Rehardenable Materials Systems with Diffusion Barrier for Three-Dimensional Printing

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ABSTRACT

Three-Dimensional Printing (3DP) is a solid freeform fabrication process being developed for the direct manufacture of functional tooling and prototypes from a computer solid model. One of its many important applications is the fabrication of metal tooling for plastic injection molding. In order to achieve a fully dense 3DP metal tool, the sintered powder skeleton is infiltrated with a molten alloy, which has a melting point lower than the skeleton material. However, the choices of materials systems are limited by the interactions of the metal powders and infiltrants during the infiltration process. Currently, the materials system with the best wear resistance for 3DP metal tooling consists of 420 stainless steel powder and bronze infiltrant. However, it only has an overall hardness of 25 HRC because the bronze infiltrant is soft and not hardenable. A hardenable 3DP metal system is desirable.

The main goals of this thesis research are: 1) to improve the flexibility of choice of metal powders and infiltrants by using a diffusion barrier to isolate them; and 2) to demonstrate the diffusion-barrier approach with steel and hardenable copper-alloy infiltrant.

The model materials systems in this study consist of stainless steel and tool steel powder skeletons with Cu-20Ni-20Mn infiltrant. It was demonstrated that TiN coating deposited on steel substrates by CVD successfully prevented the reaction between the steel and molten Cu-20Ni-20Mn at 1200 °C. In general, TiN coating on tool-steel substrates demonstrated better diffusion-barrier behavior than the stainless-steel substrates. The optimum thickness of the TiN coating was determined to be in the range of 0.5 to 1 μm. Fracture strength of the TiN coating as high as 560 MPa can be achieved for a 0.5 μm thick TiN coating on 440 C stainless steel bar. A 0.8 μm TiN-coated H13 tool-steel powder skeleton was successfully infiltrated with Cu-20Ni-20Mn infiltrant. Age hardening at 450 °C for one day resulted in a high macrohardness of 40 HRC, surpassing the current 3DP metal system for injection molding tooling. Future works on the study of other diffusion barrier materials and fluidized-bed CVD for metal powders could result in more 3DP metal systems with better properties and ease of processing.

Thesis Supervisor: Samuel M. Allen
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DEDICATION

To God, Bell, and my family
for all of your love and support.
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CHAPTER 1  INTRODUCTION

The increasing competitive global market forces manufacturers to respond by improving their products through higher quality, lower cost, and shorter time to market. Reducing development time from conception to first sales has become essential for maintaining a competitive edge for technological and consumer product industries. Being first to the market has several advantages, including greater profits due to higher initial prices and increased market share, an innovative image, and attraction of quality people.\textsuperscript{[1]} Rapid prototyping (RP) has emerged as a significant tool to greatly shorten the product development cycle.

Numerous RP techniques have been developed in industry, academia and government research institutes.\textsuperscript{[2]} For example, Stereolithography (SLA) and Selective Laser Sintering (SLS) are the two most widely used RP systems, with a system price ranging from $100,000 to $800,000. One common feature for these RP techniques is that only parts of uniform composition can be produced and materials are usually limited to polymers, which have intrinsically low hardnesses and low strengths for actual usage in tooling and commercial products. Though many variations and new RP techniques are developed to include structural materials like metals and ceramics, they come short compared with Three Dimensional Printing (3DP), a state-of-the-art RP technique invented at MIT.\textsuperscript{[3-5]} The details of the 3DP processes, its advantages, the current status and motivation for improvements are explained in the following sections.

One of the main applications of 3DP is the fabrication of toolings for plastic injection molding. The choices of materials systems are limited by the interactions of the metal powders and infiltrants during the infiltration process. The main goals of this thesis research are: 1) to improve the flexibility of choice of metal powders and infiltrants by using diffusion barrier to isolate them; and 2) to demonstrate the diffusion barrier approach with steel and hardenable copper-alloy infiltrant.
1.1 **THREE DIMENSIONAL PRINTING**

1.1.1 **Printing Process**

![Diagram of 3D printing process](image)

**Figure 1.1** Three-dimensional printing process.

Three Dimensional Printing uses ink jet technology to selectively bind powders and form complex objects. A schematic for a typical 3DP process is shown in Figure 1.1. This process creates a solid object by printing sequential two-dimensional layers. Each layer begins with spreading of a thin layer of powder over the surface of a powder bed. A slicing algorithm obtains detailed information for every layer from a CAD model of the desired part. Selective application of a liquid binder joins particles where the object is to be formed using a technology similar to ink-jet printing. Printing is accomplished by moving a printhead over the powder bed in a raster-scan or vector pattern. The binder jet is composed of droplets, which are allowed to impact the powder bed in areas where the
powder is to be joined. A piston, which supports the powder bed and the part in progress, then lowers so that the next powder layer can be spread and selectively joined. This layer-by-layer process repeats until the part is completed. Loose powder is then removed by a vacuum cleaner and a brush. The remaining binded powders form a 3-D skeleton, called "green part". The density of this green part is 58-60 vol. pct. for spherical monomodal powder. The remaining ~ 40 vol. pct. is porosity and the binder.

3DP has been used to produce complex components with a wide range of materials systems including ceramics⁶, glasses⁷, metals⁸, and polymers⁹. Unbound powder in the powder bed temporarily supports unconnected portions of the components, allowing overhangs, undercuts, and internal volumes to be created. This is especially useful for the construction of conforming cooling channels in plastic-injection mold tools.

Further, different materials can be dispersed through separate nozzles, which is a concept analogous to color ink jet printing. Materials can be deposited as particulate matter in a liquid vehicle, as dissolved matter in a liquid carrier, or as molten matter. The proper placement of droplets can be used to control the local composition and to fabricate components with true three dimensional composition gradients. For example, gradual blending of materials with different coefficient of thermal expansion (CTE) for sensors and actuators is possible with 3DP. Ceramic materials can be coated on metal parts for high temperature applications. Species that impart wear resistance can be selectively deposited near the wear-prone surfaces such as in tooling and replacement hip joint. Internal residual stresses can be modified with second phases to strengthen or toughen materials. The potential of this ability is numerous.¹⁰ Therics, a pharmaceutical company from the 3DP Consortium, uses its 3DP-based TheriForm™ technology to fabricate oral dosage forms and implantable products with complex structure and composition for time-released drug delivery. Z Corp, one of the fastest-growing RP equipment suppliers, manufactures the Z402C color 3D printer, which is able to build colored rapid prototypes to enhance visual communication among product designers and customers. Studies show that people prefer colored finite-element stress plots on a real 3D object over a confusing two-dimensional rendering on paper.¹¹
The versatility of materials systems and its ability to fabricate functionally graded parts separate 3DP from other RP techniques.

1.1.2 Application to Injection Molding Tooling

A major application of the 3DP process is the fabrication of tool sets for casting and injection molding. According to Freedonia Group, US demand for injection molded plastics is projected to increase 3.5 percent annually to 16.1 billion pounds in 2005, valued at $9.8 billion (resin content only).\textsuperscript{[12]} The demand for plastics processing machinery is forecast to climb three percent annually (including price increases) to $2.8 billion in 2005. Injection molding equipment will remain the largest market segment, accounting for close to half of total demand.\textsuperscript{[13]} Any technical improvement on the injection mold fabrication will generate a significant return. With delivery times that can range from four to more than 16 weeks (depending on size and complexity), traditional tool-making remains one of the slowest and most expensive steps in the injection molding business. On the other hand, three-dimensional printing has demonstrated superiority in the fabrication of injection molds as it can reduce tool-making time to a matter of days.\textsuperscript{[14]} The advantage is most pronounced in tooling that involves complex shapes and surfaces.

Extrude Hone, one of the 3DP licensees, utilizes 3DP in their ProMetal Rapid Tooling Systems to creating metal components and tooling for injection molding and casting. Production time is reduced and molded part quality is improved by printing embedded conformal cooling channels in the mold (Figure 1.2) and truss structure on the backside of the mold for thermal mass reduction (Figure 1.3). These advanced features are impossible to make with conventional machining.

Due to the demand of high hardness, strength, and toughness for injection molds, the metal powder skeleton cannot be used alone because of its porosity and low green strength. Additional processing steps collectively referred to as “post-processing”,

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involving debinding, sintering and infiltration, are required to achieve full density. This is explained in the following section.

**Figure 1.2** Cutaway of injection molding with conformal cooling channels.  
**Figure 1.3** Metal tool with 3D truss structure for thermal isolation of injection mold cavity.

1.1.3 Post-Processing

The post-processing of the 3DP tools has four main steps: (1) debinding/reduction; (2) sintering; (3) infiltration; and (4) heat treatment if necessary (Figure 1.4). The debinding/reduction step is carried out to evaporate polymeric binders or to reduce reactive-salt binders. The part is usually held at a temperature of 200 °C and 500 °C for a short period of time. Polymeric-binder residue may help bonding the powders or activating the sintering.

The next step is sintering. The sole purpose of this step is to enhance the strength of the skeleton in preparation for the infiltration. The skeleton is held at a temperature of at least half of the melting point of the skeleton material for a period of time. Neck formation among the powders is essential to the success of the infiltration. The green part is usually heated to 1200 °C for one hour if steel powders are used, resulting in a typical shrinkage of less than 1.5%. As the dimensional tolerance of injection mold tooling is very tight, efforts were made to reduce the shrinkage and its variation in the sintered part.
through the use of reactive salt binder\cite{15}, activated sintering, and brazing slurry\cite{16}. These binder systems can lead to neck growth at much lower temperatures than for neck growth by sintering alone. Linear shrinkage can be reduced to less than 0.2 pct. using such methods.

![Diagram of the 3DP process](image)

**Figure 1.4** Post-processing for 3DP metal tool.

The third step is the liquid-metal infiltration that makes the porous skeleton into a fully dense tool. The skeleton and the infiltrant are heated to a temperature above the melting point of the infiltrant, but below that of the skeleton. In the course of the process, the liquid infiltrant flows into the continuous porous skeleton by capillary action and fills the voids. An infiltration stilt made of the same material as the skeleton is used to support the tool during infiltration and to prevent erosion of the tool by infiltrant. Once the skeleton has been infiltrated, a near net-shape tool is ready (Figure 1.5). The tool may need final machining and heat treatment, however, depending on the purpose of the tool.
Figure 1.5  Metal injection mold before (right) and after (left) infiltration.

If the tool materials are hardenable (such as a tool steel powder skeleton and some copper alloy infiltrants), then additional heat treatment may be desirable after infiltration. In order to meet certain functional requirements, most tools need one or more heat treatments such as annealing, solution treatment, hardening and tempering. The annealing in the 3DP process improves the machinability of the tool. The solution treatment is used mainly to homogenize the infiltrant. The tempering reduces the residual stress from quenching and improves the toughness of the steel. Since the tool is a composite system, the solution treatment of the infiltrant is required to be a simultaneous process with the steel hardening. The tempering of the skeleton is also required to be a simultaneous process of the age hardening of the infiltrant. This poses another constraint on the choice of materials systems.

1.2 MATERIALS SYSTEMS FOR INJECTION MOLDING TOOLING

Currently, most challenges associated with post-processing are related to the infiltration process. Thermodynamically and kinetically, the liquid infiltrant may have strong reaction tendency with the skeleton material, due to (1) solubility and phase
formation between infiltrant and skeleton, and (2) fast diffusion rates. Once this reaction occurs, complications arise, such as the change of the melting point of the infiltrant, interdiffusion, erosion, residual porosity, and dimensional expansion.

1.2.1 316L/Bronze

The pioneer metal system for 3DP was successfully developed by Steven Michaels at MIT, which is a 60 vol% 316L stainless steel skeleton with 40% bronze (Cu-10Sn) infiltrant.\textsuperscript{[17]} This system is chosen because the 316L stainless steel has excellent corrosion resistance and the molten bronze does not react with the skeleton very much during infiltration. The element exchange between the skeleton and the infiltrant is less than 1%. However, the major disadvantage of the system is low hardness (~60 HRB), which is due to the fact that 316L is not hardenable and bronze is intrinsically a soft material. This may imply a short lifetime for the tool because of strong mechanical friction during plastic injection. A hard material system is desirable as the wear resistance is roughly proportional to its hardness.

1.2.2 420/Bronze

Honglin Guo launched an extensive research to develop a hard 3DP tool.\textsuperscript{[18]} He discovered the 420 stainless steel/bronze (Cu-10Sn) system, which has a much higher hardness at around 25 HRC. This is because 420 is harder than 316L and it hardens during furnace cooling after infiltration. Similar to 316L/bronze system, there is only a few percent exchange of iron and copper in the 420/bronze system. In actual production, AMP, a project participant, has successively produced close to one hundred thousand plastic products without any major repairs, using a 3DP metal mold made of the 420/bronze system. It was a milestone of the 3DP materials system development.

Though the 420/bronze is a substantial improvement over the 316L/bronze materials system, tool life is still short comparable to conventional pure steel mold. It is good enough for prototype and short run application. However, in order to catapult 3DP
tool into the market of mass production, development of materials systems of higher hardness and improved properties (e.g., heat conductivity, EDM performance, weight, corrosion resistance, etc.) are required. Attempts have been made to incorporate hardenable infiltrants (copper alloys, nickel brazing alloys, etc.) with hardenable steel skeleton. They all failed as there is a strong reaction between the infiltrant and the steel skeleton, mainly due to the mixing of nickel in infiltrants with the iron in steel skeleton.

1.2.3 W/Cu-20Ni-20Mn

The steel skeleton was changed to refractory metals (Cr, Mo, W, etc.) and infiltrated with hardenable copper infiltrant (Cu-20Ni-20Mn, Cu-15Ni-8Sn, etc.) Refractory metals are chosen because they have moderate hardness and the solubility and diffusion of infiltrant elements in the refractory metal is usually smaller and slower. There were some successes. For example, W/Cu-20Ni-20Mn can achieve a hardness as high as 37 HRC. However, due to the difficulties in sintering refractory metal powder, weight of the infiltrated part, and the poor electrical discharge machining (EDM) performance, it is far from an ideal materials system for 3DP tooling applications.

1.2.4 Steel/Cu-20Ni-20Mn

As a representative of the rehardenable infiltrants, Cu-20Ni-20Mn has a superior rehardenability. It can be hardened to 52 HRC by age hardening from an annealed state with initial hardness in the medium Rockwell B range. If the reaction with a steel skeleton is eliminated or prevented, it would be an ideal candidate for the next generation of 3DP metal tooling material system as the infiltrated part could reach a hardness around 40 HRC for many steel skeletons. A practical scenario would be that the infiltrated part is machined, polished in the soft state, and hardened to the desired hardness after final heat treatment. The commercial potential is considerable as the composite hardness would be comparable to conventional pure steel tool.
Table 1.1 summarizes the development of hardenable materials systems from the conventional 3DP tooling systems to the proposed steel/Cu-20Ni-20Mn system with the use of diffusion barrier.

<table>
<thead>
<tr>
<th>Conventional Materials Systems</th>
<th>New Materials System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skeleton</td>
<td>316L s.s.</td>
</tr>
<tr>
<td>Infiltrant</td>
<td>Bronze</td>
</tr>
<tr>
<td>Hardness</td>
<td>60 HRB</td>
</tr>
<tr>
<td></td>
<td>420 s.s.</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.1** Improvement of 3DP tool hardness enabled by the use of diffusion barrier. Highlighted materials are rehardenable by heat treatment.

### 1.3 Goal

The goal of this research is to develop a rehardenable 3DP system of high dimensional accuracy and hardness by use of a diffusion barrier between powder skeleton and liquid infiltrant. Experimental result is based on the study of the steel/Cu-20Ni-20Mn model system. A diffusion barrier is used to prevent diffusion and reaction between the steel skeleton and the molten Cu-20Ni-20Mn infiltrant. The success of this research will result in rehardenable materials systems with superior properties compared with the existing 3DP systems. Tool life can be greatly increased with an improved product quality. In addition, more materials systems with tailored properties can benefit from the use of diffusion barrier as it virtually eliminates the most challenging limitation in the 3DP process---reaction during infiltration that severely limits the choices of materials systems.

The objective of this thesis is to demonstrate that diffusion barrier is an effective means to solve the reaction problem during 3DP processing and lay the foundation for the next generation 3DP metal tooling with superior materials properties.
1.3.1 Thesis Organization

Chapter 2 presents an overview of the materials selection processes for choosing an effective diffusion barrier for steel substrates and Cu-20Ni-20Mn infiltrant. Selection criteria are drawn from theoretical analysis, published solubility and diffusivity data, and commercial availability of the diffusion-barrier materials and their processing.

Chapter 3 investigates the effectiveness of titanium nitride as a diffusion barrier through computer calculations and reaction experiments. Both flat steel substrates and sintered steel powder skeleton are used. Coating properties and performance are evaluated for various coating thicknesses from different coating service vendors. Microstructures, compositions and reactions at the diffusion-barrier interfaces for different steel substrates and coating thicknesses are studied. A comparison of gated infiltration to conventional infiltration is also presented.

Chapter 4 presents the mechanical properties of the materials system. Tensile strength and fracture characteristics are studied using tensile tests and electron microscopy, respectively.

Chapter 5 summarizes the heat treatment procedures and hardening response of the materials system.

Chapter 6 discusses the applicable range of TiN diffusion barrier that can be successfully applied to the steel/Cu-20Ni-20Mn materials system.

Chapter 7 summarizes the major findings in this dissertation. Discussions of the results and suggestions for improvement and future work are also presented.

Appendices contain basic information about the thermodynamics and kinetics of diffusion barrier (reaction, diffusion length estimation, etc.), materials properties data Thermo-Calc results, and estimation of residual stress in the diffusion barrier after deposition.
1.4 REFERENCES


8. Michaels, S., Sachs, E., Cima, M.J., “Metal Parts Generation by Three Dimensional Printing” in Proceedings of the SFF Symposium, Univ. of Texas, Austin, TX, 244-250 (1992).


CHAPTER 2 SELECTION OF DIFFUSION BARRIER

The purpose of the diffusion barrier is to prevent the diffusion and reaction between the molten infiltrant and the sintered steel powder skeleton during infiltration. It can minimize the dimensional change of the infiltrated part and preserve the compositions of the skeleton and infiltrant within the range of hardenability. Selection of suitable diffusion barriers is challenging because of numerous constraints.

2.1 TYPES OF DIFFUSION BARRIER

According to Nicolet\textsuperscript{[1]}, three models have been proposed for successful diffusion-barrier behaviors: sacrificial barriers, stuffed barriers and passive compound barriers. The operating mechanisms of these barriers and some of their applications are described in this section.

2.1.1 Sacrificial Barriers

A sacrificial barrier maintains the separation of A and B only for a limited duration. As shown in Figure 2.1, sacrificial barriers exploit the fact that reactions between adjacent films in turn produce uniform layered compounds AX and BX that continue to be separated by a narrowing X barrier film. However, this kind of barrier is only effective before X is consumed completely by A and B. If the reaction rate kinetics of both AX and BX are known, then either the effective lifetime or the minimum thickness of barrier required may be predicted. The use of sacrificial barriers is very common in the Al metallization on Si semiconductor devices to prevent the formation of spikes at the Al-Si interface.\textsuperscript{[2]} A well-known example is the Ti sacrificial barrier, which reacts with Si to form Ti\textsubscript{3}Si and with Al to form TiAl\textsubscript{3}.\textsuperscript{[3]}
2.1.2 Stuffed Barriers

Stuffed barriers rely on the segregation of impurities along rapid diffusion paths such as grain boundaries to block further passage of two-way atomic exchanges there. The marked improvement of the diffusion barrier properties of Mo and Ti-W films used in semiconductor devices when they contain small quantities of intentionally added N or O impurities is apparently due to this mechanism.\(^4\) Impurity concentration of \(\sim 10^1\) to \(10^3\) atomic percent are typically required to saturate grain boundaries and induce stuffed-barrier protection.

2.1.3 Passive Compound Barriers

Ideal barrier behavior exhibiting chemical inertness and negligible mutual solubility and diffusivity is sometimes approximated by compounds. Refractory metal carbides, nitrides, borides and silicides are good examples of compound barriers. In fact, TiN is presently one of the most widely used barrier materials in Cu- and Al-based metallization in the semiconductor industry.\(^5\)\(^9\)

An enormous amount of research has been done on the development of diffusion barriers for Cu and Al metallization of semiconductor devices. Various materials have been studied. These materials mainly include the transition metals from groups IVA to
VIII in the Periodic Table.\textsuperscript{[10-13]} They function as sacrificial barrier by forming silicides with the Si substrate and intermetallic phases with Al or Cu on the other side. In addition, passive-compound barriers such as TiN, TaN, and TiB\textsubscript{2} are becoming more popular as they are chemically inert and possess low diffusivities and solubilities in and with Al, Cu, and Si.\textsuperscript{[14-17]} Stuffing of the grain boundaries in TiN diffusion barriers with N\textsubscript{2}, NH\textsubscript{3}, and O\textsubscript{2} have mixed results.\textsuperscript{[18-20]} Amorphous alloys and single crystals have also been very attractive as diffusion barriers mainly because of the absence of grain boundaries for short-circuit diffusion.\textsuperscript{[21-23]}

Despite the wealth of information on the use of diffusion barriers in the semiconductor industry, the success mainly came from empirical knowledge and collaborative research efforts. Comparing the infiltration process in 3DP with typical semiconductor processing, the diffusion barrier on the steel skeleton is in contact with molten Cu alloy at a much higher temperature ($\sim$1200 °C) than the typical failure temperatures of diffusion barriers used in electronic materials ($\sim$400 °C to 600 °C).\textsuperscript{[14]} The functions and requirements of diffusion barrier could be quite different. A fundamental understanding of the materials properties and a systematic approach to the diffusion-barrier selection process is essential. However, information and experience collected from the field of electronic materials can serve as a reference to the development of diffusion barrier here.

The remainder of this chapter outlines a systematic approach for the selection of diffusion barriers for the development of rehardenable materials system in 3DP.

\section{2.2 Selection Methodology}

Due to the existence of a broad family of materials (e.g., ceramics, metals, polymers, and composites) and different coating techniques (e.g., CVD, PVD, electroplating, etc.), it is impractical to find the suitable diffusion barrier material by testing all available materials. In view of this, the selection process of diffusion barrier is
carried out with reference to the materials selection procedure developed by Ashby.\textsuperscript{[24]}

The process flow chart of the strategy of materials selection can be found in Appendix A.

Basically, Ashby's approach is an engineering one. It searches the available engineering materials by matching their attributes to the intended function with the help of materials selection charts. In this dissertation, the selection process is assisted by theoretical understanding of the fundamental principles that define the properties of a diffusion barrier material. For example, melting point, diffusivity, solubility, compound formation, adhesion, and wetting are related to each other through the interatomic cohesive forces. A good understanding of these relationships helps to establish the ranking of a small group of candidates and to suggest a better candidate if the design is changed.

Each material is characterized by a set of attributes, which include its mechanical, thermal, electrical, and chemical properties; its processing characteristics; its cost and availability; etc. This is called the property-profile. Selection involves seeking the best match between the property-profile of materials in the kingdom and that required by the design, which is in this case the use of a diffusion barrier to prevent the reaction between the steel skeleton and Cu-20Ni-20Mn infiltrant for 3DP metal tooling.

The basic selection process is based on three main steps: screening and ranking, supporting information and local conditions.

The first of these, screening, eliminates candidates that cannot do the job at all because one or more of their attributes lies outside the limits imposed by the design. Property limits do not, however, help with ordering the remaining candidates. To do this, optimization criteria are required in the ranking step. Such optimization criteria are found in the material indices, which measure how well a candidate that has passed the limits can do the job. For example, diffusion coefficient, coefficient of thermal expansion and adhesion to the steel skeleton are some of the important material indices for the ranking of diffusion-barrier candidates.
The outcome of the screening and ranking step is a short list of candidates that satisfy the quantifiable requirements of the design. To proceed further, *supporting information* is needed. Supporting information differs greatly from the property data used for screening. Typically, it is descriptive, graphical or pictorial: case studies of previous uses of the material, details of its diffusion-barrier performance, effects of processing parameters, etc. Finally, the short list can be narrowed to a final choice.

However, the final choice between competing candidates will often depend on local conditions: on the existing in-house expertise and equipment, on the availability of local suppliers, and so forth. For example, the deposition of diffusion barrier material on individual powder is certainly limited by the available techniques (e.g., fluidized-bed CVD and electroplating) and the coating recipes for a limited number of materials.

With the above selection methodologies in hand, the candidate material for diffusion barrier in 3DP metal tooling is selected in the following sections.

2.3 **Selection Constraints**

In general, the requirements and constraints for a successful diffusion barrier can be grouped into three main areas: Thermodynamic constraints, kinetic constraints and processing constraints.

2.3.1 **Thermodynamic Constraints**

Ideally, a suitable diffusion-barrier material must be thermodynamically stable with respect to the skeleton and the infiltrant at the sintering and infiltration temperatures. No new phase should be formed that can deteriorate the property of the diffusion barrier. The mutual solubilities of the diffusion barrier material with the skeleton and infiltrant should be minimal. If these criteria are met, the diffusion-barrier property of the diffusion barrier is preserved while at the same time the hardenability of the skeleton and infiltrant
is retained. In addition, the diffusion barrier must wet very well by the binder and the infiltrant. The wetting behavior is governed by the interfacial energies of the materials involved. Furthermore, the sintering temperature of the diffusion barrier should be lower than the melting point of the skeleton, while the melting point of the diffusion barrier should be higher than that of the infiltrant. These constraints apply assuming diffusion-barrier coating is done on individual powder. However, if coating is done on sintered powder skeleton, the constraints of wetting by binder and sintering temperature of diffusion barrier can be removed.

2.3.2 Kinetic Constraints

Besides the requirement of minimal solubilities in the skeleton and infiltrant, the diffusivities of elements through the diffusion barrier should be low enough so that there is no substantial elemental exchange between the skeleton and infiltrant during the infiltration step. The combination of the temperature-dependent diffusivity values, mode of diffusion and time of diffusion determines the minimum thickness of the diffusion barrier, which in turn is limited by the allowed volume ratio of diffusion barrier to the powder skeleton.

2.3.3 Processing Constraints

The effectiveness of a diffusion barrier material also depends on its film quality. The most important criterion is its adhesion to the skeleton. There should be a good chemical bonding between the diffusion barrier and the skeleton. From a thermodynamic standpoint, the work to break the bonding is related to the specific surface energies of film and substrate as well as the interfacial energy. This is material and processing (e.g., impurity, film stress, etc.) dependent.

Furthermore, many processing steps in 3DP, like sintering, infiltration and heat treatment, involve thermal cycling of the coated skeleton. The most demanding one is the infiltration step where materials are commonly heated to around 1200 °C. Consequently,
thermal stress results from the difference in the coefficients of thermal expansion (CTE) between the diffusion barrier and skeleton. Moreover, any thin-film coating techniques unavoidably introduce intrinsic stress to the film. For examples, tensile stress results from coalescence stresses during film formation.\textsuperscript{[25]} On the other hand, compressive stress can result from the shot-peening effect in sputtering at low pressure.\textsuperscript{[26]} In any case, the combined intrinsic and extrinsic stresses can lead to spallation or crack formation in the film, which can act as the site for initial attack of the steel substrate by the molten infiltrant. Thus, it is desirable to keep the stress in the diffusion barrier after deposition or during infiltration below the yield stress value of the film. In general, the yield stress of a thin film is related to the film thickness and grain size, which in turn are processing dependent.\textsuperscript{[27]}

Finally, a suitable technique is required to deposit a uniform, dense and thin diffusion barrier on the powders. A uniform diffusion barrier ensures complete coverage and protection of the skeleton. A dense diffusion barrier has lower porosity and pinhole density. Thus, diffusion through the coating can be reduced. This is an important processing criterion. A thin coating ensures that the volume ratio to the powder skeleton is small enough so that it does not degrade the desired properties of the whole tool. Currently, fluidized-bed CVD has the ability to put a thin coating on individual powder particles. Custom-made coating techniques involving a powder-mixing device coupled to conventional thin-film deposition techniques are also possible alternatives. A more practical approach is to deposit the barrier material directly on the sintered powder skeleton by CVD technique. The advantage of this approach is that the requirements of wetting by binder and sintering of the diffusion barrier material can be eliminated. No special powder coating technique is required.

In summary, all the constraints in choosing a suitable diffusion barrier are listed below:

1. Thermodynamic constraints:
   a. Non-reactive to the skeleton and infiltrant at high temperature.
b. Low mutual solubility with the skeleton and infiltrant.
c. Good wetting with the binder and infiltrant.
d. Sintering temperature lower than the melting point of the skeleton, $\sim 1500 ^{\circ}C$.
e. Melting point higher than that of the infiltrant, $\sim 1100 ^{\circ}C$.

2. Kinetic constraint:
   a. Low diffusivities in the diffusion barrier.

3. Processing constraints:
   a. Good agreement of the coefficients of thermal expansion of the diffusion barrier and skeleton.
   b. Low film stress compared to the yield stress.
   c. Uniform, dense and thin coating by suitable thin film deposition technique.

2.4 SCREENING

The next step is to screen and rank the diffusion barrier candidates according to the given constraints.

The model materials system studied in this dissertation is composed of a steel skeleton and Cu-20Ni-20Mn infiltrant. The liquidus of Cu-20Ni-20Mn is 1060 $^{\circ}C$. Thus, the melting point of the diffusion barrier should be above 1200 $^{\circ}C$, which is the typical infiltration temperature for this materials system. From this primary constraint, it is easy to single out candidate metals and ceramics from the broad materials class. Though there are composite materials with high melting points (e.g. cermets), they are not applicable for thin-film applications.

The periodic trend of the melting points of each element in the Periodic Table is shown in Figure 2.2.\textsuperscript{[28]} It is very clear that the first three periods of all transition metals
from group IIIA to VII† along with Be, B, C and Si fulfill the melting point constraint (Lanthanides and Actinides are excluded because of radioactive hazard, cost, and lack of industrial acceptance.) On the other hand, almost all common nitrides, carbides, borides, and oxides of transition metals have melting points well exceeding 1200 °C.†

![Melting Points of Elements](image)

**Figure 2.2** Melting points of the elements as a function of the subgroup of the Periodic Table. Elements with melting point higher than 1200 °C are screened out as diffusion barrier candidates.†

† Here, the old IUPAC group numbering system is used as shown in Fig 2.2. They correspond to group 3 to 10 in the new IUPAC group numbering system.
2.5 RANKING

In the ranking step, the diffusion barrier candidates are ranked by their performance with regard to the constraints of solubility, reaction and diffusivity. Further elimination of less applicable candidates is accomplished.

2.5.1 Thermodynamic Constraints

2.5.1.1 Solubility

It is generally recognized that all metals and compounds show some solubility in the solid state. Binary phase diagrams of most elements are readily available to offer the solubilities in the primary solid solutions and intermediate phases. However, some binary systems are not completely assessed, and in many higher-order alloys like tool steels, there is a scarcity of data. Commercial thermodynamic software such as Thermo-Calc\textsuperscript{[30]} can be used to construct phase diagrams of complex multi-component alloys using thermodynamic data and models. With the advance of computational materials science, materials properties such as solubility and phase formation can also be predicted from first principles.\textsuperscript{[31]} However, this is beyond the scope of this dissertation.

In the early work for the development of diffusion barrier for 3DP metal systems, Guo\textsuperscript{[32]} initiated an engineering approach for the selection of diffusion barrier based on published binary alloy phase diagrams. He predicted the reaction tendency between the steel skeleton and diffusion barrier according to the mutual solubilities of Fe with the elemental diffusion barrier. He found that only Sc, Y, Zr and Hf showed minimum solubility with Fe at 1100 °C. Other elements have either unlimited solubility or a large solubility in Fe or vice versa. Since those four elements are seldom used as coating materials, Guo concluded that there was not a suitable diffusion barrier made of just a single element. However, it should be noted that the cutoff limit of the maximum solubility considered by Guo was arbitrary and weight percent rather than atomic percent...
was used. Regarding kinetic constraints, Guo pointed out a minimum barrier thickness of 10 μm is required to survive the dissolution into Fe, which is based on a typical diffusivity value of 10^{-10} cm^2/s for one hour at 1100 °C. The barrier would be too thick for typical size of steel powder (diameter ~ 50 μm) used in 3DP. However, the result was based on simple diffusion models for diffusion in a continuous solid solution, which assumed the crystal structures of the diffusion barrier and Fe are the same.

In view of the common use of single-metal diffusion barrier in electronic materials systems, it is too early to ignore any potential single-element candidate at this stage. Many metals have high solubility in Al, Cu and Si and yet they are used as sacrificial barrier. Here, the interactions of the selected candidates with Fe are revisited. Solubility limits for the Fe-side and barrier-side are extracted from the binary phase diagrams. Then, diffusion barrier candidates will be grouped according to the type of binary phase diagram. Finally, a system-dependent diffusion length calculation will be applied to each type of phase diagram according to the possible diffusion or reaction process in the system. Those systems with lower solubility or slower reaction/diffusion will be given a higher ranking.

Aside from the present work, a more fundamental treatment in predicting solubility in solid solution can be found in Appendix B. The understanding of the underlying principle governing solubility, reaction and diffusivity can help the development of other diffusion barriers such as metallic alloys, refractory nitrides and multi-layer diffusion barriers. Furthermore, if there is a design change of the skeleton material or the infiltrant, the validity of the use of a certain diffusion barrier can be checked before an extensive experimental research effort is made for developing a new system.

From the binary alloy phase diagrams, solubilities of diffusion barrier candidates with Fe are obtained (see Table B.1 to Table B.3 in Appendix B). Some of the elements form complete solid solution with Fe while others have limited or extended solubilities with the formation of intermetallic compounds. They are denoted by type 1
and type 2 phase diagram in this text respectively. Among them, the most promising ones are Sc, Y, Zr, Nb, Hf, Ta and W, where limited solubility (< 5 at. pct.) are observed. It should be noted that besides Sc and Y, the other five elements belong to the refractory metals (transition metals having melting points higher than that of Fe). Moreover, they are farthest away from Fe among all transition metals in the Periodic Table as predicted by the Hume-Rothery rules[35] and Darken-Gurry map.[36]

On the other hand, ceramic or compound materials have intrinsically low solubility with other elements. This is mainly due to their narrow composition range and deep free-energy vs. composition curve, which is manifested in their high melting points. For example, TiN and TiC are very common diffusion barriers in semiconductor industry and hard coatings in tooling industry. Binary phase diagrams cannot be used here. With the use of Thermo-Calc, solubility values of these compound diffusion barriers with Fe, steel or the Cu-20Ni-20Mn infiltrant can be obtained. A simple calculation of the mutual solubility by mixing 0.5 mole of TiN with 0.5 mole of Fe at 1200 °C resulted in the following values expressed in mole fractions:

\[ S_{Fe}^{TiN} = 2.2 \times 10^{-2} \]
\[ S_{Ti}^{Fe} = 1.4 \times 10^{-3} \]
\[ S_{Ni}^{Fe} = 4.1 \times 10^{-7} \]

where \( S_{ij}^{j} \) is the solubility of element \( i \) in matrix \( j \). Thus, the solubility resistance of TiN is comparable to the refractory metals and sometimes exceed them.

For an actual materials system, different alloying elements can affect the solubility. A more sophisticated technique using computer calculation (e.g., Thermo-Calc) to study the solubility and reaction of the final few diffusion-barrier candidates with steel and Cu-20Ni-20Mn infiltrant is essential. However, the simple screening process illustrated in this section is an effective method in screening out a small list of candidates with very good diffusion-barrier potential regarding limited solubility.
2.5.1.2 Reaction

In type 1 system, the diffusion barrier forms complete solid solution with Fe. The thickness of the diffusion barrier required is calculated by using the simple thin-film diffusion model in Appendix C. These elements in general have a diffusivity value of \(10^{15}\) to \(10^{14}\) m\(^2\)/s at 1200 °C. An estimated diffusion-barrier thickness of 2 to 5 μm is required to prevent complete dissolution in Fe for 30min.

In type 2 system, intermetallic phases are formed with limited solubility in the primary solid solution. In most cases, the growth of the intermediate phase is diffusion-controlled and follows the parabolic growth law:

\[
W_p = 2\left(\sqrt{S_M^2 D_M t} + \sqrt{S_{Fe}^2 D_{Fe} t}\right)
\]

Eqn. 2.1

where \(S_M\) is the solubility of Fe in the diffusion barrier material M; \(D_M\) is the diffusivity in M-rich solution; and similar expressions for \(S_{Fe}\) and \(D_{Fe}\). Details of the calculations are carried out in Appendix C. It has been estimated a thickness of 1 μm is enough to compensate for the compound formation. Among the candidate barrier elements, Ta, W and Nb are determined to be the most promising. Compared with type 1 systems where there is complete solubility, refractory metal is a better choice. Furthermore, as the solubility and diffusivity is generally smaller in the nitrides, carbides, and borides of refractory metals, TiN and TiC are expected to perform even better than the refractory metals.

As a concluding remark for the thermodynamic constraints of solubility and reaction, it is expected that refractory metals like Ta, W, Nb and Hf and ceramic compounds like TiN and TiC are good candidates for diffusion-barrier materials. The above conclusion is based on solubility and reaction with Fe alone. In an actual 3DP metal system, steel and Cu-20Ni-20Mn are used and there may be more interactions with other alloying elements. In view of this, the stable-compound diffusion barriers are preferred over pure refractory metals based on thermodynamic considerations.
2.5.2 Kinetic Constraints

During the service lifetime of the diffusion barrier, it should prevent diffusional mixing of the skeleton materials and infiltrant on both interfaces. Thus, a thick enough film is required besides satisfying the thermodynamics constraints mentioned in the preceding section. The minimum thickness of the diffusion barrier can be estimated by scaling with the diffusion length:

\[ h = 2\sqrt{Dt} \]  
\textbf{Eqn. 2.2}

There are two important parameters: diffusivity of elements in the barrier and infiltration time. Conventional 3DP processing of metal parts requires a typical infiltration time of 1 hour. This can be greatly reduced to as short as 5 minutes with the use of gated infiltration. More on gated infiltration will be described in Chapter 3.

Diffusivity depends on the nature of the barrier and the operating temperature. In general, the activation energy of diffusion scales with the melting point of the matrix material. In crystalline materials, the diffusivity depends also on transport path. A convenient summary of resulting diffusion parameters is given by Balluffi and Blakely for the class of FCC metals:

\[ D_L \approx 0.5 \exp \left( -17.0 \frac{T_M}{T} \right) \text{cm}^2/\text{s}; \]  
\textbf{Eqn. 2.3a}

\[ \delta D_b \approx 1.5 \times 10^{-8} \exp \left( -8.9 \frac{T_M}{T} \right) \text{cm}^2/\text{s}; \]  
\textbf{Eqn. 2.3b}

\[ A_d D_d \approx 5.3 \times 10^{15} \exp \left( -12.5 \frac{T_M}{T} \right) \text{cm}^4/\text{s} \]  
\textbf{Eqn. 2.3c}

The scaling can be realized by the diffusion process where a diffusing atom moves by distorting an elastic lattice of matrix atoms. It has to overcome the elastic force that the matrix atoms exert on the solute. Such energy barrier from the elastic force is a measure of the bond strength, which is manifested in the melting point.

Diffusivity should be low in refractory metals and compounds as they possess the highest melting points among other materials. The contribution from each mechanism depends on temperature, grain size, and dislocation density. At a typical reduced temperature of \( T/T_M = 0.4 \) – 0.5 for infiltration temperature at 1200 °C with refractory-metal diffusion barrier, grain-boundary diffusion is dominant when the grain size of the
film is less than 50 nm. Diffusion of the elements through the diffusion barrier is an admixture of diffusion mechanisms that results in an initial rapid penetration down the short-circuit network of the grain boundaries. Diffusion then slows down as atoms leak into the lattice from the grain boundaries. A detailed mathematical treatment of this can be found by the works of Fisher\textsuperscript{[38]}, Whipple\textsuperscript{[39]}, and Suzuoka\textsuperscript{[40]}. 

Diffusivity data for some refractory metals and TiN, TiC are obtained.\textsuperscript{[41, 42]} At a temperature of 1200 °C, typical diffusivity values of the order $10^{-15}$ m$^2$/s are found for Fe diffusing in Ta, W and Nb while Fe has a diffusivity of only $10^{-17}$ m$^2$/s in TiN. No data is available for diffusion in TiC but it is expected to be of the same order of TiN. From Eqn. 2.2, the required minimum thickness of the diffusion barrier for an infiltration time of 30 min is only 3 μm and 0.3 μm for refractory metals and TiN respectively. These values are of the same order of the estimation from reaction consideration in section 2.5.1.2.

So far, TiN and TiC rank higher than Ta, W and Nb in terms of thermodynamic stability and diffusion barrier ability. Other factors are also considered to further differentiate these candidates.

2.5.3 Other Considerations

Table 2.1 is a summary of the factors that differentiate the refractory metals and refractory metal nitrides and carbides. Complete properties of all refractory metals and refractory nitrides and carbides can be obtained from the references. Ranges of values are only shown for Ta, W, Nb, TiN, and TiC as they are the most promising diffusion-barrier candidates in their respective group. A highlighted box in the column means that material has a better performance in that category.
<table>
<thead>
<tr>
<th></th>
<th>Refractory metals (Ta, W, and Nb)</th>
<th>TiN</th>
<th>TiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in Fe</td>
<td>~1%</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Reaction with steel</td>
<td>May form carbides and intermetallics</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>Diffusivity at 1200 °C</td>
<td>(~10^{-15}) m(^2)/s)</td>
<td>(~10^{-17}) m(^2)/s)</td>
<td>(~10^{-17}) m(^2)/s)</td>
</tr>
<tr>
<td>Wetting</td>
<td>Metal-metal</td>
<td>Metal-ceramic</td>
<td>Metal-ceramic</td>
</tr>
<tr>
<td>Coefficient of thermal expansion close to steel?</td>
<td>4.6-7.1 µm/m·K</td>
<td>9.4 µm/m·K</td>
<td>7.4 µm/m·K</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>54-174 W/m·K</td>
<td>29 W/m·K</td>
<td>20 W/m·K</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>5-15 µΩ·cm</td>
<td>22 µΩ·cm</td>
<td>53 µΩ·cm</td>
</tr>
<tr>
<td>Ductility</td>
<td>Metal</td>
<td>Ceramic</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Vickers hardness</td>
<td>60-300 HV</td>
<td>1900 HV</td>
<td>2600 HV</td>
</tr>
<tr>
<td>Density (weight)</td>
<td>8.6-19.3 g/cm(^3)</td>
<td>5.4 g/cm(^3)</td>
<td>4.9 g/cm(^3)</td>
</tr>
</tbody>
</table>


**Table 2.1** Comparison of the merits of refractory metals and refractory nitrides and carbides as diffusion barrier.

A successful diffusion barrier should have a small solubility with the substrates, minimal reaction and small diffusivity. Both TiN and TiC are superior to the refractory metals. However, it is expected that the refractory metal diffusion barriers should have a better wetting behavior with the infiltrant as the interface is metal-metal in nature. The coefficient of thermal expansion (CTE) of TiN is very close to steel (10-12 µm/m·K). Thus, the thermal residual stress after the coating process should be minimal, resulting in
better adhesion of the diffusion barrier. The remaining factors are less important as their effect to the final 3DP part is not significant because of the small volume fraction of the diffusion barrier in the part. One exception is that the ductility of ceramic coatings is very low and it may affect the mechanical properties (tensile strength and fracture mechanism, etc.). By considering all the factors, it is more desirable to use TiN as the primary diffusion barrier for rehardenable materials systems in 3DP metal tooling. The main selection criteria are its chemical stability and low diffusivity.
2.6 REFERENCES


CHAPTER 3  TITANIUM NITRIDE DIFFUSION BARRIER

Among the diffusion-barrier candidates suggested in Chapter 2, ceramic diffusion barriers are expected to be the most promising material because of their thermodynamic stability and low diffusivities of other elements. TiN is chosen for its widespread use in the semiconductor industry as diffusion barrier and in the tooling industry as a hard coating. For examples, in the semiconductor industry, TiN was employed to reduce Ti-Pt interdiffusion for the Ti-Pt-Au beam-lead metallization as early as 1979.\(^1\) It was also used as diffusion barrier to prevent degradation of Si solar cell with the conventional Ti-Pd-Ag metallization.\(^2\) TiN diffusion barrier has also been successfully tested for a Ni metallization to PtSi layers on a Si substrates.\(^3\) A 750 Å TiN barrier maintained the integrity of the contact after 90 min at 600 °C. The majority use of TiN diffusion barrier, however, is in the Al and Cu metallization. TiN is known to be an efficient diffusion barrier between Al and Si up to 500 °C anneal for a duration of one hour.\(^4\text{-}^6\) Similarly, TiN is also shown to inhibit Cu-Si interaction up to 650 °C.\(^7\text{-}^9\)

The use of TiN is beneficial because of its superior properties, which include good wear and corrosion resistance, a low friction coefficient, chemical stability, and low diffusivity. Moreover, material properties, processing technologies, and functional characteristics of TiN are well documented. Thus, it can be readily accepted by metal tool manufacturers.

Although there are many studies on the use of TiN as a diffusion barrier in the literature, most of the work was focused on solid-state reactions and diffusion at moderate temperature. Thus, the effectiveness of TiN as a diffusion barrier for molten Cu alloys has yet to be explored. In this chapter, the reactions of a thin TiN diffusion barrier with various steel substrates and with Cu-20Ni-20Mn infiltrant are presented. TiN-coated flat steel bars and sintered steel powder skeletons were both used for complete analysis of TiN diffusion-barrier properties. Mechanical properties such as fracture strength of the coating and hardening response of the infiltrated part will be discussed in chapter 4 and 5.
3.1 THERMODYNAMIC STABILITY OF TiN

The thermodynamic stability of TiN diffusion barrier was first investigated before any extensive experimental effort was made on the TiN-coated steel. Computer calculation using Thermo-Calc was used to predict the reactions between TiN, iron, steel, and Cu-20Ni-20Mn, followed by experimental work to determine the optimum processing parameters, such as TiN-coating thickness, steel substrates, and infiltration procedures, for actual use in 3DP metal tooling.

3.1.1 Computer Calculation with Thermo-Calc

3.1.1.1 TiN and Fe

In order to simulate the reaction behavior of TiN and Fe, the input for the system was 0.1 mole of TiN and 0.9 mole of Fe. The ratio was chosen as it is approximately the expected amount of TiN diffusion barrier that might be used on fine steel powder. Ideally, the final composition of the infiltrated 3DP part consists of about 55 vol. pct. of steel skeleton, 5 vol. pct. of TiN diffusion barrier, and 40 vol. pct. of Cu-20Ni-20Mn infiltrant. The database is a user-defined database based on the SSOL and KP databases in Thermo-Calc. Ti, N, Fe, Cu, Ni, Mn, and all other alloying elements in steel are included in the user database. Figure 3.1 shows the change in mole fraction of different phases in the TiN/Fe system as the temperature changes. It shows that there is only little reaction between TiN and Fe, which is indicated by the steady phase mole-fractions. Calculations with other molar ratio of TiN to Fe also showed similar results. At 1200 °C, there are 0.102 mole of TiN and 0.898 mole of BCC Fe, only a change in 2%.
Figure 3.1  Phase mole fraction vs. temperature of TiN/Fe.

The change in composition of the TiN phase can be obtained from Figure 3.2. Only 2.5 at. pct. of Fe is expected to dissolve in TiN at 1200 °C at equilibrium. However, as the diffusivity of Fe in TiN is $3.27 \times 10^{17}$ m$^2$/s, it does not have time to establish the equilibrium during a typical infiltration time of 30 min if the TiN thickness is thicker than 0.2 μm. On the other hand, there is negligible amount of Ti and N dissolved in FCC Fe. Thus, it is concluded that TiN is a very stable diffusion barrier with respect to an Fe substrate.
Figure 3.2  Mole fraction of elements in TiN vs. temperature of TiN/Fe.

3.1.1.2 TiN and Steels

Similar calculations were carried out for other TiN/steel systems. Results are included in Appendix E. Figure 3.3 shows the mole fraction of TiN in the TiN/steel-systems and the composition of TiN plotted against the carbon activity for 12 different steels at 1200 °C. The mole fraction of TiN in the system ranges from 0.102 to 0.118 for 316L and M2 respectively. In TiN, iron concentration ranges from 2 at. pct. to 6.5 at. pct. while carbon concentration ranges from 0.6 at. pct. to 7.2 at. pct. On the other hand, the concentrations of titanium and nitrogen remain essentially equal. As the diffusivities of iron and carbon in TiN are of the order of $10^{-17}$ m$^2$/s,$^{10}$ the actual content of iron and carbon in TiN is expected to be lower than the calculated equilibrium values during the short infiltration time.
Figure 3.3  Thermo-Calc calculation of mole fraction and composition of TiN in the TiN-steels systems. Data are extracted from Appendix E.

3.1.1.3  TiN and Cu-20Ni-20Mn

The reaction between TiN and Cu-20Ni-20Mn was also investigated using the same technique and procedure for the TiN/Fe calculation. 0.1 mole of TiN and 0.9 mole of Cu-20Ni-20Mn were input into Thermo-Calc using the SSOL and KP databases. Figure 3.4 shows that there is no reaction between TiN and Cu-20Ni-20Mn. Calculation of the composition of TiN also confirms the fact that Cu-20Ni-20Mn does not dissolve in TiN. The calculated solidus and liquidus of Cu-20Ni-20Mn are 1047 °C and 1077 °C respectively, with a very narrow solidification range of 30 °C. This is in excellent agreement with experimental values, where the solidus and liquidus are 1030 °C and 1060 °C respectively.\(^{11}\) Upon cooling, the ordered phase NiMn is predicted to form at around 825 °C, which is responsible for the age hardening of Cu-20Ni-20Mn.\(^{12}\) However, the actual order-disorder transformation temperature is known to be below 530
The hardening process and response for pure Cu-20Ni-20Mn and infiltrated steel parts will be discussed in Chapter 5.

![Graph showing phase mole fraction vs. temperature of TiN/Cu-20Ni-20Mn.]

**Figure 3.4** Phase mole fraction vs. temperature of TiN/Cu-20Ni-20Mn.

### 3.1.2 Experimental Test

Two simple experimental tests were done to confirm the chemical stability of TiN with an Fe substrate and with the Cu-20Ni-20Mn infiltrant.

#### 3.1.2.1 Test 1: TiN on Fe Plate

A 1-cm square iron plate (99.995% purity) with a thickness of 0.25 mm was coated with 3 μm-thick TiN by chemical vapor deposition (CVD). This coating on this Fe plate was done along with one of the TiN CVD batches of steel bars, which will be described in section 3.2. The TiN-coated Fe plate was encapsulated inside an argon-filled quartz tube. It was then annealed at 1200 °C for 1 hour inside an air furnace. The TiN-coated Fe plate was then cross-sectioned, mounted in epoxy, and polished for
examination under a scanning electron microscope (SEM). Composition analysis was done with the use of electron microprobe analysis (EMPA) and energy dispersive spectroscopy (EDS). Figure 3.5 shows the cross section of the TiN-coated plate. There is a clear interface between the TiN film and Fe plate. Only about 1 at. pct. of Fe was found in the TiN layer by EMPA. No trace of Ti and N was found in the Fe substrate. These results are in agreement with the prediction from computer calculation using ThermoCalc.

![Figure 3.5](image)

**Figure 3.5** Cross section of 3 μm thick TiN coating on Fe plate, after an annealing at 1200 °C for 1 hour.

3.1.2.2 Test 2: TiN Coated WC-Co Carbide Tooling Insert with Cu-20Ni-20Mn

A quick test of the reaction between TiN and Cu-20Ni-20Mn was done with a TiN-coated carbide tooling insert. The carbide insert from Valenite® is made of WC-12% Co, with a 4 μm thick TiN hard coating. The TiN-coated carbide insert was chosen as it was readily available and TiN adheres well to WC-Co. The thermodynamic stability of
TiN with WC-Co would not affect any reaction occurring on the other side at the TiN/Cu-20Ni-20Mn interface.

The carbide tooling insert was put inside an alumina crucible with a small chunk of Cu-20Ni-20Mn ingot. They were then heated to 1200 °C for 1 hour with a ramping rate of 8 °C/min inside a CM tube furnace. Forming gas (95 vol. pct. of Ar with 5 vol. pct. of H₂) was passed through the tube to maintain a reducing atmosphere throughout the experiment. A heating/cooling rate of 8 °C/min and the use of forming gas were used for all experiments described in this dissertation unless stated otherwise.

Figure 3.6 shows the cross section of the cooled specimen. The interfaces on both sides of the TiN coating are very sharp and there was negligible amount of elemental exchange between various substances. Thus, it confirms the chemical stability of TiN towards Cu-20Ni-20Mn.

![Figure 3.6](image)

**Figure 3.6** Cross section of 4 μm thick TiN coating on WC-12%Co, which was in contact with molten Cu-20Ni-20Mn at 1200 °C for 1 hour.
3.2 TiN on Flat Steel Substrates

After the successful results from the chemical stability test of TiN with Fe and Cu-20Ni-20Mn, the use of TiN as a diffusion barrier was then studied on flat steel substrates. Chemical vapor deposition of TiN on steel bars was used as it is the preferred choice of coating process for steel powders. The wetting of molten Cu-20Ni-20Mn to the TiN coating, adhesion, and reactions at the interfaces between Cu-20Ni-20Mn, TiN and steels were examined. TiN coating on flat steel substrates also simplifies the study of mechanical properties, which will be described in the next chapter.

3.2.1 Steel Substrates

Twelve common steel substrates covering a broad spectrum of alloying elements were used for the wetting experiment. Representatives from different groups of tool steels (H13, S7, M2, O1, A2 and D2) and stainless steels (17-4PH, 316L, 420 and 440C) were used. Pure iron, low-carbon steel (1018), and a typical alloy steel (4142) were also used for comparison. Table D.1 in Appendix D lists the compositions of the steel bars supplied by the vendors.

3.2.2 TiN Coating by CVD

Flat ground steel bars measured 1/4 × 1/2 × 2 inches were cut from factory stock. One end of the bar was milled to a cross section measuring 1/4 × 1/4 inches, representing the center of the gauge length of a tensile specimen. The bars were finely polished, with 0.05 μm alumina slurry in the final step. Coating of the polished bars was done by CVD from three different vendors\(^2\) according to the reaction in Eqn. 3.1. Typical processing temperature is 1000 °C and the gas feed proportions are TiCl\(_4\) (1-2 %); N\(_2\) (22-26 %); and

---

\(^2\) IonBond Inc. for 0.2 μm and 0.5 μm TiN coating; Ti-Coating for 3 μm TiN coating; and Toll Coating Service for 1 μm and 6 μm TiN coating.
H₂ (77-72 %). The average batch-thicknesses of the TiN coating in this study were 0.2 μm, 0.5 μm, 1 μm, 3 μm and 6 μm.

\[ 2 \text{TiCl}_4 + N_2 + 4 \text{H}_2 \rightarrow 2 \text{TiN} + 8 \text{HCl} \quad \text{(at 1000 °C)} \]  

**Eqn. 3.1**

### 3.2.3 Variation of TiN Thickness vs. Carbon Activity in Steels

The TiN-coated steel bars were cross-sectioned and polished. TiN coating thickness was measured by SEM. It was found that TiN thickness varied with different steel substrates from the same CVD batch process. For example, the thickness of the TiN film varied from 1.43 μm in 17-4PH to 3.86 μm in O1 steel in the CVD batch process intended for a 1 μm thick TiN coating. In order to investigate the substrate-effect on the growth of TiN film on steel bars, the carbon activities in different steels were calculated using Thermo-Calc. All the values were evaluated at 1000 °C, which corresponds to the deposition temperature of the TiN film. Figure 3.7 shows a plot of TiN film-thickness versus the carbon activity in the steel. There is a linear relationship between the TiN film thickness and the carbon activity.
Figure 3.7  Plot of TiN thickness versus carbon activity in steels for the CVD batch process intended for a 1 μm thick TiN coating.

3.2.3.1 Discussion

The linear relationship was also observed in the growth of CVD TiC films on steels.\textsuperscript{[14, 15]} It has been found that the thickness ($d_{TiC}$) of the TiC film can be described by a diffusion process\textsuperscript{[16]}:

$$d_{TiC} = at^{1/2}$$  \hspace{1cm} \text{Eqn. 3.2}

where $a$ depends on the carbon content in the gas phase and in the base material. The coefficient $a$ can be estimated for steels from

$$a = \gamma \alpha_c$$  \hspace{1cm} \text{Eqn. 3.3}

where $\alpha_c$ is the carbon activity in the steel and $\gamma$ is a constant. A high carbon activity promotes the growth of TiC film since carbon activity is a measure of the availability of
carbon and its tendency of reaction. Formation of TiC is thermodynamically favorable as it can lower the free energy of the system, and thus the carbon activity.

In the case of the TiN deposition on steels, the observed linear behavior suggests that carbon in the steel also assists the growth of TiN film. One possible explanation is that during the nucleation stage of the film, free carbon reacts with Ti-radical from the gas, forming small nuclei of TiC or possibly TiCN. The exact composition of the nuclei depends on the partial pressures of the reactants and temperature of the system. The formation of these compound nuclei on steel is thermodynamically more favorable than the formation of Ti nuclei on pure iron. It is speculated that as the nucleation barrier is lowered, nucleation rate increases and initiates a chain reaction: subsequent incoming Ti- and N-radicals grow faster on TiC or TiCN than on Fe because of the preferred affinity to TiN and TiC.

The aforementioned explanation is further supported from the study of ion-plated TiN on 304 stainless steel by Shieu et al.\(^{[17]}\) who found that during the ion-plating of TiN films on 304 stainless steel there is a deficiency of nitrogen near the TiN-steel interface. The early-deposited TiN layer is non-stoichiometric. This suggested that if more carbon is available in the early growth stage of TiN\(_x\) (\(x < 1\)), the conversion of Ti into TiC\(_x\)N\(_y\) (\(x, y < 1\)) can be faster, resulting in a thicker film.

In conclusion, carbon from the steel promotes the growth of TiN film. However, the availability of the carbon is related to the carbon activity in the steel rather than the actual carbon content. The reason is that in heavily alloyed steels like stainless steels (Cr > 12 wt. pct.), M2 (high Cr, Mo, and W content), and D2 (high C but also high Cr content), carbon is locked up in the carbides (e.g., M\(_6\)C in M2; M\(_2\)C\(_3\) in D2; and M\(_{23}\)C\(_6\) in 440C) or in the Cr-stabilized ferrite matrix (e.g., in 420 stainless steel). Therefore, such steels have low values of carbon activity and thus thinner TiN coatings. The effect of carbon activity is best seen by comparing M2 and O1 in Figure 3.7 with reference to their compositions in Table D.1 in Appendix D. Both steels contain about 0.9 wt. pct. of carbon. However, the TiN deposits on O1 are almost 70 percent thicker than M2. The
difference can be attributed to the high carbon activity in O1 as it is almost free of other alloying elements, with only 0.5 wt. pct. of Cr in it.

Careful examination of the as-deposited TiN coatings on steels revealed that an interfacial phase is present at the TiN/steel interface (Figure 3.8). However, no such interfacial phase was found at the TiN/Fe interface as shown in Figure 3.5. It is believed that the interfacial phase at the TiN/steel interface contains substantial amount of carbon, which may be the precursor to the rapid growth of TiN.

**Figure 3.8** Cross section of 1 μm batch TiN coating on M2 steel bar. TiN film thickness is 2.36 μm. Occasional TiN particles can be found on the film surface.
3.2.4 Wetting of Cu-20Ni-20Mn and Contact Angle Measurement

3.2.4.1 Experimental Procedures

Small pieces of Cu-20Ni-20Mn were placed on 1 cm square × 0.25 mm thick TiN-coated iron plates (99.995% purity). They were then heated to 1200 °C inside the tube furnace with standard condition mentioned in section 3.2.1. When the temperature reached 1200 °C, the system was cooled immediately to room temperature. Thus, the TiN coating was presumably in contact with molten Cu-20Ni-20Mn for about 30 min, assuming the Cu alloy completely melted at 1060 °C (liquidus) and solidified at 1030 °C (solidus).

3.2.4.2 Results and Discussions

The molten Cu-20Ni-20Mn wetted the TiN coating surfaces and smooth beads were formed on the TiN coatings. The samples were then cross-sectioned at the center of the bead and polished. Reactions at the Cu-20Ni-20Mn/TiN/Fe interfaces were studied and contact angle was measured with SEM.

Figure 3.9 shows the cross section of a Cu-20Ni-20Mn/TiN/Fe sample. The thickness of the TiN coating is 0.9 µm, which is expected from the 1 µm TiN CVD batch. The contact angle was found to be 10°. However, the contact angles varied among other samples. In general, the contact angle varied from 10° to 25°. The higher contact angle observed could be due to the oxide contamination on the TiN surface, which resulted in poorer wetting. Nevertheless, this is an encouraging result as it showed that the wettability of TiN is good for Cu-20Ni-20Mn infiltrant. Good wettability results in higher infiltration height, shorter infiltration time required, and reduced porosity in the infiltrated parts.
Figure 3.9  Cross section of Cu-20Ni-20Mn bead on 0.9 μm TiN-coated pure iron plate.

3.2.5 Reaction Experiment

3.2.5.1 Experimental Procedures

The reaction of Cu-20Ni-20Mn to TiN-coated steel was studied by inserting a thin plate (thickness ~ 1 mm) of Cu-20Ni-20Mn between two TiN-coated bars of the same steel substrates. The whole assembly was placed horizontally inside an alumina crucible and put inside a tube furnace with flowing forming gas. The system was then heated to 1200 °C with a ramping rate of 8 °C/min. The molten infiltrant wetted and joined the coated bars upon cooling, forming a tensile-test specimen (Figure 3.10). The tensile bars were subsequently used for the study of fracture strength and mode of fracture of the interfaces. Detailed descriptions of the tensile-test experiment and results will be presented in chapter 4. Some of the joined samples were cross-sectioned, mounted, and polished. The interactions at the interfaces between the infiltrant, the TiN diffusion barrier and the steel substrates were examined by SEM. Composition was analyzed using EMPA and EDS.
Figure 3.10  Joining of TiN-coated steel bars with Cu-20Ni-20Mn.

3.2.5.2 Results

Twelve different steel substrates mentioned in section 3.2.1 with various TiN thicknesses were examined by SEM. The reaction to molten Cu-20Ni-20Mn can be summarized into five categories, from ideal diffusion barrier behavior to complete failure. Table 3.1 shows the schematics and descriptions of these five categories of behavior.
<table>
<thead>
<tr>
<th>Category</th>
<th>TiN coating</th>
<th>Adhesion to steel</th>
<th>Reaction of steel with Cu-20Ni-20Mn</th>
<th>Schematics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Intact</td>
<td>Adhered to steel</td>
<td>No reaction</td>
<td><img src="Cu-20Ni-20Mn.png" alt="Schematic" /></td>
</tr>
<tr>
<td>2</td>
<td>Intact</td>
<td>Adhered to steel</td>
<td>Localized reaction zone</td>
<td><img src="Reaction_Zone.png" alt="Schematic" /></td>
</tr>
<tr>
<td>3</td>
<td>Intact</td>
<td>Adhered to steel</td>
<td>Continuous reaction zone</td>
<td><img src="Continuous_Reaction_Zone.png" alt="Schematic" /></td>
</tr>
<tr>
<td>4</td>
<td>Intact</td>
<td>Detached from steel</td>
<td>Continuous reaction zone</td>
<td><img src="Continuous_Reaction_Zone.png" alt="Schematic" /></td>
</tr>
<tr>
<td>5</td>
<td>Broken up</td>
<td>Detached from steel</td>
<td>Continuous reaction zone</td>
<td><img src="Continuous_Reaction_Zone.png" alt="Schematic" /></td>
</tr>
</tbody>
</table>

**Table 3.1** Summary of the interaction of Cu-20Ni-20Mn with TiN-coated steel bars.

Representative SEM micrographs of these five types of interactions are shown in Figure 3.11 to Figure 3.15:
**Figure 3.11** *Category 1:* 2.36 μm TiN on M2 steel with Cu-20Ni-20Mn. TiN coating is intact and adheres to the steel. No reaction between Cu-20Ni-20Mn and steel.

**Figure 3.12** *Category 2:* 0.52 μm TiN on H13 steel with Cu-20Ni-20Mn. TiN coating is intact and adheres to the steel. Localized reaction zone is present at the site where the TiN diffusion barrier has an opening.
Figure 3.13  Category 3: 0.75 μm TiN on 440C steel with Cu-20Ni-20Mn. TiN coating is intact and adheres to the steel. However, continuous reaction zone approximately 15 μm thick is seen beneath the TiN diffusion barrier.

Figure 3.14  Category 4: 2.39 μm TiN on O1 steel with Cu-20Ni-20Mn. TiN coating is intact but detached from the steel. Continuous reaction with steel is seen beneath the lifted-off TiN diffusion barrier.
Figure 3.15  *Category 5*: 0.2 μm TiN on 17-4PH stainless steel with Cu-20Ni-20Mn. TiN coating is broken up and detached from the steel. Massive reaction with steel occurs due to the failure of the TiN diffusion barrier.
<table>
<thead>
<tr>
<th>Steel</th>
<th>0.2 μm</th>
<th>0.5 μm</th>
<th>1 μm</th>
<th>3 μm</th>
<th>6 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>17-4PH</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>420</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>1018</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>H13</td>
<td>5</td>
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<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>4142</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>4</td>
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<td>S7</td>
<td>2</td>
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<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>M2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>A2</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>440C</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>D2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

**Table 3.2** Summary of the reactions of Cu-20Ni-20Mn to TiN-coated steel bars, according to the categories illustrated in Table 3.1. Those combinations of coating thickness and steel substrates yielding good diffusion-barrier results are highlighted.

Table 3.2 summarizes all the results according to the categories illustrated in Table 3.1. Those thickness-substrate pairs with good diffusion-barrier results fall into category 1, which are highlighted in Table 3.2. The average score was calculated based on the occurrence of each category in that batch. In general, a lower value indicates a better diffusion barrier in that batch.

For the 5 different TiN batch thicknesses studied here, the 1-μm batch TiN coating yielded the best result for diffusion-barrier behavior. In this batch, most of the substrates fall into category 1 where the TiN coating adhered well to all substrates and formed a continuous intact diffusion barrier. No reaction between Cu-20Ni-20Mn and
steel substrates occurred. For H13 and 4142, a localized reaction zone was found. The hemispherical shape of the reaction zone indicates the reaction originated from a point source through the TiN diffusion barrier. Close examination revealed that the TiN coating was broken at that specific location.

For those two batches with thickness larger than the 1-\(\mu\)m batch, the results were the worst. Most of the substrates fall into category 4 where the TiN coating was intact but detached from the substrate, apparently due to spallation. Molten Cu-20Ni-20Mn could easily get underneath the lifted-off region and react with the steel substrates. However, it should be noted that the superior performance of the 6 \(\mu\)m TiN-coated M2 stood out from the rest.

When the thickness of the TiN diffusion barrier was reduced below about 0.5 \(\mu\)m, there was a steep deterioration of the performance. The 0.5 \(\mu\)m batch had mixed results, which were generally dominated by category 2 features. There were many localized reaction zones adjacent to the TiN coating, which indicates the possibility of the presence of pinholes or loose structures on the TiN coating. The 0.2 \(\mu\)m batch was even worse than the 0.5 \(\mu\)m batch in this regard. For those substrates with low carbon content, like 316L, 17-4PH, and 440C, the TiN coating was broken up and massive reaction occurred between Cu-20Ni-20Mn and the steel substrates. This category 5 feature indicates the lower limit of useful TiN coating thickness has been reached.

Comparing the substrates, the top performers are 17-4PH, H13, S7, M2, and D2. The TiN coatings all adhered well to the substrates for various thicknesses and exhibited good protection. Furthermore, M2 stands out from the rest of the group and is the only substrate that has good adhesion and protection from the TiN diffusion barriers of all thicknesses. It should be noted that M2 is characterized by its low chromium, high carbon, and high alloy-element (Mo, W, and V) composition. The presence of various carbides in the substrate could help to stabilize the deposited TiN film.
3.2.5.3 Discussion

In Chapter 2, the minimum thickness of TiN diffusion barrier was estimated to be about 0.3 μm based on diffusion length estimation. Thermodynamic consideration also suggested a similar value of the minimum thickness of TiN, which is in the sub-micron range. If the TiN thickness is thinner than this value, like in the 0.2 μm batch, Cu-20Ni-20Mn can react with the steel substrates through diffusional process or actual reaction with the TiN coating itself. Moreover, the probability of the presence of pinholes and other imperfections arising from the coating process increases with a decreasing coating thickness. It is suggested that the general failure observed in the 0.2 μm batch specimen is related to the excessive pinholes and defects on the TiN diffusion barrier that allow the molten Cu-20Ni-20Mn to come into contact with the steel substrates.

The majority of category 2 features observed in the 0.5 μm batch indicates that the TiN diffusion barrier is thick enough to prevent global diffusional attack of Cu-20Ni-20Mn. However, pinhole density is high enough so that localized reaction zones originating from the pinholes could still result. An improved CVD-coating process could lower the pinhole density for thinner coating thickness.

The excellent results from the 1 μm batch TiN coating could arise from the disappearance of pinhole defects with the increased thickness of the coating. However, as the thickness further increased, both accumulated intrinsic stresses and extrinsic stresses also increased. These stresses could lead to spallation, which is mainly observed in the 3 μm batch and the 6 μm batch.

3.2.6 Acid Test

3.2.6.1 Experimental Procedures

In order to investigate the presence of pinhole defects in thin coatings, an acid test was used. A concentrated hydrochloric acid solution (50 vol. pct. HCl with 50 vol. pct. of
H₂O) was prepared, which preferentially attacks the steel substrates. As-received TiN-coated bars were immersed into the acid for a duration ranging from 1 hour to 1 day. At the end of the acid cycle, the samples were rinsed and dried. Both surface morphology and cross section were examined under SEM.

### 3.2.6.2 Results and Discussion

When the TiN-coated steel bars were immersed into the acid, gas bubbles were observed, showing the reaction of HCl with steel, forming H₂ gas. However, the onset time and rate of gas evolution depended on the TiN thickness and steel substrates. Thick coatings (1 μm, 3 μm, and 6 μm batches) did not have much reaction with the acid. A small amount of initial gas evolution in these batches is due to the adhered gas on the samples. For the 0.5 μm and 0.2 μm batches, continuous gas evolution was observed for some specimens.

Figure 3.16 shows the cross section of 174-PH steel from the 1 μm TiN batch that has been in contact with acid for 5 hours. No observable erosion was observed on the TiN coating surface. The cross section also reveals no evidence of pinhole defects. This result in general applies to all coated substrates in the 1 μm batch.

![Cross section of 17-4PH stainless steel from the 1 μm TiN batch after immersion in 50% HCl for 5 hours.](image)

**Figure 3.16** Cross section of 17-4PH stainless steel from the 1 μm TiN batch after immersion in 50% HCl for 5 hours.
Figure 3.17 and Figure 3.18 are the surface micrographs of M2 steel from the 0.5 μm and 0.2 μm batches respectively. They have been immersed in the acid for 1 day. For the 0.5 μm TiN-coated M2, no detectable pinholes were found. On the other hand, the 0.2 μm TiN-coated M2 reveals the presence of pinholes. The locations of pinholes are marked by the island region in Figure 3.18. The acid reacted with the steel substrates through the pinholes and damaged the surrounding TiN layer. The average pinhole separation is about 300 μm, corresponding to a pinhole density of $1.1 \times 10^5$ μm$^2$. This shows that for the M2 substrate, there is a transition from pinhole to no-pinhole TiN coating when the TiN thickness is increased from 0.2 μm to 0.5 μm. This explains the observation of transition from localized reaction zone to ideal diffusion barrier behavior in the reaction experiment with molten Cu-20Ni-20Mn as shown in Table 3.2.

![Image of surface micrograph of TiN-coated M2 steel](image)

**Figure 3.17** Surface of TiN-coated M2 steel from the 0.5 μm TiN batch after immersion in 50% HCl for 1 day. Horizontal lines were scratch remains from surface polishing of the M2 steel substrate before the TiN coating.
Figure 3.18 Surface of TiN-coated M2 steel from the 0.2 \( \mu \text{m} \) TiN batch after immersion in 50\% HCl for 1 day.

In conclusion, the observation of continuous or localized reaction zone observed in the reaction experiment with molten Cu-20Ni-20Mn could be attributed to the presence of pinholes in the as-deposited TiN coatings on the steel bars. The molten Cu-20Ni-20Mn initiated the reaction with steels at the pinhole and the degree of reaction depends on the pinhole density, which is TiN-thickness related.

3.2.7 Long Contact-Time Reaction Test

The excellent diffusion barrier behavior observed in the 1 \( \mu \text{m} \) batch prompted a more demanding test for the TiN diffusion barrier. With the standard heating cycle in the reaction test with Cu-20Ni-20Mn, the specimens were in contact with molten Cu-20Ni-20Mn for about 30 min. The liquid-contact time was extended for several steel substrates from the 1 \( \mu \text{m} \) batch in order to test the service limit of the TiN diffusion barrier. Figure 3.19 shows a 17-4PH stainless steel from the 1 \( \mu \text{m} \) batch that was in contact with molten Cu-20Ni-20Mn at 1200 \( ^\circ \text{C} \) for 3 hours. The coating was intact and adhered well to the
substrate. No reaction between Cu-20Ni-20Mn and steel occurred. The actual thickness of the TiN coating on the steel is 2 μm. From the parabolic scaling of diffusion length, or diffusion-controlled reaction, it is estimated that a coating thickness of 0.8 μm is enough if the specimen is required to be in contact with the molten Cu-20Ni-20Mn for just 30 min. In view of this, a gated infiltration technique was developed for the use with thin diffusion barrier. Gated infiltration, which will be described in the following sections, requires only fractions of the standard infiltration time, yet enables a full infiltration of a sintered powder skeleton. The use of thinner diffusion barriers is beneficial as it can lower the cost and retain the original material properties of the infiltrated part.

![Figure 3.19](image)

**Figure 3.19** Cross section of 17-4PH stainless steel from the 1 μm TiN batch in contact with molten Cu-20Ni-20Mn at 1200 °C for 3 hours.

### 3.3 TiN on Sintered Steel Powder Skeleton

With the success of TiN diffusion barrier that prevented the interdiffusion and reaction between flat steel substrates and molten Cu-20Ni-20Mn, TiN diffusion barrier
was then applied to sintered steel powder skeletons. Results in section 3.2 suggests that the ideal TiN coating thickness should be in the vicinity of 1 μm, with a minimum thickness of about 0.5 μm. This serves as the guideline for steel-powder skeleton coating.

3.3.1 TiN Coating Process

Three tool steel powders (H13, M2, and D2) and three stainless steel powders (17-4PH, 420, and 440C) were selected for the study because they are commonly used and readily available. Their compositions, which cover a wide range of carbon content, are listed in Table D.2 in Appendix D. The nominal size of the powders are around 50 μm, with the exception of D2 tool steel, which is 75 μm. Steel powders were poured into alumina crucible measuring 1/4 x 3/4 x 4 inches. The powders were tapped to ensure a uniform powder distribution and high green density. Sintering was done in a tube furnace by heating to 1200°C for an hour in forming gas (95% Ar and 5% H₂). The forming gas was used to reduce the oxides on the steel powders and assist sintering. The ramping and cooling rates were 8 °C/min.

The sintered powder skeletons have good green strengths and could be handled easily. The sintered powder skeletons were then coated by a thin layer of TiN by CVD, which was done by IonBond Inc. In the initial test run, the coating process that would result in a TiN target thickness of 2 μm for flat steel substrates was used, to take into account that the sintered steel skeletons were porous and the effective area was larger than the flat substrates. There could be a "loading" effect to the CVD system, which results in thinner coating in the interior of the skeleton. Thus, the expected TiN thickness on the steel skeletons would be smaller and fall in the desired range of 0.5 to 1 μm.

3.3.2 TiN-Coated Steel Powder Skeletons

The TiN coating on the steel skeleton was examined by breaking the coated skeleton and observing with SEM. The uniformity of the coating, the coating thickness,
and the effect to skeleton geometry was studied. Figure 3.20 shows the broken surface of the TiN-coated D2 steel powder skeleton with a targeted batch thickness of 2 \( \mu m \) for flat steel substrates. Figure 3.21 is the neck region between two TiN-coated D2 powders. Both micrographs show that the TiN coating covered uniformly all powder surfaces including the neck region.

**Figure 3.20** Fractured surface of TiN-coated D2 steel powder skeleton intended for a batch thickness of 2 \( \mu m \) for flat steel substrates. Circular white patches on the powders are the broken neck regions joining adjacent powders before fracture.
Figure 3.21  Neck region of the TiN-coated D2 steel powder skeleton in Figure 3.20.

Figure 3.22  Broken neck region of TiN-coated D2 steel powder skeleton, exposing the cross section of the TiN coating.
Close examination of the broken neck region (marked by white patches on the TiN-coated powders in Figure 3.20) revealed the ductile fracture surface of the steel and the cross section of the TiN coating, which enabled a direct measurement of the coating thickness (see Figure 3.22). The TiN coating thickness on D2 steel skeleton was then estimated to be 0.21 μm only. Comparing to the targeted batch thickness of 2 μm, the coating thickness on the skeleton was only about 10% of that on flat steel substrates. Similar results were obtained for other steel powder skeletons. The TiN coatings were uniform on all powders. The thicknesses of the coatings on different steel skeleton were measured in the same way as the D2 steel. Table 3.3 shows the average TiN coating thickness on different steel skeletons. It shows that for those steel skeletons with lower carbon content than that in D2, the TiN thickness was even smaller. The coating thickness for these low-carbon skeletons was only about 5% of that on flat steel substrates.

<table>
<thead>
<tr>
<th>Steel</th>
<th>17-4PH</th>
<th>H13</th>
<th>420</th>
<th>M2</th>
<th>440C</th>
<th>D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN thickness (μm)</td>
<td>0.09</td>
<td>0.1</td>
<td>0.12</td>
<td>0.11</td>
<td>0.1</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 3.3 TiN thickness on different steel powder skeleton for a target batch thickness of 2 μm on flat steel substrates.

3.3.3 Gated Infiltration (Thin TiN Diffusion Barrier)

3.3.3.1 Experimental Procedures

Infiltrations of the TiN-coated skeletons with molten Cu-20Ni-20Mn were then performed in the tube furnace to test the actual performance of the TiN coating as a diffusion barrier. In the conventional infiltration process, the steel skeleton is heated together with the solid infiltrant in the same crucible. When the infiltrant melts, it starts infiltrating into the skeleton as the temperature keeps rising to the infiltration temperature, which is usually about 100 °C higher than the melting point of the infiltrant. The infiltrating skeleton and the infiltrant are held at the infiltration temperature for an
hour to ensure complete infiltration of the voids in the skeleton. However, for reactive materials systems, the contact time of the skeleton to molten infiltrant is too long and results in strong erosion. In view of this, gated infiltration was used for the subsequent infiltration of the TiN-coated skeletons.

In gated infiltration, the powder skeleton and the infiltrant are separated but heated together in the furnace until thermal equilibrium at the infiltration temperature is reached. An actuator coupled to the outside of the furnace is used to trigger the contact of the skeleton with the molten infiltrant. This can be done in two ways: 1) by removing a "gate" between the skeleton and the infiltrant or 2) by bringing the skeleton into contact with the molten infiltrant. In the current experiment, the latter method was adopted.

![Schematic of gated infiltration](image)

**Figure 3.23** Schematic of gated infiltration. The TiN-coated skeleton is brought to contact with molten infiltrant after thermal equilibrium is established.

A schematic of the experimental setup for the gated infiltration of TiN-coated steel powder skeletons with Cu-20Ni-20Mn infiltrant is shown in Figure 3.23. The crucible, steel skeleton, and infiltrant were all placed inside the tube furnace with running forming gas. The whole setup was then heated to the infiltration temperature of 1200 °C.
at a ramping rate of 8 °C/min. Thermal equilibrium was reached after 30 min at 1200 °C. Then the actuator was pushed against the slider, which supported the TiN-coated steel skeleton. Eventually, the skeleton was dropped into the molten Cu-20Ni-20Mn infiltrant and infiltration readily occurred. After five min, the cooling cycle started and the whole setup was cooled to room temperature at a rate of 8 °C/min.

The infiltrated skeletons were then sectioned, mounted, polished, and examined under SEM. Other sections were cut and heat treated to study the hardening response. Hardening results are presented in Chapter 5.

3.3.3.2 Results

For all the six TiN-coated steel skeletons, full infiltration was observed for all the tool steels (H13, M2, and D2). On the other hand, the stainless steels (17-4PH, 420, and 440C) did not have good infiltration. Only the lower part of the skeleton in contact with the infiltrant was infiltrated.

Figure 3.24 shows the cross sections of the TiN-coated steel skeletons after infiltration. The thin dark layer on all the powders is the TiN diffusion barrier. Although there was no massive reaction between the steel skeletons and the infiltrant, two kinds of reaction zones were observed: 1) A uniform reaction zone with a penetration depth on the order of 5 μm beneath the TiN diffusion barrier in the steel powder, and 2) Clusters of reaction zones outside the TiN diffusion barrier with sizes on the order of 10 μm. The uniform reaction zone near the powder surface indicated that the TiN diffusion barrier was not thick enough to prevent interdiffusion of the steel and Cu-20Ni-20Mn. This is expected as the TiN coating thickness was only 0.1 to 0.2 μm thick, which is smaller than the estimated minimum thickness requirement of 0.3 μm. On the other hand, the reaction clusters outside the TiN coating suggested that there were weak spots on the TiN coating where localized fast diffusion and reaction occurred.
Figure 3.24  Cross sections of the TiN-coated steel skeletons with Cu-20Ni-20Mn infiltrant. (a)-(c): H13, M2, and D2 steel respectively. (d)-(e): higher magnifications near the edge of the powders. The thin dark layer on the powder surface is the TiN diffusion barrier. Average thickness is 0.1 to 0.2 μm. Clusters of reaction zones can be seen on the powder surface.
Chapter 3  

Titanium Nitride Diffusion Barrier

The compositions of the steel skeletons, the infiltrants, and the reaction zones inside and outside the TiN diffusion barrier were determined with microprobe. Results are tabulated in Table 3.4 to Table 3.6. Composition analysis shows that the reaction zone is a mixture of steel and infiltrant. However, it is rich in Fe, Ni and Mn. As a result, the infiltrant was depleted of Ni and Mn, with three to five wt. pct. of Fe dissolved in it. Other alloying elements in the steel did not have much participation in the diffusion and reaction with Cu-20Ni-20Mn. These alloying elements are presumably locked up in the carbides in the steel powders. The consequence of the Fe impurity in Cu-20Ni-20Mn and the preferential depletion of Ni and Mn in the infiltrant would result in a change in infiltrant hardening response. This will be addressed in Chapter 5.

<table>
<thead>
<tr>
<th>Composition in wt. pct.</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>H13 powder</td>
<td>91.2</td>
<td>4.5</td>
<td>1.5</td>
<td>1.6</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uniform reaction zone</td>
<td>54.7</td>
<td>15.9</td>
<td>10.4</td>
<td>11.2</td>
<td>4.1</td>
<td>1.3</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Cluster reaction zone</td>
<td>37.0</td>
<td>33.2</td>
<td>12.6</td>
<td>13.5</td>
<td>1.7</td>
<td>0.6</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Infiltrant</td>
<td>5.0</td>
<td>69.9</td>
<td>8.8</td>
<td>14.9</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 3.4  Composition of infiltrated TiN-coated H13 steel skeleton.

<table>
<thead>
<tr>
<th>Composition in wt. pct.</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2 powder</td>
<td>77.4</td>
<td>4.5</td>
<td>5.2</td>
<td>6.9</td>
<td>3.6</td>
<td>4.8</td>
<td>2.3</td>
<td>10.7</td>
</tr>
<tr>
<td>Uniform reaction zone</td>
<td>63.0</td>
<td>4.2</td>
<td>5.2</td>
<td>6.9</td>
<td>3.6</td>
<td>4.8</td>
<td>2.3</td>
<td>10.7</td>
</tr>
<tr>
<td>Cluster reaction zone</td>
<td>63.8</td>
<td>8.9</td>
<td>8.7</td>
<td>8.6</td>
<td>3.3</td>
<td>1.6</td>
<td>0.9</td>
<td>10.7</td>
</tr>
<tr>
<td>Infiltrant</td>
<td>3.7</td>
<td>78.6</td>
<td>3.8</td>
<td>11.5</td>
<td>0.4</td>
<td>0.5</td>
<td>0.3</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 3.5  Composition of infiltrated TiN-coated M2 steel skeleton.

<table>
<thead>
<tr>
<th>Composition in wt. pct.</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2 powder</td>
<td>86.3</td>
<td>11.8</td>
<td>0.8</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uniform reaction zone</td>
<td>58.1</td>
<td>10.1</td>
<td>12.7</td>
<td>11.2</td>
<td>7.9</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Cluster reaction zone</td>
<td>49.1</td>
<td>16.0</td>
<td>19.5</td>
<td>11.7</td>
<td>3.1</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Infiltrant</td>
<td>4.7</td>
<td>72.5</td>
<td>8.7</td>
<td>13.4</td>
<td>0.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 3.6  Composition of infiltrated TiN-coated D2 steel skeleton.
3.3.4 Acid Test

In order to study the origin of the reaction zones in the infiltration experiment, an acid test similar to that described in section 3.2.6 was performed. The as-received TiN-coated steel skeletons were immersed in a concentrated hydrochloric acid solution (50 vol. pct. HCl with 50 vol. pct. H₂O) for 30 min. The samples were then rinsed and dried. Surface morphology of the TiN coating and steel powders was examined under SEM. Figure 3.25 shows the comparison between different steel powders.

If there were defects or pinholes on the TiN-coated steel powders, the acid would preferentially attack the steel substrates through these pinholes. Figure 3.25 shows that many pinholes were present on the stainless steel powder skeletons. However, no observable pinholes were found on the tool-steel powder skeletons. A longer immersion time revealed few pinholes on the tool-steel powder skeletons. This matched the observation in the infiltrated steel powder skeletons.
Figure 3.25 Surface of TiN-coated steel skeletons after immersion in 50% HCl for 30 min. Pinholes were revealed as the acid preferentially attacked the steel powder, leaving holes on the powder surfaces.
3.3.5 Discussion

The observation of pinholes and reaction zones on the TiN-coated steel skeletons is consistent with that on the TiN-coated flat steel bars. The thickness of the TiN diffusion barrier on these steel skeletons was only 0.1 to 0.2 μm. This is smaller than the estimated minimum thickness requirement of 0.3 μm from section 2.5.2, which considered the diffusion length of the elements through the TiN coating at 1200 °C for 30 min. Thus, uniform diffusion through the TiN occurred. For a diffusivity of $1 \times 10^{-17}$ m$^2$/s in TiN, the time of diffusion through a 0.1 μm thick TiN coating is estimated to be 4 min according to Eqn. 3.4:

$$h = 2\sqrt{Dt}$$

Eqn. 3.4

For a total diffusion time of 30 min, there would be a diffusion inside the steel powders in the remaining 26 min. For a typical diffusivity of $1 \times 10^{-14}$ m$^2$/s in the steel, the penetration depth of the uniform reaction zone in the powder is found to be about 8 mm. This is in good agreement of the measured penetration depth of the reaction zone in the powders as shown in Figure 3.24.

On the other hand, the reaction experiments on flat steel bars in section 3.2.5 predicted that localized reaction zones could form when the TiN coating thickness is less than approximately 0.5 μm. Acid test of the 0.2 μm TiN-coated flat M2 steel bar in section 3.2.6 also confirmed the presence of pinholes on the TiN coating (Figure 3.18).

The partial infiltration of some specimens, especially the TiN-coated stainless steel skeletons, could be due to the blocking of infiltrant by the reaction zone clusters outside the TiN coating. The new phase in the reaction zone contained about 50% of Fe. It is expected to a solid phase at the infiltration temperature. This was verified with a ThermoCalc calculation, which predicted that solid Fe-rich phase will form if there are more than 20 at. pct. of Fe in Cu-20Ni-20Mn at 1200 °C. Another factor that contributed to the poor infiltration of the stainless steel skeletons could be due to the native oxide on the stainless steel powders. This could change the chemistry of the deposited TiN film and thus altered the wetting behavior of the molten Cu-20Ni-20Mn on these skeletons.
In conclusion, although there were localized reactions between the steel skeletons and the Cu-20Ni-20Mn infiltrant through the pinholes on the TiN diffusion barrier, the result was encouraging. No massive reaction between the steel powders and Cu-20Ni-20Mn infiltrant occurred. The geometry of the TiN-coated skeleton was maintained. In view of the successful result of the TiN-coated flat steel bars, the thickness of the TiN coating on the steel skeleton was increased in the second batch. It was expected that the optimum thickness of 1 μm could be reached by changing the CVD coating process.

3.3.6 Gated Infiltration (Thick TiN Diffusion Barrier)

3.3.6.1 Experimental Procedures

The sintering of steel powders, the coating of TiN diffusion barrier, and the infiltration procedures were the same as before. However, the coating recipe was changed for a TiN target thickness of 10 μm on flat steel substrates. From the experience of the previous batch coating of steel skeletons, the effective TiN thickness on the steel skeleton was about 5 to 10 percent of that on flat steel substrates. Thus, it was expected that the TiN thickness in this batch would be 0.5 to 1 μm.

3.3.6.2 Results

Full infiltration was observed for D2 tool steel. However, H13 and M2 tool steels only had good infiltration on the outside surface of the skeleton bars, while the interior was not infiltrated. The skin depth of the infiltration front from the surface was about 5 mm. As before, the stainless steels (17-4PH, 420, and 440C) did not have good infiltration. Infiltration only occurred near the base of the skeleton, which was in contact with the molten Cu-20Ni-20Mn.

Figure 3.26 shows the TiN-coated D2 steel skeleton bar after infiltrating with Cu-20Ni-20Mn. There was no distortion or erosion of the specimen and the inscribed
marking on the skeleton bar is clearly shown in the picture. The role and effectiveness of the TiN diffusion barrier can be seen by comparing the TiN-coated skeleton with the uncoated skeleton in Figure 3.27. In Figure 3.27, there is massive erosion and distortion of the steel skeleton due to the rigorous reaction with the molten Cu-20Ni-20Mn infiltrant.

**Figure 3.26** TiN-coated D2 steel skeleton with Cu-20Ni-20Mn infiltrant. No distortion and or erosion was observed.

**Figure 3.27** Uncoated D2 steel skeleton with Cu-20Ni-20Mn infiltrant. Massive distortion and erosion due to reaction with molten Cu-20Ni-20Mn infiltrant.
The thickness of the TiN coating on each steel skeleton was determined from the cross section of the specimens. Table 3.7 lists the result of measured TiN thicknesses on different steel skeletons. The TiN thickness agreed with the predicted range of 0.5 to 1 μm.

<table>
<thead>
<tr>
<th>Steel</th>
<th>17-4PH</th>
<th>H13</th>
<th>420</th>
<th>M2</th>
<th>440C</th>
<th>D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN thickness (μm)</td>
<td>0.5</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Table 3.7** TiN thickness on different steel powder skeleton for a target batch thickness of 10 μm on flat steel substrates.

There was no uniform reaction zone inside the powders, which showed that the TiN coating is thick enough to prevent global interdiffusion of steel and Cu-20Ni-20Mn. The size and the density of reaction zones outside the TiN coating were also reduced considerably with a thicker TiN diffusion barrier. The micrograph of the TiN-coated D2 steel skeleton in Figure 3.28 is a representative of all the steel skeletons except H13 tool steel, which did not show any reaction zones.

**Figure 3.28** Cross section of the TiN-coated D2 steel skeleton infiltrated with molten Cu-20Ni-20Mn infiltrant.
For the TiN-coated H13 steel skeleton, no observable reaction zone was found on the powder surface (see Figure 3.29). Figure 3.30 shows the details near the neck region between two steel powder particles. It shows that the TiN coating is pinhole-free, conformal and uniform on the powder surface. As a concluding remark, the uncoated H13 skeleton with Cu-20Ni-20Mn infiltrant is also shown in Figure 3.31 for comparison. Without the TiN diffusion barrier, the Cu-20Ni-20Mn infiltrant reacts strongly with steel and causes massive reaction and erosion.

Figure 3.29 Cross section of the TiN-coated H13 steel skeleton infiltrated with molten Cu-20Ni-20Mn infiltrant.
Figure 3.30  The TiN coating on the H13 steel skeleton is pinhole-free, conformal and uniform.

Figure 3.31  Cross section of the uncoated H13 steel skeleton infiltrated with molten Cu-20Ni-20Mn infiltrant.
3.4 SUMMARY

TiN is an effective diffusion barrier to prevent reaction between both flat and powder steel substrates and the molten Cu-20Ni-20Mn infiltrant. The optimum thickness of the TiN coating was determined to be about 1 μm. For thicknesses below 0.5 μm, defects such as pinholes on the TiN coating hindered its usefulness. Localized reaction zone resulted at the pinhole sites. If the TiN coating is thinner than 0.3 μm, global uniform diffusion through the TiN coating into the steel powders occurred. Elemental exchange between the substrate and the infiltrant mainly of Fe, Ni, and Mn resulted in a change in the Cu-20Ni-20Mn composition. The hardening behavior of the infiltrant would then be affected accordingly.

For the infiltration of TiN-coated steel skeletons with a TiN thickness from 0.1 to 0.2 μm, full infiltration occurred for tool steel substrates while stainless steel substrates did not give good infiltration. For thicker TiN coatings (0.5–0.8 μm), only D2 tool-steel skeleton had full infiltration. M2 and H13 tool-steel skeletons only had partial infiltration on the skeleton surface with an average infiltration depth of 5 mm. The stainless steel skeletons did not have good infiltration at all. The reason of poor infiltration could be due to the blocking of the Cu-20Ni-20Mn infiltrant by the solid phase in the reaction zone, which is a mixture of Fe and Cu-20Ni-20Mn. D2 steel skeletons always have the best infiltration, which may be due to the larger average powder size and wider fluid-flow channels between the powders. Another reason of the poor infiltration could be due to the oxide formation on the TiN coating as it heated up to the infiltration temperature.

The most encouraging result is the 0.8 μm TiN-coated H13 steel skeleton. There was no reaction zone on the powder surface. This could be due to its slightly thicker TiN coating than the that of other steels, which were about 0.6 μm. It is expected that further increasing the TiN coating thickness to approximately 1 μm will result in improved diffusion barrier behavior for more steel systems.
3.5 References


CHAPTER 4 TENSILE TEST AND FRACTURE STRENGTH

In metal tooling applications, mechanical properties such as fracture strength and hardness are important parameters in determining tool performance and service life. A high hardness usually results in a better wear resistance.\textsuperscript{[1]} This is especially important in metal tooling for injection molding applications, which is a major use of 3DP-fabricated metal parts. In Chapter 4 and Chapter 5, the effects of the addition of a TiN diffusion barrier on the mechanical properties of 3DP metal parts are presented. In this chapter, the TiN-coated tensile bars joined end-to-end as described in Chapter 3 were used to determine the fracture strength and mode of fracture. Hardening responses of Cu-20Ni-20Mn, steel substrates, and infiltrated tool-steel skeletons will be presented in Chapter 5.

4.1 EXPERIMENTAL PROCEDURES

Steel bars with TiN coatings of different thickness as described in Chapter 3 were used to determine the fracture strength and mode of fracture of the interfaces between Cu-20Ni-20Mn, the TiN diffusion barrier, and various steel substrates. The bars measured $1/4 \times 1/2 \times 2$ inches. One end of the bar was milled to a cross section of $1/4 \times 1/4$ inches, representing the center of the gauge length of a tensile specimen. After coating with a thin layer of TiN, two bars were joined together by inserting a thin plate (thickness $\sim 1$ mm) of Cu-20Ni-20Mn between them. The assembly was placed horizontally inside an alumina crucible and put inside a tube furnace with running forming gas. The system was then heated to 1200 °C with a ramping rate of 8 °C/min. The molten infiltrant wetted and joined the coated-bars upon cooling, forming a tensile test specimen (Figure 4.1). The dimensions of the joined bars follow that outlined in the ASTM E8 specifications.\textsuperscript{[2]}
Figure 4.1  Joining of TiN-coated steel bars with Cu-20Ni-20Mn.

The tensile bars were then subjected to tensile loading with an Instron tensile testing machine. The load was applied through the pins passing through the holes near the end of the bar, with a typical strain rate of the order of 0.01/min. The load-displacement curve of the tensile bar was monitored until the bar was pulled apart. The color, texture, and morphology of the fracture surfaces were studied with an optical microscope and SEM. Ideally, the cross section of the joined bar should be $1/4 \times 1/4$ inches. However, the molten infiltrant may not fill all the space in the gap during the joining stage. The true cross sectional area of the fracture surface was measured by a caliper after the tensile test. Results showed that the measured cross sectional area was at least 90% of the maximum
cross sectional area. Fracture strength of the interface was then calculated by dividing the load at which the tensile bar broke by the measured cross sectional area of the fracture surface.

4.2 Fracture Strength

All the load-displacement curves were linear up to the point at which the tensile bars were broken. Little or no yielding was observed. Figure 4.2 shows the stress-strain curve from the tensile test for a 0.2 μm TiN-coated D2 tensile specimen, which is typical of all tensile specimens. Table 4.1 shows the fracture strength of all the tensile bars obtained from the tensile test. The five highest values in each batch are highlighted. Among all the steel substrates, 17-4PH, H13, 4142, S7, 440C, and D2 consistently have high values of fracture strength in all batches. The result in Table 4.1 is also plotted in Figure 4.3 to illustrate the dependence of fracture strength on TiN coating batch thicknesses and steel substrates.

![Stress-Strain Curve](image)

**Figure 4.2** The stress-strain curve for the 0.2 μm TiN-coated D2 steel tensile bar from the tensile test.
Table 4.1 Fracture strength of TiN-coated steel bars jointed by Cu-20Ni-20Mn. The five highest values in each batch are highlighted.

From Figure 4.3, it is readily seen that fracture strength generally increased with a decrease in the TiN coating thickness. Both the 0.2 μm batch and 0.5 μm batch have much higher average fracture-strength values than the thicker coatings. The distribution of fracture strength in the 0.2 μm batch has a narrow range of 300 MPa to 500 MPa while the 0.5 μm batch has a broader range (200 MPa to 550 MPa). The average fracture strength for both the 1 μm and 6 μm batch is around 200 MPa. However, the 3 μm batch has an average value of only 100 MPa. Half of the coated steel substrates in this batch even have fracture strength less than 50 MPa.
Figure 4.3 Relation of fracture strength to TiN thicknesses and substrates. Stainless steels are represented by solid symbols. Tool steels and others are represented by outlined symbols.

4.3 MORPHOLOGY OF THE FRACTURE SURFACE

The fracture surfaces of all the tensile specimens were examined by optical microscopy and SEM. In general, both fracture surfaces were smooth, shiny, and golden in color, indicating that fracture propagated along a plane in the middle of the TiN coating. The sharp fracture interfaces also suggested that the mode of tensile-test fracture was brittle in nature. However, the fracture surface became more complex for those specimens with thinner TiN coating and higher fracture strength. The morphology and mode of fracture can be grouped into three categories according to the fracture-strength values.
4.3.1 Low Fracture Strength

For the specimens with thicker TiN coatings that have fracture-strength values roughly lower than 200 MPa, fracture occurred at the TiN coating between the steel substrate and Cu-20Ni-20Mn. Both the fracture surfaces were flat, shiny, and golden in color, which indicated that the fracture plane was inside and parallel to the TiN coating.

Figure 4.4 shows the fracture surface of the TiN coating on the 440C stainless steel side from the 3 \( \mu \text{m} \) batch. The nominal thickness of TiN coating on 440C in this batch is about 3.5 \( \mu \text{m} \). Islands of full-thickness TiN layer could be found scattered on the surface. The size of the TiN islands ranges from 10 \( \mu \text{m} \) to 100 \( \mu \text{m} \) and the distribution is random. Figure 4.5 shows the area near the edge of a TiN island. Close examination revealed that the fractured TiN-coating surface is even smoother than the original TiN surface. Figure 4.6 is the opposing side of the fracture surface of the TiN coating that adheres to Cu-20Ni-20Mn. Voids were found on the TiN fracture surface. The distribution and shape of these voids are exactly the mirror image of the islands observed in Figure 4.4. Exposed free surface of solidified Cu-20Ni-20Mn could be found inside the voids (Figure 4.7).
Figure 4.4  Fracture surface of TiN coating on the 3 μm TiN-coated 440C stainless steel bar. The fracture surface on the side of the steel bar is shown here. Details of the boxed region are shown in Figure 4.5.

Figure 4.5  Edge of the island structure on the fracture surface in Figure 4.4.
Figure 4.6  Fracture surface of TiN coating on the 3 μm TiN-coated 440C stainless steel bar. The fracture surface on the side of Cu-20Ni-20Mn is shown here. Details of the boxed region are shown in Figure 4.7.

Figure 4.7  Edge of the void on the fracture surface in Figure 4.6.
These observations suggest that the fracture crack mainly propagated along a primary plane inside the TiN coating. Occasional crossover of the fracture interface occurred at certain locations where voids were formed on the TiN/Cu-20Ni-20Mn interface. Figure 4.8 illustrates a possible scenario of the crack location in the tensile bar. Trapped air bubbles could form when Cu-20Ni-20Mn melted during the heating stage of joining the TiN-coated bars. If the air bubbles could not leave the molten Cu-20Ni-20Mn alloy, they would remain trapped at the TiN/Cu-20Ni-20Mn interface when the molten Cu-20Ni-20Mn solidified. Another explanation of the void formation could be due to solidification shrinkage of molten Cu-20Ni-20Mn in the thin gap between the two bars. Any dirt or an oxidized region can change the wetting behavior of the surface. Voids from solidification shrinkage could still form without the presence of adhered air bubbles. In either case, the presence of these voids at the TiN/Cu-20Ni-20Mn interface could serve as the crack initiation site or crack crossover site, because a stress concentration is expected at these locations during the tensile test.

![Diagram of tensile test](image)

**Figure 4.8** Schematic of the cross section of the 3 µm TiN-coated 440C stainless steel tensile bar (not to scale). Crossover of fracture crack occurred at the voids between the TiN coating and Cu-20Ni-20Mn.
4.3.2 Medium Fracture Strength

For the specimens with thinner TiN coatings that have medium fracture strength values between 200 MPa and 350 MPa, fracture also occurred inside the TiN coating. Both the fracture surfaces were gold in color but not as shiny as those of the specimens of lower fracture strength.

Figure 4.9 shows the fracture surface of the TiN coating on the M2 tool-steel side from the 1 μm batch. The nominal thickness of TiN coating on M2 is 2.36 μm. It can be seen that the loss of shininess is due to the rougher fracture surface. The fracture surface is no longer a smooth flat plane but became scale-like. This indicates multiple fracture planes inside the TiN coating. The fracture planes are mostly parallel and aligned in the direction of the major fracture crack. Microscopically, the fractured surface is still smoother than the original TiN-coating surface. Moreover, islands of full-thickness TiN coating observed in the low fracture-strength specimens are still present. However, the shape of the TiN islands became irregular. Debris of Cu-20Ni-20Mn was also found on the full-thickness TiN islands. This shows that ductile fracture of Cu-20Ni-20Mn itself started to set in at this stress level.
Figure 4.9 Fracture surface of TiN coating on the 1 μm TiN-coated M2 tool steel bar. The fracture surface on the side of the steel bar is shown here. Details of the boxed region are shown in Figure 4.10.

Figure 4.10 Boxed region of the fracture surface in Figure 4.9.
4.3.3 High Fracture Strength

For the specimens that have high fracture-strength values approximately exceeding 350 MPa, the fracture surface became more complex. Striped golden patterns on a rough silver-gray background were observed.

Figure 4.11 and Figure 4.12 show the fracture surface of the TiN coating on the 17-4PH stainless steel side from the 1 μm coating thickness batch. Besides the usual fractured TiN coating and full-thickness TiN islands, more than half of the surface is now exposed with the ductile fracture surface of the steel substrate. Debris of fractured Cu-20Ni-20Mn could also be found adhering to the full-thickness TiN islands. The TiN coating was also broken up into isolated patches, which indicated that the fracture did not propagate entirely inside the TiN coating. The fracture strength of the TiN itself and the TiN/steel interface strength were presumably comparable to each other in this case.

![Fracture surface of TiN coating](image)

**Figure 4.11** Fracture surface of TiN coating on the 1 μm TiN-coated 17-4PH stainless steel bar. The fracture surface on the side of the steel bar is shown here. Details of the boxed region are shown in Figure 4.12.
4.4 DISCUSSION

4.4.1 Brittle Fracture in TiN

The smoothness of the fractured TiN surface at low strength levels indicated that brittle fracture occurred in this ceramic coating. Feature size on the fracture surface was finer than the TiN grain size on the coating surface. This is expected as the grain size increases from the TiN-steel interface to the coating surface as the film grows thicker during deposition. The fracture crack simply propagated along the fine grain boundaries, which are almost lying on the same plane parallel to the coating macroscopically. Figure 4.13 is a cross section of a tensile bar showing how the fracture crack propagated inside the TiN coating before the specimen was completely broken during the tensile test.
4.4.2 Effect of TiN-Coating Thickness on Fracture Mode

It was expected that fracture should occur at the TiN/steel or the TiN/Cu-20Ni-20Mn interfaces because there may be weak bonding between two different materials. However, tensile-test results suggested that there was a transition from simple fracture inside the TiN coating to complex fracture involving the coating-substrate interfaces. This transition in fracture mode was associated with a decrease in TiN-coating thickness and an increase in fracture strength. For thick TiN coatings, fracture strength was low and fracture occurred at a single plane in the interior of the TiN coating. As the coating thickness was reduced, fracture strength increased and multiple fracture surfaces in the interior of the TiN coating were observed. For TiN coatings thinner than about 1 μm and fracture strengths exceeding about 350 MPa, a more complex fracture mechanism was involved. Ductile steel fracture surfaces started to appear, together with the partial- and full-thickness TiN fracture surfaces, and debris of Cu-20Ni-20Mn.
The change in the fracture mode can be explained by considering the effect of TiN-coating thickness on the yield strength of the TiN coating, the fracture strength of the TiN coating, and the adhesion strength at the TiN/steel interface.

### 4.4.2.1 TiN Yield Strength

For ceramic materials like TiN, the yield strength is almost the same as the ultimate tensile strength as there is only limited plastic deformation before breaking. The tensile strength is smaller than the compressive strength in contrast to many metals. Bulk sintered TiN has a compressive strength of 972 MPa while its tensile strength is only 248 MPa.\(^3\) However, in the case of thin film, the yield strength is typically much higher than for a bulk material.\(^4\) For example, Scherzer found that the yield strength of TiN film on a steel substrate was of the order of 1.5 GPa.\(^5\) No direct measurement of the yield strength of the TiN coating was made in this study. However, as there was no spallation or rupture of the TiN coating in the as-received specimens, the yield strength should be higher than the residual stress. Assuming the residual film stress in the TiN coating is only due to thermal-mismatch with the steel substrates, it is estimated to be 1.3 GPa. Detail calculation can be found in Appendix F. Thus, the yield stress of the TiN coating should be higher than 1.3 GPa.

The increase in yield strength in thin film is partly explained by the Hall-Petch type relationship between the film yield strength, \(\sigma_y\), and its grain size, \(d\):

\[
\sigma_y = \sigma_i + kd^{-n}
\]

**Eqn. 4.1**

where \(\sigma_i\) is some intrinsic stress, independent of the grain size \(d\), and \(n\) is typically between 0.5 and 1. Since the grain size of a thin film scales with the film thickness, \(h\), the latter can be used instead of the grain size as the scaling parameter:\(^6\)

\[
\sigma_y = \sigma_i \left[1 + \beta h^{-1/2}\right]
\]

**Eqn. 4.2**

where \(\sigma_i\) and \(\beta\) are the fitting parameters. Venkatraman and Bravman\(^7\) further showed that the yield strength of polycrystalline thin films depends separately on the film thickness and the grain size. Thompson\(^8\) explained the experimental observations by
calculating the work done in sweeping a dislocation loop through the slip plane in the grain causing the grain to yield. In Thompson’s model, the film is predominantly composed of grains whose boundaries intersect both surfaces of the film. Each grain is treated as a right circular cylinder of diameter $d$ and height $h$. The yield strength depends on crystallographic texture, grain size and film thickness and is given by the expression:

$$
\sigma_y = \left( \frac{W_d \sin \phi}{b \cos \lambda \cos \phi} \right) \left( \frac{2}{d \sin \phi + h} + 1 \right)
$$

Eqn. 4.3

where $W_d$ is the energy per unit length of dislocation;
$\phi$ is the angle between the dislocation plane and the plane of the film;
$b$ is the Burgers vector;
$\lambda$ is the angle between the Burgers vector and the normal of the plane of the film;
$d$ is the grain size; and
$h$ is the film thickness.

Although the yield-strength dependence on film thickness in Eqn. 4.3 is similar to the trend observed in the fracture-strength dependence on TiN-coating thickness, the absolute yield-strength value (of the order of GPa) is almost one order-of-magnitude higher than the fracture strength results (~100 to 500 MPa) from the tensile test. In other words, the TiN coating fractured prior to yielding when an external tensile load was applied. In view of this, linear elastic fracture mechanics (LEFM) is used to explain the fracture behavior of the TiN coatings in the tensile bars.

### 4.4.2.2 TiN Fracture Strength

It is assumed that the TiN coating already possessed an intrinsic collection of structural flaws distributed laterally as well as through the coating thickness. Voids, porosity, voided or grooved grain boundaries, local regions of de-cohesion, etc. may be viewed as flaws and even incipient cracks. Such flaws were presumably formed during the TiN deposition and the joining of the tensile bars. Under tensile loading, each flaw will locally concentrate stress and the surrounding material will deform. If the stresses are
sufficiently large, they can ultimately destroy the coating by crack propagation, resulting in fracture.\[9\]

Crack formation and propagation is driven by the release of the energy in the strained system under tensile loading. Irwin\[10\] defined a strain-energy release rate, $G$, which is a measure of the energy available for crack propagation. For the TiN film on the steel substrate, the strain-energy release rate for steady crack propagation is given by:

$$G = Z \sigma^2 h (1 - v^2) / E \quad (J/m^2)$$  \hspace{1cm} \text{Eqn. 4.4}

where $\sigma$ is the applied tensile stress, $h$ is the TiN-film thickness, $E$ and $v$ are the Young’s modulus and Poisson’s ratio of the TiN film. $Z$ is a dimensionless number, of order unity, depending on the cracking pattern and elastic mismatch of the film and substrate.\[11\] Fracture occurs when $G$ reaches the critical value, $G_c$, which is the toughness of the material. $G_c$ is a function of both material properties such as the bonding, microstructures and elastic-plastic constitutive behavior, and mechanical parameters such as the loading mode mixity (ratio of shear to normal stress) near to the crack tip.\[12\]

$G_c$ is related to the mode-I fracture toughness, $K_{lc}$, of the material by the well-known relation:\[13\]

$$K_{lc}^2 = G_c \tilde{E}$$  \hspace{1cm} \text{Eqn. 4.5}

where $\tilde{E} = E / (1 - v^2)$ for plane strain. Values of $K_{lc}$ for TiN film was found to range from 1 to 3 MPa m$^{1/2}$, depending on the film-deposition methods, substrates, and measuring techniques.\[14-16\] Comparing Eqn. 4.4 and Eqn. 4.5 yields the following relation between the fracture strength, $\sigma_f$, and TiN-film thickness:

$$\sigma_f^2 h = K_{hc}^2$$  \hspace{1cm} \text{Eqn. 4.6}

Here, $Z$ is approximated by unity. Compilation of the product on the left hand side of Eqn. 4.6 from the tensile test results in Table 4.1 allows estimation of the fracture toughness of the TiN film. Eqn. 4.6 also predicts that thinner films should have a higher fracture strength.
However, because the TiN coating was sandwiched between two compliant metal layers (steel and Cu-20Ni-20Mn), elastic shielding effects should be taken into account to interpret the meaning of $K_{lc}$. By using a simple energy argument or application of J-integral, Wang et al.\textsuperscript{[17]} established the relation between the macroscopic, or apparent fracture toughness, $K_{lc}^\infty$, and the intrinsic fracture toughness, $K_{lc}$:

\[
K_{lc}^\infty = \left(\frac{1+\alpha}{1-\alpha}\right)^{1/2} K_{lc}
\]

\textbf{Eqn. 4.7}

where Dundurs’ elastic mismatch parameter, $\alpha$, in Eqn. 4.7 is given by:

\[
\alpha = \frac{\tilde{E}_s - \tilde{E}}{\tilde{E}_s + \tilde{E}}
\]

\textbf{Eqn. 4.8}

where $E_s$ is the Young’s modulus of the substrate and $E$ is the Young’s modulus of the TiN film. For a typical value of $\tilde{E}_s = 200$ GPa for the steel substrate and $\tilde{E} = 590$ GPa for the TiN film\textsuperscript{[5,18]}, $\alpha$ is equal to -0.49. Substituting the value of $\alpha$ into Eqn. 4.7 yields:

\[
K_{lc}^\infty = 0.59 K_{lc}
\]

\textbf{Eqn. 4.9}

An equivalent statement concerning the elastic shielding in Eqn. 4.9 is that the load needed to fracture the sandwiched tensile bar (a stiff TiN film between two compliant metal layers) would be lower than that needed to fracture a geometrically similar tensile bar made entirely from TiN. As a result, $K_{lc}$ in Eqn. 4.6 should be replaced by $K_{lc}^\infty$.

For a typical value of $K_{lc} = 1$ MPa m$^{1/2}$ for the TiN film and for a film thickness of 6 $\mu$m, Eqn. 4.6 predicts that the fracture strength, $\sigma_f$, of the film should be about 240 MPa. Similarly, for a 1 $\mu$m film, $\sigma_f$ should be about 590 MPa. Comparing to the fracture strength results in Table 4.1, Eqn. 4.6 agrees qualitatively to the observed trend of the increase in fracture strength with a reduction in film thickness, given the random nature of the distribution in fracture strength in brittle material.\textsuperscript{[19]}

It should be noted that Eqn. 4.6 also predicted that the fracture strength for the tensile bars with 0.5 $\mu$m and 0.2 $\mu$m thick TiN coating should reach a much higher value. This was not observed in the tensile test. There appeared to be a cut-off fracture strength
value around 500 MPa where further decrease in TiN thickness did not result in higher fracture strengths. The reason is due to the change in fracture mode from in-layer fracture to interface fracture as the coating thickness is reduced.

### 4.4.2.3 TiN/Steel Interfacial Fracture Strength

In general, a straight crack in a stiff layer between two compliant substrates is configurationally unstable.\[^{20}\] Hutchinson et al. calculated that the crack inside such brittle layer would deflect away from the center-line if there is a fracture mode mixity.\[^{21}\] The origin of mode mixity includes effects of loading direction, difference in elastic properties of the layer and substrates, and asymmetric geometry. The consequence is that if there is even a slight component of shear stress in the tensile test due to misalignment or non-uniformity of the tensile bars, the in-layer crack will be driven toward one interface or the other.

For a thick TiN coating, the coating thickness is large compared to the roughness of the TiN/steel interface. The chance of a crack touching the interface is low. On the other hand, there is a high probability that the crack in a thin TiN coating could originate close to the interface or reach the interface during unstable crack propagation. As a result, the fracture strength is limited by the interface toughness. Laeng et al.\[^{22}\] and Perry et al.\[^{23}\] found that the adhesion strength of the TiN/steel interface was relatively constant and only increased slightly with the coating thickness. The TiN/steel interface adhesion strength also depended on the hardness of steel substrates.

Evans et al.\[^{24}\] found that if the interface toughness is comparable to that of the coating material, then the interface crack will interact with flaws in the layer adjacent to the interface, and nucleate microcracks. The effect of the mixed mode loading is to grow these microcracks back towards the interface. The resulting fracture surface will be covered with tiny chunks of the coating material. This is in agreement with the observation of the fractographs in Figure 4.11 and 4.12.
The discussion of the fracture-strength dependence on TiN-coating thickness can be summarized in Figure 4.14. Figure 4.14 shows the experimental fracture strength data obtained from the tensile test, along with the prediction from Eqn. 4.6. For thick coatings, the fracture strength was low and fracture occurred solely inside the TiN coating, forming smooth and golden fracture surfaces. As the film thickness decreased, the fracture strength increased according to Eqn. 4.6. Eventually, the fracture strength was comparable to the interface strength of the TiN/steel interface. There was a mixing between coating interior fracture and interfacial fracture. Such transition to mixed fracture mode was observed in the tensile specimens with coating thickness around 0.5 μm to 1 μm, corresponding to a fracture strength level of about 500 MPa.

![Fracture strength vs TiN coating thickness](image)

**Figure 4.14** Comparison of the change in the TiN coating fracture strength to the interface strength of the TiN/steel interface.

### 4.4.3 Comparison of Fracture Strengths

We have discussed in the above section that the increase in fracture strength as the TiN-coating thickness decreased is mainly due to the relative change in the in-layer fracture strength of the TiN coating and interface strength at the TiN/steel interface. The
maximum fracture strength is limited by the interface strength. The maximum fracture strength achieved in this study is the 0.5 \( \mu \text{m} \) TiN coated 440C stainless steel bar, which is 560 MPa. However, it is expected that the fracture strength should be higher in the TiN-coated powder skeleton where the TiN coating forms a three-dimensional connected network rather than a planar interface. There is a strong mode mixity as the loading direction is no longer perpendicular to all coating surfaces. The fracture strength in mode II (shear-mode fracture) loading is substantially higher than that in mode I.\(^{[21,25,26]}\)

Although there is a general dependence of fracture strength according to Eqn. 4.6, there is also variation in fracture strength values for different substrates inside the same batch. This could be due to the minor difference in film thickness or in adhesion of TiN to different steel substrates. The adhesion of TiC on steels, for example, can be increased by pre-depositing a thin cobalt film on the steel substrates.\(^{[27,28]}\) The improved adherence is related to the increased mobility of carbon atoms on the cobalt surface which provides a greater TiN nucleation density on the surface and, therefore, a stronger bond. Similarly, the difference in carbon activities in the steel bars could affect the adhesion of the TiN coating. Furthermore, since the fracture strength is statistical in nature, more measurements are required to determine the average fracture strength of each steel substrate in each batch.

The apparent high fracture-strength values of the 0.2 \( \mu \text{m} \) coating thickness specimens were due to the mixed contribution from the ductile fractures of steel substrate and Cu-20Ni-20Mn. This is the result of the failure of the thin diffusion barrier (see section 3.2.5 in Chapter 3). The TiN diffusion barrier was so thin that it was either broken up by the attack of Cu-20Ni-20Mn or lifted off from the substrate. Fracture no longer occurred along the interior of the TiN coating or at the TiN-steel interface. The TiN coating was effectively a dispersed layer of hard particles on the steel substrate. Consequently, the primary mode of fracture was changed to ductile fracture in the Cu-20Ni-20Mn matrix, with mixed contribution from the fracture in the broken coating. Examination of the fracture-surface morphology confirmed this explanation. Thus, the fracture strength is effectively determined by that of Cu-20Ni-20Mn, which is
independent of the steel substrate. This is manifested in the narrowness of the fracture strength values in the 0.2 µm batch compared to the 0.5 µm batch in Figure 4.3.

The poor performance of the 3 µm batch could be due to the coating process itself as the 3 µm batch was done by a different vendor than that used for all other specimens. Examination of the as-received TiN-coated bars from the 3 µm batch showed that the golden color was not as bright as those from the other batches. Patches of discoloration were also observed on the surface. These could indicate a defective coating process. The TiN coating could be contaminated by oxides and impurities, which would result in lower observed fracture strengths.

4.5 SUMMARY

From the tensile test of TiN-coated steel bars, it was found that in general fracture strength increased as the TiN coating thickness decreased. Fracture strength as high as 560 MPa can be achieved for a 0.5 µm thick TiN coating on 440C stainless steel bar. Fracture occurred at a plane inside and parallel to the TiN coating for low fracture strength level. For thinner coatings and higher fracture strengths, fracture at the TiN-steel interface was also observed. An increase in fracture strength of the coating and a slight decrease in the TiN-steel adhesion strength as the coating thickness was decreased was responsible for the change in fracture mode.

The high average fracture strength observed in the 0.5 µm batch TiN diffusion barrier suggested that it is the desired coating thickness. However, from the results in Chapter 3, the 1 µm TiN diffusion barrier performed better in preventing the Cu-20Ni-20Mn infiltrant from reacting with the steel substrates. Thus, there is a trade-off of fracture strength and diffusion barrier performance. As a manufacturing guideline, TiN coating of thickness ranging from 0.5 µm to 1 µm can be used. The minimum thickness that does not cause reaction failure can be determined for each specific steel substrate.
4.6 **TENSILE STRENGTH OF INFILTRATED SKELETON**

In Chapter 3, a process was described in which TiN-coated steel powder skeletons were infiltrated with molten Cu-20Ni-20Mn at 1200 °C by gated infiltration. The tensile strengths and fracture behavior of these infiltrated skeletons were then studied by tensile test and SEM. Since only the D2 steel skeleton with 0.7 μm TiN coating was fully infiltrated, only one tensile test was performed on the infiltrated skeletons. However, this can serve as a reference for all other steel substrates if they were fully infiltrated. As a control, a solid D2 steel bar of the same geometry and heat treatment (1200 °C for 30 min) as the infiltrated TiN-coated D2 skeleton was subjected to tensile test too.

Tensile test results showed that the infiltrated TiN-coated D2 skeleton broke at 265 MPa at 0.6% strain while the solid D2 steel bar broke at 1320 MPa at 3.7% strain. Moreover, the stress-strain curves suggested that the TiN-coated D2 skeleton is brittle while there was little yielding of the solid D2 bar before it broke.

Examination of the fracture surfaces of the TiN-coated D2 skeleton showed that both sides of the fracture surfaces were golden in color, which suggested that the fracture occurred inside the TiN coating. This kind of fracture behavior is similar to that observed in the TiN-coated flat steel bars described in the preceding sections. Figure 4.15 is a micrograph of the fractured surface of the TiN-coated D2 skeleton. The fracture crack propagated along the TiN coating from one steel powder to another, crossing over the Cu-20Ni-20Mn infiltrant between the powders. Figure 4.16 illustrated the break-away of Cu-20Ni-20Mn from the TiN coating on the steel powders and the fracture of the TiN coating itself. In conclusion, both TiN coating fracture and Cu-20Ni-20Mn/TiN detachment were the two main fracture mechanism in the infiltrated TiN-coated D2 skeleton.
Figure 4.15 Fracture surface of the Cu-20Ni-20Mn infiltrated D2 steel powder skeleton with 0.7 μm TiN coating.

Figure 4.16 Break-away of Cu-20Ni-20Mn from the TiN coating on the steel powder and the fracture of TiN coating.
For comparison, the fracture surface of the solid D2 steel bar is also shown in Figure 4.17 and 4.18. There is a mix of ductile and brittle fracture.

**Figure 4.17** Fracture surface of solid D2 steel bar.

**Figure 4.18** Ductile fracture in the Fe matrix and the void formation surrounding the carbide particles.
4.7 REFERENCES


CHAPTER 5 HEAT TREATMENT AND HARDENING

Hardness is an important parameter in determining the 3DP metal tool performance especially in metal tooling for injection molding where high wear resistance is preferred. For the steel skeleton, depending on the desired application, a wide selection of hardness ranging from 40 HRC to 60 HRC can be chosen for different types of steel and heat treatments.\textsuperscript{[1]} Machining and surface finishing can be done in the soft annealed state and the tool can be rehardened with subsequent hardening treatments including austenitizing, quenching, and tempering. For the Cu-20Ni-20Mn infiltrant, its hardness can be increased dramatically from the high Rockwell B range from the ingot to as high as 45 HRC with optimal age hardening.\textsuperscript{[2]} Further increase in hardness is possible with cold working, although it is not applicable to 3DP infiltrated parts.

In this chapter, the hardness of the TiN-coated steel powder skeleton that has been infiltrated with Cu-20Ni-20Mn was studied. First, background of the age hardening behavior of Cu-20Ni-20Mn is presented, followed by experimental results on the measured hardness with various heat treatment conditions. Then the effect of Fe addition to the hardening response of Cu-20Ni-20Mn was studied to determine the allowed extent of reaction between the steel skeleton and Cu-20Ni-20Mn infiltrant. The heat treatment conditions used for age hardening of Cu-20Ni-20Mn were also applied to the steels to determine the hardening compatibility. Finally, the rehardenability of the infiltrated skeleton with the TiN diffusion barrier under the optimum heat treatment condition will be presented to assess its application to metal tooling by the 3DP process.

5.1 Cu-20Ni-20Mn INFLICTANT

In a 3DP metal part, about 60 vol. pct. of the part consists of the sintered steel powder skeleton and the remainder of the volume is filled by the Cu-20Ni-20Mn infiltrant. If a 0.5 μm thick TiN diffusion barrier is deposited on the steel powder skeleton
with a typical powder size of 50 μm, there will be just an additional 5 vol. pct. of TiN in the 3DP part. Thus, the final hardness of a finished 3DP metal part depends mainly on the contribution from both the skeleton and infiltrant. A high hardness requires a compatible heat treatment that can yield good hardening responses from the skeleton and the infiltrant.

5.1.1 Background

The alloy of Cu-20Ni-20Mn was first developed in the 1940s as a possible substitute for the Cu-Be alloys. Dean et al. found that the composition range capable of maximum hardening corresponded roughly to the pseudo-binary line from copper to the compound MnNi in the Cu-Ni-Mn alloy system. The composition range that has the ability to harden is marked in Figure 5.1.

![Figure 5.1](image)

The hardenable [○], non-hardenable [•], and brittle [+] region in the Cu-Ni-Mn system.

At moderate to high temperatures and over a broad composition range, the Cu-Ni-Mn alloy exists as a single FCC γ solid solution. Though the phase equilibria in this alloy system have not been studied in detail, two major phase transformations occur in this
alloy: (1) transformation of the $\gamma$ solid solution and (2) order-disorder transformation. A summary and review of this alloy system can be found in Gupta's article.\cite{4}

According to Gupta, several investigations have been carried out in the 1970's to understand the low-temperature transformation of the $\gamma$ solid solution at the Cu-rich end as well as along the pseudo-binary line Cu-MnNi. There is a general agreement that the FCC $\gamma$ solid solution on cooling transforms to produce $\gamma$ phase (FCC, lean in Mn and Ni) and MnNi ordered phase (lean in Cu), represented by $\gamma \Rightarrow \gamma + \text{MnNi}$. The mechanism of transformation appears to vary with the temperature of transformation. For example, in Cu-20Ni-20Mn, a discontinuous precipitation reaction occurs between 250 $^\circ$C and 350 $^\circ$C whereas a spinodal decomposition occurs between 350 $^\circ$C and 530 $^\circ$C. No transformation of the $\gamma$ phase occurs in this alloy above 530 $^\circ$C. The critical transformation temperature is shown in the Cu-MnNi isopleth along the pseudo-binary line (Figure 5.2).\cite{5} The order-disorder transformation was also observed in Cu-Ni-Mn. The critical temperature for the order-disorder transformation of the MnNi$_3$ type structure also decreased as the copper concentration increased.

![Figure 5.2](image)

**Figure 5.2** Cu-MnNi isopleth. The critical transformation temperature of $\gamma \Rightarrow \gamma + \text{MnNi}$ decreases towards the Cu-rich side.
Dean *et al.* [2, 3] studied the mechanical properties of the Cu-Ni-Mn system extensively. They found that the addition of copper improved the ductility of the alloys but did not inhibit ordering or hardening. For various alloys with compositions along the Cu-MnNi pseudo-binary line, hardnesses as high as 45 HRC to 50 HRC were reported. *The optimum heat treatment consists of a solution treatment at 650 °C for an hour, followed by aging at 350 °C to 450 °C from a few hours to a few weeks.* Near maximum hardness can be achieved approximately after 12 hours. Typical time-hardness curves for different aging conditions are shown in Figure 5.3.

![Figure 5.3](image.png)

**Figure 5.3** Time-hardness curves for Cu-20Ni-20Mn with different aging temperatures. The specimens in the top chart were annealed at 650 °C for an hour before aging. The specimens in the bottom chart were cold-rolled without annealing before aging.[2]

In a comment to Dean *et al.*'s work,[2] Hood stated that an unusual and highly desirable characteristic of these alloys is their insensitivity to cooling rate from the solution temperature. Hood found that the air-cooled and water-cooled samples had identical time-hardness curves on being aged. Furnace-cooled samples may partially
harden on passing through the transformation temperature. Hardening can then be continued at the normal rate by reheating to the aging temperature. Isothermal hardening can be accomplished either by quenching from the solution temperature to the aging temperature or by slow cooling from the solution temperature to the aging temperature and holding for the required time.

Another advantage of this alloy is that hardening occurs via an order-disorder transformation mechanism. The process is reversible and can be repeated any number of times. A hardened sample can be softened again by heating it at an intermediate temperature between the aging temperature and solution temperature where “resolution” takes place. The amount of “resolution” is primarily a function of temperature rather than time. It is therefore possible to “draw” the hardness back to any predetermined value with considerable accuracy. Full hardness can be restored after drawing by reheating to the aging temperature.

5.1.2 Age Hardening and Results

As a control for the hardening experiment of the infiltrated steel-powder skeletons, the heat treatment of the pure Cu-20Ni-20Mn was first done to compare with the published result. Small chunks (~ 1 cm³) of Cu-20Ni-20Mn were cut from the cast ingots. After polishing and cleaning, the specimens were encapsulated inside glass tubes, which were filled with argon gas. Some of the specimens were solution treated before age hardening.

Solution treatments were done by putting the encapsulated specimen inside the air-furnace at 650 °C for an hour. At the end of the solution treatment step, three different cooling procedures were used: 1) furnace-cooling, where the specimens in the tubes were left cooling inside the air furnace; 2) air-quenching, where the tubes were broken and the specimens were cooled in open air; and 3) water-quenching, where the tubes were broken and the specimens were quenched in water at room temperature. The estimated cooling rates for these different cooling procedures were of the order of 5 °C/min, 50 °C/min, and
500 °C/min for the furnace-cooled, air-quenched, and water-quenched conditions respectively.

Specimens with different solution treatments and those without solution treatment were resealed again inside the glass tubes with argon. Age hardening was carried out inside the air furnace at 350 °C, 400 °C, and 450 °C for one day. Results of the final hardness are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Solution Treatments</th>
<th>Aging Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>350 °C</td>
</tr>
<tr>
<td>No Solution Treatment</td>
<td>58 HRB</td>
</tr>
<tr>
<td>650 °C for 1 hr, furnace-cooled</td>
<td>63 HRB</td>
</tr>
<tr>
<td>650 °C for 1 hr, air-quenched</td>
<td>65 HRB</td>
</tr>
<tr>
<td>650 °C for 1 hr, water-quenched</td>
<td>70 HRB</td>
</tr>
</tbody>
</table>

Table 5.1 Age hardening of Cu-20Ni-20Mn with different solution treatments and aging conditions (aging time = 1 day).

As a reference, the original hardness of Cu-20Ni-20Mn ingot after solution treatment at 650 °C for an hour was found to be in the range of 40 HRB to 50 HRB. Similarly, in a separate experiment, the hardness measured after the Cu-20Ni-20Mn ingot was molten and cooled in the tube furnace was only about 40 HRB. To illustrate the extent of hardening response, results in Table 6.1 are plotted in Figure 5.4 with the hardness values converted to Vickers hardness numbers. It shows that there was a general increase in hardness with aging temperature. Maximum hardness of 35 HRC was achieved for an aging of one day at 450 °C. It can be accomplished through direct aging without solution treatment or aging preceded by solution treatment at 650 °C for an hour with furnace-cooling.
Figure 5.4  Change in age hardening response of Cu-20Ni-20Mn with aging temperature.

The maximum hardness achieved in this experiment is lower than the maximum hardness obtained by Dean et al., which was 45 HRC.[2] The reason of the discrepancy could be due to the absence of any cold working before the heat treatment that Dean et al. used in their experiments. Cold-rolling can reduce the grain size and improve the compositional homogeneity of the specimen, which lead to a more rapid and complete hardening response. Another explanation for the discrepancy could be due to the non-ideal composition of the Cu-20Ni-20Mn ingot used in this study. The nominal composition of the ingot was found to consist of 58.13 at. pct. Cu, 21.46 at. pct. Ni, and 20.41 at. pct. Mn. The deviation from the required 1:1 ratio of Ni to Mn producing maximum hardenability could contribute to the difference in the measured hardness. Nevertheless, a hardness of 35 HRC under the current heat treatment condition already compared favorably with that attained by Cu-Be alloys.

From the above result, it can be concluded that the optimum heat treatment condition consists of an age hardening treatment at 450 °C for one day. The solution treatment step is optional as its effect on age hardening is not significant. If this direct
aging treatment is used for the infiltrated skeleton, the maximum temperature the steel skeleton experiences is only 450 °C. This can maintain a good hardness in the steel without exposing to a high tempering temperature at the 650 °C solution-treatment temperature during the solution treatment step of the Cu-20Ni-20Mn infiltrant. Higher tempering temperature usually results in a lower hardness for steel. The effects of these treatments on various steel substrates are discussed in Section 5.2.

5.1.3 Effect of Iron Addition on Age-hardening of Cu-20Ni-20Mn

In Chapter 3, we see that if the TiN diffusion barrier fails, iron from the steel powder skeleton can leak out through the cracks on the diffusion barrier and react with the Cu-20Ni-20Mn infiltrant. This can affect the age-hardening response of the Cu-20Ni-20Mn infiltrant. In order to quantify the effect of iron addition to the age hardening of Cu-20Ni-20Mn, different amounts of Fe were systematically added to Cu-20Ni-20Mn. Ingots of different compositions were made by melting the mixtures at 1450 °C inside the tube furnace. The alloy ingots were then subjected to the same optimum age-hardening procedures of Cu-20Ni-20Mn as described in the previous section. Microstructures of the ingots and age-hardening results are shown in Table 6.2. It was found that for an Fe content lower than 2 at. pct., a homogeneous solid solution of Fe and Cu-20Ni-20Mn was formed. An increase in Fe content from 4 at. pct. up to 30 at. pct. resulted in discontinuous Fe-rich fine dendrites in a Cu-20Ni-20Mn rich matrix. Complex dendritic networks of different dendrites and eutectic structures were found when the Fe content was higher than 35 at. pct. and up to 50 at. pct.

The hardening response of the ingots with different Fe content is shown in Figure 5.5. The hardness values are converted to Vickers hardness for comparison. It shows that a hardening response persisted with the addition of Fe in Cu-20Ni-20Mn up to about 30 at. pct. However, the high hardness in the Rockwell C range expected from age-hardening of pure Cu-20Ni-20Mn can be achieved only for an alloy with Fe composition less than 1 at. pct. Thus, it is essential to have a good diffusion barrier to prevent any reaction between the steel powder skeleton with the Cu-20Ni-20Mn infiltrant.
Table 5.2  Hardness of Cu-20Ni-20Mn with different Fe addition. Compositions that have good hardening response are highlighted.

Figure 5.5  Effect of Fe addition to hardening response of Cu-20Ni-20Mn. Hardness values are converted to Vickers hardness numbers for comparison.
5.2 **STEEL SUBSTRATES**

Although Cu-20Ni-20Mn can be hardened with the optimum hardening condition of 450 °C aging for one day, this may not be a good tempering condition for the steels. Similarly, if the solution treatment at 650 °C for 1 hour of Cu-20Ni-20Mn is also applied to the steel substrate, the hardness could decrease due to the high annealing temperature. Furthermore, the infiltration temperature of 1200 °C is higher than the typical austenitizing temperature for steel. Thus, a complete study of the heat treatment response of the steel substrates is essential to optimize the final heat treatment condition that is applicable to the infiltrated part. Standard heat treatment conditions for the tool steels and stainless steels can be found in several sources.\[^{1,6,7}\]

In order to study the effect of the age hardening treatment for Cu-20Ni-20Mn on the steel substrates, small sections of the steel bars were cut from the tensile test specimens in Chapter 4. These specimens had been heated at a rate of 8 °C/min to 1200 °C and cooled at 8 °C/min in the tube furnace to room temperature. Their hardness was measured before being sealed inside the glass tubes. This is listed in the “austenitizing” column in Table 5.3. Half of the specimens were then subjected to annealing at 650 °C for an hour before tempering at the age-hardening temperatures of Cu-20Ni-20Mn, ranging from 350 °C to 450 °C. The other half of the specimens was tempered directly after the austenitizing treatment without any annealing treatment. The hardness after each heat treatment step is summarized in Table 5.3.

The changes in hardness for each steel as a result of various heat-treatment steps were plotted in Figure 5.6 to Figure 5.12. The effect of the additional annealing step (corresponding to the solution-treatment step for Cu-20Ni-20Mn) to tempered hardness can be studied through the comparison plots.
<table>
<thead>
<tr>
<th></th>
<th>Austenitizing (1200 °C, 0hr)</th>
<th>Annealing (650 °C, 1hr)</th>
<th>Tempering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>350 °C, 1 day</td>
</tr>
<tr>
<td>174PH</td>
<td>37</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>38</td>
<td>42</td>
</tr>
<tr>
<td>420</td>
<td>44</td>
<td>39</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>440C</td>
<td>48</td>
<td>40</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>H13</td>
<td>55</td>
<td>53</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>52</td>
<td>53</td>
</tr>
<tr>
<td>S7</td>
<td>50</td>
<td>46</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>52</td>
<td>51</td>
</tr>
<tr>
<td>M2</td>
<td>53</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>52</td>
<td>51</td>
</tr>
<tr>
<td>A2</td>
<td>56</td>
<td>56</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>55</td>
<td>57</td>
</tr>
</tbody>
</table>

**Table 5.3** Summary of the hardness of steel bar after different heat treatment cycles. Hardness values are in Rockwell C scale.

**Figure 5.6** Hardening response of 17-4PH stainless steel for different heat treatments.
Figure 5.7  Hardening response of 420 stainless steel for different heat treatments.

Figure 5.8  Hardening response of 440C stainless steel for different heat treatments.
Figure 5.9  Hardening response of H13 tool steel for different heat treatments.

Figure 5.10  Hardening response of S7 tool steel for different heat treatments.
Figure 5.11  Hardening response of M2 tool steel for different heat treatments.

Figure 5.12  Hardening response of A2 tool steel for different heat treatments.
Chapter 5

After the austenitizing treatment of steels at 1200 °C, 17-4PH and 420 stainless steels had a hardness level in the 35 HRC to 45 HRC range while all the tool steels with 440C stainless steels had a higher hardness level in the 50 HRC to 55 HRC range. For 17-4PH, 420, and H13, the hardness values matches reasonably well with the as-quenched hardness values in the literature.\[1\] However, the hardness values for the higher-alloyed steels like S7, M2, A2, and 440C are lower than those expected from standard quenching, which has a typical hardness value higher than 60 HRC.

Nevertheless, these relatively high hardness values suggested that martensite transformation occurred during the furnace cooling. This could be a result of the moderately high cooling rate of 8 °C/min in the tube furnace after the austenitizing treatment. Although this cooling rate is smaller than that normally achieved by quenching in air, water, or oil, this is still much higher than the typical slow cooling rate (8 to 22 °C/hr) required for annealing treatment.\[7\] As a result, formation of ferrite was suppressed while martensite transformation took place. The amount of retained austenite, and thus as-quenched hardness, depends on the martensitic transformation temperature, $M_s$. $M_s$ is strongly affected by the carbon content in the steel, along with minor contributions from other alloying elements.\[8\] Highly-alloyed steels like S7, M2, A2, and 440C mentioned above all have low $M_s$. Thus, the martensitic transformation was not likely completed during the moderate cooling in the furnace. This explains the lower as-quenched hardness observed in these steels.

Subsequent annealing at 650 °C for one hour resulted in a lower hardness for all steels studied. For the annealed specimens, further tempering led to even lower hardness except M2 tool steel, which seems to be insensitive to these heat treatment conditions. On the other hand, if the annealing step was eliminated, the hardness of these steels can be retained in the 50 HRC to 55 HRC level except 17-4PH and 420 stainless steels, which even showed substantial hardening response from tempering.

From the hardening response observed in these specimens, it was found that the hardness of these steel bars could not be restored if they are softened after the annealing
step at 650 °C for an hour. As this is close to the $A_1$ temperature of steels, it is believed that recovery or recrystallization annealing occurred in the tempered martensite that led to the formation of bainitic mixtures of ferrite and coarsened carbides. This structure is softer than the martensite and could not be subsequently hardened. In view of this, it is suggested that the 650 °C annealing step for steel (corresponds to the solution treatment of Cu-20Ni-20Mn) be removed. Results in the age hardening of Cu-20Ni-20Mn also suggested that this solution treatment is not critical to attain a high hardness.

As a conclusion, it was found that the age hardening procedure suggested for Cu-20Ni-20Mn would not significantly affect the hardness of steels if the whole infiltrated part is age hardened directly at 450 °C for one day without solution treatment at high tempering temperature. Estimated by the rule of mixtures, the final hardness of an infiltrated part composed of 60 vol. pct. steel and 40 vol. pct. Cu-20Ni-20Mn could be in the range of 40 HRC to 45 HRC.

5.3 HARDNESS OF INFILTRATED SKELETON

Sections of the infiltrated TiN-coated skeletons were heat treated to study the hardening response. Heat treatment procedures followed those discussed in the previous section. Rectangular plates measuring $1/4 \times 3/4 \times 1/4$ inches were cut from the infiltrated skeletons that have the thicker TiN coating (0.6 to 0.8 μm) and polished. Care was taken to ensure the top and bottom surfaces of the plates were parallel. This is essential for accurate measurement of macrohardness. They were then sealed inside glass tubes and heat treated at 450 °C for one day.

Both macrohardness and microhardness of the infiltrated skeletons were measured by a Rockwell hardness tester and a microhardness tester, respectively. Most of the specimens could only be hardened to 10 to 15 HRC. Microhardness measurements on the steel powders and the infiltrant showed that the steel powders retained their respective high hardness in the range of 40 to 50 HRC. However, there was no significant age
hardening response from the Cu-20Ni-20Mn infiltrant. The microhardness of the infiltrant was only in the 10 to 15 HRC range, which is far less than the expected hardness of 35 HRC. However, this is expected as there was reaction between the steel powders and the Cu-20Ni-20Mn infiltrant through the defects on the TiN coatings. A new phase formed at the reaction zones, which changed the composition of the remaining infiltrant. The infiltrant became depleted of Ni and Mn, driving the overall composition outside the hardenable region in the Cu-Ni-Mn ternary system. Figure 5.1 shows that if the amount of Ni and Mn is less than about 10 wt. pct., the alloy lost its hardening ability. The composition analysis of the infiltrant in section 3.3 also confirmed the depletion of Ni and Mn in the infiltrant due to the diffusional reaction.

The exceptions to the above observations are the H13 and D2 specimens. Excellent hardening was obtained for the infiltrated H13 skeleton. Macrohardness of 40 HRC was measured in the H13 specimen. Microhardness test revealed that the H13 powders hardened to 55 HRC while the Cu-20Ni-20Mn infiltrant hardened to 45 HRC. It should be noted that the macrohardness of the H13 specimen is lower than the measured microhardness values of both the H13 powders and Cu-20Ni-20Mn infiltrant. This could be due to cracks formed around the indentation during the macrohardness measurement, which will be addressed in the next section. Nevertheless, the success of the H13 specimen with the high hardness achieved is due to the effectiveness of the thick TiN diffusion barrier (0.8 μm in this case) that prevented the reaction between the steel powders and the infiltrant (see Figure 3.29). The original compositions were preserved and optimum age hardening response resulted. It should be noted that the hardness achieved by the Cu-20Ni-20Mn infiltrant inside the infiltrated skeleton was higher than that achieved by the Cu-20Ni-20Mn ingot. This could be due to the suppressed grain growth in the confined space between the powders in the former case.

Though the hardness achieved by the infiltrated D2 skeleton was not as high as that by the H13 specimen, it still had a macrohardness of 28 HRC. The microhardness of the D2 powder and the infiltrant were 55 HRC and 20 HRC respectively. The lower
hardness of the infiltrant compared to that achieved by that in the H13 specimen could be due to a slight localized diffusional reaction with the D2 steel powder.

5.3.1 Indentation Crack from Hardness Test

Figure 5.13 reveals cracks radiating from the indentation site during the macrohardness test of the 0.8 μm TiN-coated H13 specimen that had been age hardened. The apparent lower macrohardness relative to the microhardnesses of both the powders and infiltrant could be due to these indentation cracks. The crack formation permits the indenter to drive further into the specimen during loading, which results in a lower macrohardness reading. Figure 5.14 also confirmed that the crack propagated along the TiN coating, which is consistent to the fracture specimens discussed in Chapter 4.

![Crack formation around the indentation site from macrohardness test](image)

**Figure 5.13** Crack formation around the indentation site from macrohardness test.
5.4 CHARPY IMPACT TEST ON INFILTRATED SKELETON

In tooling applications, frequent mechanical shock or impulse loading of the metal tool is expected. Thus, it is also useful to measure the impact energy by Charpy Impact Test, which is a measure of the toughness of the specimen. Again, the 0.7 μm TiN-coated D2 steel skeleton and solid D2 steel bar were used. The TiN-coated D2 steel skeleton and one of the solid D2 bar has the same heat treatment, consisting of an infiltration at 1200 °C followed by aging at 450 °C for one day. As a comparison, a fully annealed solid D2 bar was used. The annealing treatment is done by heating to 870 °C for one hour at a heating rate of 5 °C/min, followed by a slow furnace cooling to room temperature at 22 °C/hr. The specimens were then cut and the Charpy test was carried out according to the procedures outlined in ASTM Standard E23.\textsuperscript{[9]}
Table 5.4 summarizes the experimental results relating to the hardness and Charpy impact energy for each specimen.

<table>
<thead>
<tr>
<th></th>
<th>Hardness (HRC)</th>
<th>Charpy Impact Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid D2 bar (fully annealed)</td>
<td>20</td>
<td>22.2</td>
</tr>
<tr>
<td>Solid D2 bar (same heat treatment as D2 skeleton)</td>
<td>50</td>
<td>8.8</td>
</tr>
<tr>
<td>0.7 μm TiN-coated D2 skeleton with Cu-20Ni-20Mn infiltrant</td>
<td>28</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table 5.4 Comparison of hardness and Charpy impact energy for the solid D2 steel bar and the 0.7 μm TiN-coated D2 skeleton with Cu-20Ni-20Mn infiltrant that has been age hardened at 450 °C for 1 day.

It can be seen that the inverse relation of hardness vs. impact energy holds for these 3 specimens: higher hardness generally has a lower impact energy. The infiltrated D2 skeleton with 0.7 micron TiN has a slightly higher hardness than the fully annealed D2 bar. However, its impact energy is only half of that of the annealed D2 bar. Assuming a linear relation of hardness vs. impact energy for the solid D2 bar, a solid D2 bar with a hardness of 28 HRC would have an impact energy about 18.6 J. Thus, the infiltrated skeleton is considered more brittle than a solid D2 bar with the same hardness. This is presumably due to the preferred fracture of TiN coating during the impact test. In the second case, although the infiltrated skeleton has a much lower hardness than the hardened D2 bar with the same heat treatment, the impact energies were almost the same. In this case, the ductility of Cu-20Ni-20Mn was overcome by the brittleness of TiN.

5.5 SUMMARY

Optimum heat treatment condition for the Cu-20Ni-20Mn infiltrant was found to consist of an age hardening at 450 °C for one day. Solution treatments at 650 °C for an hour is optional as it did not significantly affect the hardening response of Cu-20Ni-
20Mn. The steel substrates under the same heat treatment of the Cu-20Ni-20Mn did not show any over-tempering effect, provided they were not subjected to the 650 °C annealing step prior to aging at 450 °C. Average hardesses of 45 to 55 HRC could be obtained for the steel substrates.

Both macro- and micro-hardnesses of the infiltrated TiN-coated skeletons were measured. A very high macrohardness of 40 HRC was obtained for the H13 steel specimen. Microhardness results showed that the H13 steel powder hardened to 55 HRC while the infiltrant hardened to 45 HRC. This is due to the effectiveness of the TiN coating preventing reaction between the H13 steel powders and the molten Cu-20Ni-20Mn infiltrant. Other steel specimens did not show significant hardening response as the TiN coating was not thick enough and pinhole-free to suppress the interaction of steel and infiltrant that resulted in a compositional change of the Cu-20Ni-20Mn infiltrant. Consequently, the hardenability was significantly affected.

Charpy test revealed that the TiN-coated steel skeleton with Cu-20Ni-20Mn infiltrant has a ductility only comparable to a brittle solid D2 steel bar, which has been hardened to a hardness of 50 HRC. The reason is the preferred fracture occurring at the brittle TiN coating.
5.6 REFERENCES


CHAPTER 6  TIN FILM THICKNESS

A central question to the development of TiN diffusion barrier is the determination of the minimum thickness of the diffusion barrier that can be used to protect the steel powders from reacting with the Cu-20Ni-20Mn infiltrant. Although a thick coating can prevent any diffusion and reaction between the powder and infiltrant, it could substantially change the mechanical properties of the final part as TiN is a brittle ceramic. A thick coating also increases cost and time for the extra deposition process. This chapter serves as a summary on the discussion of determining a suitable range of the TiN coating thickness that is applied to the steel/Cu-20Ni-20Mn materials system.

6.1 MINIMUM THICKNESS

From the diffusion analysis in Chapter 2, the diffusivity of most elements in TiN is of the order of $1 \times 10^{-17}$ m$^2$/s at the infiltration temperature of 1200 °C. This corresponds to a diffusion length of about 0.3 µm for 30 min, which is the typical infiltration time. Thus, it is expected that a minimum thickness of 0.3 µm is required to prevent any interdiffusion of the materials on both sides of the TiN diffusion barrier.

However, the minimum thickness of the TiN coating can be further reduced if we can allow a certain amount of Fe that would leak out to the Cu-20Ni-20Mn infiltrant. The amount of Fe should not significantly change the Cu-20Ni-20Mn composition so that the hardenability of the Cu 20Ni-20Mn infiltrant can be preserved. From Chapter 5, it was experimentally determined that the maximum amount of Fe that can be allowed in Cu-20Ni-20Mn was about 1 at. pct without degrading its hardenability. The following analysis determined the thickness of TiN coating that would allow 1 at. pct. of Fe to dissolve in molten Cu-20Ni-20Mn infiltrant at 1200 °C with a duration of 30 min.
Since the TiN coating is very thin compared to the powder size, one-dimensional diffusion analysis is used here. From Chapter 3, it was calculated that the solubility of Fe in TiN at 1200 °C is 2.5 at. pct. The diffusivity of Fe in TiN is of the order of $1 \times 10^{-17}$ m$^2$/s. During the isothermal treatment step of the gated infiltration (1200 °C for 30 min), the TiN coating is assumed to be saturated with 2.5 at. pct. of Fe if the TiN coating thickness is less than the diffusion length of 0.3 μm. Figure 6.1(a) shows the composition profile of Fe in the powder/TiN-coating/Cu-20Ni-20Mn system before infiltration starts.

![Diagrams](image)

**Figure 6.1** Diffusion of Fe through the TiN diffusion barrier: (a) $t=0$, before infiltration; (b) $t=t^*$, intermediate step; (c) $t=T=30$ min, when 1 at. pct. of Fe is dissolved in the Cu-20Ni-20Mn infiltrant.

When the molten Cu-20Ni-20Mn is brought into contact with the TiN-coated powders (Figure 6.1(b)), Fe leaks out from the TiN/Cu-20Ni-20Mn interface and dissolves quickly in Cu-20Ni-20Mn, which acts as a fast solute sink. The composition in the Cu-20Ni-20Mn infiltrant is assumed to be homogeneous since the diffusivity of Fe in molten Cu-20Ni-20Mn is much higher than that in TiN. On the other hand, Fe is supplied from Fe powder at the Fe/TiN interface, which is maintained at the equilibrium solubility of 2.5 at. pct. As the TiN coating thickness is very thin, a quasi-steady state diffusion
profile is assumed through the TiN layer. Figure 6.1(c) shows the final composition profile after 30 min of diffusion when 1 at. pct. of Fe is dissolved in the Cu-20Ni-20Mn infiltrant.

Using Fick’s law, the flux in the TiN layer is given by:

\[ J = D \frac{\Delta C}{h} \]  
\textbf{Eqn. 6.1}

where \( D \) is the Fe diffusivity in TiN, \( C \) is the concentration of Fe, \( h \) is the TiN coating thickness. Equating the mass flow through the TiN diffusion barrier, the number of moles of Fe atoms passed through the TiN layer is

\[ M_1 = JST \]  
\textbf{Eqn. 6.2}

where \( S \) is the total surface area of the Fe powders (same as the TiN coatings) and \( T \) is the diffusion time (30 min). On the other hand, the number of moles of Fe in the Cu-20Ni-20Mn infiltrant is given by

\[ M_2 = 1\% \left(1 - f\right)V \]  
\textbf{Eqn. 6.3}

where \( f \) is the packing fraction of the Fe powders and \( V \) is the total volume of the system. Continuity requires that \( M_1 = M_2 \). At \( t = T \), \( \Delta C = 2.5 - 1 = 1.5 \) at. pct. (Figure 6.1 (c)). Substituting Eqn. 6.1 into Eqn. 6.2 and equating with Eqn. 6.3 yields

\[ \frac{V}{S} \frac{h}{DT} = \frac{1 - f}{1.5} \]  
\textbf{Eqn. 6.4}

Since the powder skeleton is slightly sintered, its structure and packing can be approximated by a BCC lattice, with the void between the powders filled with Cu-20Ni-20Mn. For a BCC lattice, the packing fraction, \( f \) is equal to 68%. The volume-to-powder-surface ratio is

\[ \frac{V}{S} = \frac{4}{3\sqrt{3}\pi}d \]  
\textbf{Eqn. 6.5}

where \( d \) is the powder diameter. Substituting the expressions for \( f \) and \( V/S \) into Eqn. 6.4, results in the relation of the minimum thickness of TiN coating with powder diameter:

\[ hd = 0.344 \mu m^2 \]  
\textbf{Eqn. 6.6}
Eqn. 6.6 is plotted in Figure 6.2. Figure 6.2 shows that if a smaller powder is used, the required minimum thickness of TiN coating is increased. The reason is that smaller powders have a higher surface-area-to-volume ratio, which allows more Fe to be diffused through the TiN coating. Thus, the Fe concentration would increase faster in the Cu-20Ni-20Mn infiltrant. As a result, a thicker TiN coating is required.

![Graph](image)

**Figure 6.2** Relation of minimum TiN diffusion barrier thickness to powder size for a diffusion time of 30 min at 1200 °C that would result in 1 at. pct. Fe dissolved in molten Cu-20Ni-20Mn infiltrant.

For a typical powder size of 30 μm, the required minimum thickness of TiN coating can be as small as 0.01 μm if we allow 1 at. pct. of Fe to be dissolved in Cu-20Ni-20Mn after infiltration for 30 min at 1200 °C. This result is an order of magnitude smaller than that obtained by the “no-leaking” estimation where no Fe is allowed to be diffused through the TiN diffusion barrier and dissolved in Cu-20Ni-20Mn.

The significance of Eqn. 6.6 suggests that if a pin-hole free TiN diffusion barrier can be deposited on the skeletons, the minimum thickness of the TiN coating can be
reduced to the order of 0.01 μm. This corresponds to only about 2 vol. pct. of TiN in the whole part for a powder size of 30 μm. It is expected that the mechanical properties could be improved significantly with the use of thinner TiN coating.

In Chapter 3, TiN-coated steel bars with different TiN thicknesses were brought into contact with molten Cu-20Ni-20Mn. The reactions were studied and it was found that localized reaction zones on the TiN coating started appearing for those specimens with a TiN coating less than 0.5 μm. The reason is due to the presence of pinholes and defects in the TiN coating where the infiltrant can easily attack the steel substrates. This was confirmed by the acid test, which reveals the distribution of pinholes on the TiN coating surface. Thus, from a processing standpoint, it is advisable to have a minimum thickness of 0.5 μm to ensure a pinhole free TiN diffusion barrier under. However, a change in coating processing vendors or the use of other coating techniques like PVD with refined processing procedures could produce a thinner film with higher quality that can be used for diffusion barrier in this materials system.

6.2 Maximum Thickness

Ideally, a thicker TiN film guarantees that it can prevent any interdiffusion between the steel skeletons and Cu-20Ni-20Mn infiltrant. However, a thick film could result in spallation from the steel substrates due to thermal mismatch stress. The stress originates from the thermal cycles during the whole 3DP processes, especially the film deposition and infiltration steps.

Apart from the stress issue, the main limiting factor is the change in properties of the final part due to the presence of the TiN coating. Since TiN is a brittle ceramic, it will make the final part more brittle and more difficult to machine although it could increase the macrohardness to a certain extent. Thus, it is preferable to keep the overall volume fraction of the TiN coating smaller than an arbitrary limit, say, 10 vol. pct. However, the maximum thickness of the TiN coating also depends on the powder size. A large powder
allows the use of a thicker coating for the same TiN volume fraction. Figure 6.3 shows the relation between TiN coating thickness and powder size for a given allowable volume fraction of TiN in the whole 3DP part. Here, it is assumed that the powder skeleton occupies 60 vol. pct. of the total volume and the rest is shared by the TiN coating and the infiltrant.

If 10 vol. pct. of TiN coating is allowed in the final part, the thickness of the TiN can range from 0.5 μm to 2.5 μm corresponding to a powder diameter from 20 μm to 100 μm. For a typical powder size of 50 μm, the maximum thickness of the TiN coating is 1.3 μm in this case. However, if only 5 vol. pct. of TiN is allowed in the final part, the maximum thickness of the TiN coating that can be put on the powder skeleton is only 0.7 μm.

![Graph showing the relation between TiN coating thickness and powder size for different target TiN volume fraction in the final 3DP part.](image)

Figure 6.3 Relation between TiN coating thickness and powder size for different target TiN volume fraction in the final 3DP part.

In conclusion, a minimum thickness of the order of 0.01 μm is enough to allow only 1 at pct. of Fe to be dissolved into molten Cu-20Ni-20Mn at 1200 °C for a 30 min
diffusion time through the TiN diffusion barrier. This serves as the theoretical guideline for the subsequent development of TiN diffusion barrier. However, experimental results suggested that a minimum TiN thickness should generally be used to prevent reaction between the steel powders and Cu-20Ni-20Mn infiltrant under the current batch CVD deposition from the outside vendors selected for this research. On the other hand, the maximum thickness is constrained by the target volume fraction of TiN in the final 3DP part. A larger powder can allow a thicker TiN coating for a given target TiN volume fraction.
CHAPTER 7   DISCUSSION AND CONCLUSIONS

The important contribution of this work has been to develop rehardenable materials systems for 3DP metal tools through the use of a diffusion barrier. A successful diffusion barrier can prevent any diffusion and reaction between the powder skeleton and molten infiltrant. Thus, the original compositions and the hardenabley of the powder and infiltrant materials can be preserved. Following is a summary of the major findings in this dissertation.

1. TiN coating is an effective diffusion barrier that can prevent diffusion and reaction between steel powders and molten Cu-20Ni-20Mn at 1200 °C.

2. A high hardness of 40 HRC was achieved for the 0.8 μm TiN-coated H13 steel skeleton with Cu-20Ni-20Mn infiltrant that had been age hardened at 450 °C for 1 day. The hardness is higher than that of the current material system (420 steel powder with bronze infiltrant) for 3DP metal tooling application, which is 25 HRC.

3. Fracture strength of the TiN coatings on flat steel substrates was found to vary from 100 MPa to 500 MPa for 12 different steel substrates with TiN coating thicknesses ranging from 0.2 μm to 6 μm. There was a general increase in fracture strength with a decrease in TiN coating thickness. Fracture primarily occurred inside the TiN coating.

4. The minimum TiN thickness for good diffusion-barrier performance was experimentally determined to be 0.5 μm with the coating processes done by the selected outside vendors. The presence of pinholes and defects in thinner coatings form localized reaction zones. Optimum TiN thickness was found to be around 1 μm. Film spallation was observed for thicker coatings. A theoretical minimum TiN coating thickness was estimated to be of the order of 0.01 μm if 1 at. pct. of
Fe is allowed to be dissolved in the Cu-20Ni-20Mn infiltrant, which still preserved the hardening response of the Cu-20Ni-20Mn infiltrant.

5. Full infiltration was only observed in 0.7 μm TiN-coated D2 steel skeleton and 0.1-0.2 μm TiN-coated D2, M2, and H13 steel skeletons with Cu-20Ni-20Mn infiltrant at 1200 °C.

6. Despite the ability to prevent reaction between the steel powders and Cu-20Ni-20Mn infiltrant and the increase in hardness of the materials system with the use TiN diffusion barrier, it was compromised with the brittleness of TiN itself, which was shown by the low Charpy impact energy and fracture strength of the infiltrated TiN-coated steel skeleton.

7.1 Selection of Diffusion Barrier

The selection of diffusion barrier was based on a systematic methodology that incorporates theoretical analysis, data from thermodynamic and kinetic databases, processing constraints, and computer calculation by Thermo-Calc. Two classes of materials were determined to be potential candidates for diffusion barrier isolating steel skeleton and Cu-20Ni-20Mn infiltrant, namely refractory metals, and refractory metal nitrides and carbides. Among them, TiN was chosen because of its excellent performance merit based on its thermodynamic stability, low solubility and low diffusivity at high temperature, and good matching of thermal expansion with steel substrates.

Other diffusion barrier materials were also considered. Tungsten is very stable against molten Cu-20Ni-20Mn, which was confirmed by experiments and phase equilibrium calculation. However, there is substantial solubility of W in Fe. On the other hand, tantalum was also tried and it is very stable with pure Fe. However, annealing of deposited Ta film on steel substrates showed that it was converted to TaC at 1200 °C, which was confirmed by XRD. Other ceramic coatings including TiB₂ and ZrN were also
studied but they seemed to be inferior to TiN. However, more detailed studies on these diffusion barriers are encouraged when applied to other materials systems.

7.2 DEPOSITION OF DIFFUSION BARRIER

Chemical vapor deposition is the preferred choice of deposition technique for the TiN coating. Currently, it is the only process that can deposit a conformal coating to the interior of a porous skeleton. For a typical deposition temperature of 1000 °C, the residual stress in the TiN film was calculated to be 1.3 GPa (compressive). A lower stress level in the film would favor its performance as a diffusion barrier during infiltration. To reduce the thermal stress of the thin film, low-temperature CVD (LT-CVD) can be considered, which can reduce the deposition temperature to as low as 500 °C. However, the grain size of the deposited film would be reduced accordingly. A small grain size is beneficial to mechanical properties but the increased grain-boundary density could also make the film more susceptible to grain boundary attack by the molten infiltrant or increase the grain-boundary contribution to diffusivity of Fe in TiN.

7.3 INFILTRATION AND REACTION

TiN diffusion barriers with a thickness ranging from 0.2 μm to 6 μm were deposited on twelve different flat steel bars to study the ability to prevent reaction with molten Cu-20Ni-20Mn at 1200 °C. Coatings with thickness of 1 μm were very successful in isolating the steels from Cu-20Ni-20Mn. The minimum effective coating thickness was determined to be 0.5 μm. Below that, strong reaction occurred because of the presence of excessive pinholes and defects in the TiN coatings. The maximum permitted coating thickness was limited by spallation of the TiN coating, which occurred for a film thickness larger than a few μm.

Among the steel substrates, TiN coatings on tool steels in general had a better diffusion-barrier performance than on stainless steels substrates. This could be related to
the carbon activity and to the presence of native oxide on the substrate surfaces, which affect the film adhesion and growth.

Infiltration of the TiN-coated steel powder skeletons were also studied. For a TiN coating thickness from 0.1 to 0.2 μm, full infiltration occurred for tool steel substrates while stainless steel substrates did not give good infiltration. For thicker TiN coatings (0.5-0.8 μm), only D2 tool-steel skeleton had full infiltration. M2 and H13 tool-steel skeletons only had partial infiltration on the skeleton surface with an average infiltration depth of 5 mm. The stainless steel skeletons did not have good infiltration at all. The reason of poor infiltration could be due to the blocking of the Cu-20Ni-20Mn infiltrant by the solid phase in the reaction zone, which is a mixture of Fe and Cu-20Ni-20Mn. D2 steel skeletons always have the best infiltration, which may be due to the larger average powder size and wider fluid-flow channels between the powders. Another reason of the poor infiltration could be due to the oxide formation on the TiN coating as it heated up to the infiltration temperature.

Excellent diffusion barrier performance was obtained for the H13 tool-steel skeleton with a TiN coating thickness of 0.8 μm. No reaction occurred between the H13 steel powders and the Cu-20Ni-20Mn infiltrant. The TiN coating is uniform and intact after infiltration. The performance of the TiN diffusion barrier can be illustrated by comparing Figure 8.1 and Figure 8.2, which are cross sections of the infiltrated H13 skeleton with and without TiN diffusion barrier, respectively.
Figure 7.1 Cross section of the TiN-coated H13 steel skeleton infiltrated with molten Cu-20Ni-20Mn infiltrant.

Figure 7.2 Cross section of the uncoated H13 steel skeleton infiltrated with molten Cu-20Ni-20Mn infiltrant.
7.4 **Fracture of the TiN Coating**

The fracture strength of the TiN coated steel bars was evaluated with tensile tests. It was found that there was a general increase in fracture strength with a decrease in film thickness, although there was a large range of values among different steels even with the same coating thickness. Fracture occurred mainly inside the TiN coating with the crack propagating parallel to the coating surface, splitting the coating in half. As the fracture strength increased, there was a transition of fracture mode from in-layer to interfacial fracture at the TiN/steel interface. This occurred at a coating thickness of about 1 \( \mu \text{m} \) with an average fracture strength of 400 MPa. Fracture strength of the TiN coating as high as 560 MPa can be achieved for a 0.5 \( \mu \text{m} \) thick TiN coating on 440 C stainless steel bar.

Since the experimental values of fracture strength are statistical in nature, more tensile tests are required to confirm the dependence of fracture strength on coating thickness and substrate material. Fracture resistance can be improved by the use of multilayer coatings. Adhesion of the film can be improved with an increase in surface roughness of the substrates.

7.5 **Hardness of the Infiltrated Skeleton**

The Cu-20Ni-20Mn infiltrant can be hardened by spinodal and order-disorder transformation below 530 °C, with the formation of NiMn ordered phase. Systematic heat-treatment studies were carried out and it was found that a maximum hardness of 35 HRC can be achieved for an aging of one day at 450 °C, comparing to a hardness of only 50 HRB in the annealed state. Solution treatments at 650 °C for an hour is optional as it did not significantly affect the hardening response of Cu-20Ni-20Mn. Experimental results from other studies showed that Cu-20Ni-20Mn can be hardened to 45 HRC with
the solution treatment. The difference could be due to the lack of cold working in the present work and a slight difference in composition.

Different steel substrates were also subjected to the same heat treatments used for Cu-20Ni-20Mn. Both the hardness and the subsequent hardenability of the steels were reduced if they were annealed at 650 °C for one hour. On the other hand, direct tempering of the steels at 450 °C for one day did not show any deterioration of hardness. Average hardesses ranging from 45 to 55 HRC could be obtained for the steel substrates. Because of the different effects of heat treatment to the steel skeleton and Cu-20Ni-20Mn infiltrant, two heat treatment routines are proposed:

1) **Heat Treatment Schedule A (if no machining or surface finishing is required after infiltration):**
   i) Infiltration at 1200 °C and fast cooling in the furnace.
   ii) Direct age hardening at 450 °C for one day in the furnace right after infiltration.

2) **Heat Treatment Schedule B (if machining and surface finishing is required after infiltration and rehardening is required after machining and surface finishing):**
   i) Infiltration at 1200 °C.
   ii) Annealing at the typical steel annealing temperature (~800 °C-900 °C) with slow cooling in the furnace (~15-20 °C/hr).
   iii) Final machining and surface finishing of the metal part in the soft annealed state.
   iv) Austenitizing at typical steel austenitizing temperature (~1000-1100 °C)
   v) Quenching to room temperature to obtain a hard steel and soft Cu-20Ni-20Mn specimen.
   vi) Age hardening of the Cu-20Ni-20Mn and tempering of steel at 450 °C for one hour or other customized condition to obtain optimum heat treatment properties of the final part.

Both macro- and micro-hardnesses of the infiltrated TiN-coated skeletons were measured according to heat treatment schedule A. A very high macrohardness of 40 HRC
was obtained for the H13 steel specimen. Microhardness results showed that the H13 steel powder hardened to 55 HRC while the Cu-20Ni-20Mn infiltrant hardened to 45 HRC. The lower overall macrohardness could be due to the formation of indentation crack during the macrohardness measurement. Nevertheless, the high hardness level achieved in this specimen was due to the effectiveness of the TiN coating preventing reaction between the H13 steel powders and the molten Cu-20Ni-20Mn infiltrant. Other steel specimens did not show significant hardening response as the TiN coating was not thick enough and pinhole-free to suppress the interaction of steel and infiltrant.

According to Dean et al.,[1,2] hardness of the materials system could be even increased by lowering the Cu content in the infiltrant. For example, a hardness of 53 HRC could be achieved for Cu-35Ni-35Mn after aging at 450 °C for 12 hours.[2] However, this could result in a decrease in toughness.

7.6 SUGGESTIONS FOR FUTURE WORK

Currently, the use of TiN diffusion barrier to the steel/Cu-20Ni-20Mn material system is limited by the localized reaction zones on thin TiN coatings and the brittleness of TiN itself. The focus of work should be on the elimination of TiN coating defects and the use of thinner coatings.

Following are some suggestions for future work to improve the performance of TiN diffusion barrier for the steel/Cu-20Ni-20Mn system and to maximize the potential of using diffusion barriers in the development of other rehardenable materials systems for 3DP metal tooling.

7.6.1 Change in Coating Thickness

The success of the H13 steel skeleton with 0.8 μm-thick TiN diffusion barrier suggests additional experimental studies on other steel powder skeletons with a TiN
thickness close to 1 μm. This should eliminate the problem of localized reaction zones on
the TiN coating that was observed in specimens with thinner coatings. This assumed that
the current coating vendors are used for the coating deposition in the future. However, as
it was shown in Chapter 6 that the theoretical minimum thickness of the TiN coating can
be as small as 0.01 μm, it is advisable to find another coating vendor that can deposit
pinhole-free TiN film with a smaller TiN thickness towards 0.01 μm. The success of this
approach should substantially increase the mechanical properties of the final part such as
higher fracture strength and improved overall ductility.

7.6.2 Other Diffusion Barrier

Other materials systems that have strong reaction between the skeletons and
infiltrants can be revisited with the application of suitable diffusion barrier. The ceramic
and refractory metal diffusion barriers should be applicable to a wide range of materials
systems because of their exceptional physical and chemical properties at high
temperature. It should be noted that if the powder substrates contain carbide or nitride
forming agent, refractory metal diffusion barriers should generally not be considered as
they can easily form refractory metal carbides or nitrides at high temperature.

Multilayer coatings can also be considered. Specific properties of the diffusion
barrier can be obtained to optimize the interfacial reaction at the powder side and the
infiltrant side of the diffusion barrier.

7.6.3 Other Powder Coating Techniques

To maximize the flexibility of the 3DP process with diffusion barrier, the coating
of diffusion barrier on each individual powder particles could be useful. This can be done
by fluidized-bed CVD. This technique has been used for the coating of metals on many
ceramic powders to improve liquid-phase sintering. Another idea is the modification to
the conventional PVD system that can incorporate a rotating device in the system, thus
ensuring each powder particle is coated uniformly.
If ceramic diffusion barrier such as TiN is coated on steel powders before sintering, new binder and sintering technique that enables the coated powder to sinter to reasonable green strength have to be developed. The reason is that the melting point of TiN is much higher than that of steel powders. Sintering of the coated powders is very difficult as neck formation between the powders by the transport of TiN is expected to be minimal near the melting point of steel. In this case, additional materials have to be provided by the binders to form the neck between powders during sintering. Metal salts or oxides that can be reduced to metal and deposited in the neck region can be used in this case.

7.6.4 Heat Treatment

Extensive study with specific heat treatment procedures have to be developed for each materials system to optimize the mechanical properties of the final infiltrated part.

7.6.5 EDM Measurement

In order to fully characterize the TiN diffusion barrier approach for 3DP metal tooling, machining characteristics such as EDM performance are also required.

In conclusion, the use of diffusion barrier greatly improves the flexibility of choice of materials systems for 3DP metal tooling. Tailor-made materials properties can be obtained by choosing compatible powder, infiltrant, and diffusion-barrier materials. Success in the use of TiN diffusion barrier for the steel/Cu-20Ni-20Mn system demonstrated the potential of incorporating diffusion barrier as one component of metal-based materials systems for 3DP.
7.7 REFERENCES


APPENDIX A  STRATEGY FOR MATERIALS SELECTION

All Materials

**Screening**: apply property limits
(Eliminate candidates which cannot do the job)

**Ranking**: apply materials indices
(Find candidates which can do the job well)

Subset of Materials

**Supporting Information**:  
Handbooks, specialized software, 
expert systems, CD-ROMS, WWW  
(search "family history" of candidates)

Prime Candidates

**Local Conditions**  
(Does the choice match local needs, expertise?)

Final Material Choice


**Figure A.1**  The strategy for materials selection. The main steps are enclosed in bold boxes.

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APPENDIX B  SOLUBILITY

B.1 PREDICTION OF SOLID SOLUBILITY

The basic empirical rules governing the formation of solid solution and predicting solubility were first proposed in the early 1930's by Hume-Rothery and co-workers.\textsuperscript{[1]} The three rules (or factors) are known as:

1) The 15\% size rule;
2) The electrochemical effect; and
3) The relative valency effect.

In summary, a solid solution have limited solubilities (< 5 at. \%) when:

1) There is a large difference of the atomic diameter between the solute and solvent atoms;
2) Formation of stable intermediate compounds; and
3) Solute atom has lower valency than the solvent.

As shown by Waber et al. \textsuperscript{[2]} when the simple size rule alone was applied, over 90\% of the predicted insoluble systems indeed showed limited solubility. However, the rule only has moderate success in predicting systems with extended mutual solubility. Clearly, other factors play a critical role in solid-solution formation. Nevertheless, the rules are important guidelines to screen and rank the diffusion-barrier candidates. Detail discussion of the validity of the Hume-Rothery rules and recent development on the art of predicting solubility can be found elsewhere.\textsuperscript{[3, 4]}

Practically, Darken and Gurry suggested that the extent of solid solubility in a given solvent metal may be assessed by testing simultaneously both the size and electronegativity differences between solvent and solute elements.\textsuperscript{[5]} The more distant any two points are on the Darken-Gurry map, the more likely is a low mutual solid solubility between the elements involved. Because of the periodicity of the atomic size
and electronegativity in the Periodic Table, this implies an important screening guideline for solubility is to choose an element away from Fe in the Periodic Table.

To construct the Darken-Gurry map for the solvent Fe, data for atomic radius\(^6\) and electronegativities\(^7\) for all the diffusion barrier candidates from Chapter 2 are collected (For reference, Cu and Mn are also included as they are the alloying elements in the infiltrant.) An ellipse of minor axis (abscissa) of ±15% of iron’s radius and major axis (ordinate) of ±0.4 of electronegativity difference is superimposed on the scatter plot of electronegativity versus atomic radius. According to Darken, those elements outside the ellipse are expected to have limited solubility in Fe. Figure B.1 shows that limited solubility is expected for B, C, Sc, Ti, Y, Zr, Nb, Hf, Ta and W with Fe.

![Diagram](image)

**Figure B.1** The Darken-Gurry map with an ellipse drawn about the solvent Fe (■). The minor axis is ±15% of iron’s radius and the major axis is ±0.4 of electronegativity difference. All elements (●) with melting points higher than 1200 °C are displayed. Cu and Mn (▲) are included for reference.
B.2 **SOlubility Limit From Phase Diagram**

Actual solubility data for the Fe and diffusion barrier candidates at 1200 °C are extracted from binary alloy phase diagrams.\(^{8,9}\) In general, two types of phase diagram are observed for these binary systems: 1) complete solid solubility and 2) limited solubility with one or more intermetallic compounds between the primary solid solution phases. In type 1 phase diagram, unlimited mutual solubility is found for both the solute and solvent such as the Fe-Ni system at 1200 °C (Figure B.2). In type 2 phase diagram, stable intermetallic compounds are formed, which generally restrict primary solid solubility.\(^{3}\) This is illustrated in Figure B.4. An example of this system is Fe-Sc (Figure B.3) where Fe\(_2\)Sc is the intermetallic compound (Laves phases\(^{10}\)).

**Fe-Ni**

![Diagram of Fe-Ni phase diagram](image)

*Figure B.2  Example of type 1 phase diagram: Fe-Ni.*
Fe-Sc

Figure B.3 Example of type 2 phase diagram: Fe-Sc.

Figure B.4 Restriction of primary solid solubility due to stability of an intermediate phase.\(^3\)
Grouping of the elements shows that for those elements inside the ellipse, both unlimited solubility of type 1 phase diagram (Table B.1) and extended solubility of type 2 phase diagrams are found (Table B.2). Those elements outside the ellipse (Table B.3) with the exception of Ti show very limited mutual solubility (0 at. % - 5 at. %). They all belong to type 2 phase diagram, which exhibits one or more intermetallic compounds including Fe₂M, where M is the solute element. There is an excellent agreement with the prediction from the Darken-Gurry map, which predicts limited solubility for primary solid solution if there is a large difference in atomic radii and electronegativity between the solvent and solute atom.

The excess molar Gibbs energy of a solution phase is expressed as:

\[ \Delta G = \Delta H - T \Delta S \]  

**Eqn. B.1**

where \( \Delta H \) is the molar enthalpy of mixing and \( \Delta S \) is the molar excess entropy. A large difference in atomic radii usually results in large \( \Delta H \) for substitutional solid solution. Formation of intermetallic compounds with ordering of Fe and M results in a very small \( \Delta H \) for the compound phase, which is usually confined to a small compositional range. Thus, intermetallic compound is characterized by a deep and narrow free energy curve. Limited solubility results when lever rule is applied to the free energy diagram in Figure B.4.

<table>
<thead>
<tr>
<th>Diffusion Barrier Element (M)</th>
<th>Co</th>
<th>Cr</th>
<th>Ir</th>
<th>Ni</th>
<th>Os</th>
<th>Pd</th>
<th>Pt</th>
<th>Ru</th>
<th>V</th>
</tr>
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<tbody>
<tr>
<td>Unlimited mutual solubility in Fe and M</td>
<td></td>
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**Table B.1** Solubility for elements that exhibit type 1 phase diagram inside the ellipse of Darken-Gurry map.
<table>
<thead>
<tr>
<th>Diffusion Barrier Element (M)</th>
<th>Be</th>
<th>Mo</th>
<th>Re</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in Fe, at%</td>
<td>25</td>
<td>12</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Solubility in M, at%</td>
<td>1</td>
<td>7</td>
<td>N/A</td>
<td>0</td>
</tr>
</tbody>
</table>

Table B.2 Solubility for elements that exhibit type 2 phase diagram inside the ellipse of Darken-Gurry map.

<table>
<thead>
<tr>
<th>Diffusion Barrier Element (M)</th>
<th>B</th>
<th>C</th>
<th>Hf</th>
<th>Nb</th>
<th>Sc</th>
<th>Ta</th>
<th>Ti</th>
<th>W</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in Fe, at%</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>9</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Solubility in M, at%</td>
<td>N/A</td>
<td>N/A</td>
<td>0.1</td>
<td>6</td>
<td>0.1</td>
<td>0.1</td>
<td>14</td>
<td>1</td>
<td>0.1</td>
<td>5</td>
</tr>
</tbody>
</table>

Table B.3 Solubility for elements outside the ellipse of Darken-Gurry map. All exhibit type 2 phase diagram.

Boron and carbon are subsequently dropped from consideration as they have exceptionally high diffusivities in Fe because of their small size and low activation energy associated with the interstitial diffusion mechanism. Thus, the remaining candidates (in order of increasing atomic number) are Sc, Y, Zr, Nb, Hf, Ta and W, which are shaded. Except Sc and Y, they belong to the refractory metals and are farthest away from Fe among the transition metals in the Periodic Table.
B.3 REFERENCES


APPENDIX C REACTION AND DIFFUSION

C.1 TYPE 1 PHASE DIAGRAM — COMPLETE SOLUBILITY

In type 1 phase diagram, where unlimited solid solution is formed, interdiffusion occurs in a continuous solid solution. There is a composition continuity at the interface between the diffusion barrier and the Fe substrate. Assuming the film is thin compared to the size of the Fe substrate, the classical solution to the one-dimensional diffusion equation for a thin film source located at x=0 is

\[ C(x, t) = \frac{C_0 h}{\sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right) \]  

**Eqn. C.1**

where \( D \) is the diffusion coefficient of the diffusion barrier atom in Fe;
\( C_o \) is the initial concentration in the film; and
\( h \) is the film thickness.

Assume the diffusion barrier fails when \( C(0, t)/C_0 = 0.5 \), the minimum thickness of the diffusion barrier should be

\[ h = 0.5\sqrt{\pi Dt} \]  

**Eqn. C.2**

Impurity tracer diffusivities of some type 1 diffusion barrier materials in Fe are obtained and they are shown in Figure C.1.\(^{[1]}\) It should be noted that chemical diffusivities should be used in Eqn. C.2. The use of impurity tracer diffusivities here is a convenient estimate and it may involve some error. Table C.1 shows the diffusivities of those elements and the required coating thicknesses for \( t = 30 \) min at a temperature of 1200 °C.

<table>
<thead>
<tr>
<th>Diffusion Barrier Element (M)</th>
<th>Co</th>
<th>Cr</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity in Fe, ( 10^{-15} ) m²/s</td>
<td>4.9</td>
<td>48.5</td>
<td>3.3</td>
<td>4.5</td>
<td>8.6</td>
<td>12.4</td>
</tr>
<tr>
<td>Required Film Thickness, μm</td>
<td>2.6</td>
<td>8.3</td>
<td>2.1</td>
<td>2.5</td>
<td>3.5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

**Table C.1** Diffusivities and thicknesses of type 1 diffusion barriers. Diffusivities are evaluated at 1200 °C and thicknesses are calculated according to Eqn. C.2.
Figure C.1  Impurity diffusivities in Fe.$^{[1]}$
C.2 Type 2 Phase Diagram — Limited Solubility with Intermetallic Compound

In type 2 phase diagram, there is limited solubility in the primary solid solution with the formation of intermetallic phases. The intermetallic phase form at the interface between the diffusion barrier material and Fe substrate. Usually, the growth of this compound is diffusion-controlled and equilibrium concentration is established at the \(\alpha-\beta\) and \(\beta-\gamma\) interfaces as shown in Figure C.2.

\[\text{Figure C.2} \text{ Type 2 phase diagram. Metals} \alpha \text{ and} \gamma \text{ form compound phase} \beta \text{ by interdiffusion at temperature} \ T.\]

The width \(W_b\) of the intermetallic phase \(\beta\) after a time \(t\) has been derived by Kidson\(^2\):

\[W_b = \frac{2\left[\frac{(DK)_{\beta\gamma} - (DK)_{\beta\alpha}}{C_{\beta\gamma} - C_{\gamma\beta}} \times \left(\frac{(DK)_{\beta\alpha} - (DK)_{\gamma\beta}}{C_{\alpha\beta} - C_{\beta\alpha}}\right)\right]}{t^{1/2}} \quad \text{Eqn. C.3}\]

\[= k_\beta t^{1/2}\]
where $K_{ij} = \sqrt{\left(\frac{\partial C}{\partial x}\right)_{ij}}$ is evaluated at the $i$-side of the physical interface;

$D_{ij}$ is the interdiffusion coefficient at the same point;

We see that the growth of the intermetallic phase follows the diffusion-controlled parabolic growth law. Since most of the intermetallic phase is a stoichiometric compound, we can approximate $C_{\beta\gamma} = C_{\beta\alpha} = C_{\beta}$ and the concentration profile is essentially flat in the intermetallic compound. A simple expression of $W_{\beta}$ is then obtained:[3]

$$W_{\beta} = k_\gamma \sqrt{D_{\gamma} t} + k_\alpha \sqrt{D_{\alpha} t}$$  \hspace{1cm} \text{Eqn. C.4}

where $k_\gamma = \frac{(1 - C_{\beta\gamma})}{\sqrt{(C_{\gamma\beta} - C_{\beta}) C_{\gamma}}}$;

$k_\alpha = \frac{C_{\alpha\beta}}{\sqrt{(C_{\beta} - C_{\alpha\beta}) C_{\beta}}}$;

$D_i$ is the interdiffusion coefficient in the $i$-phase.

From Figure C.2, let $\alpha$ be the Fe-rich phase and $\gamma$ be the M-rich phase, where M is the diffusion barrier candidate of type 2 from Table B.3. Also, define the solubility of M in Fe as $S_{Fe}$, and the solubility of Fe in M as $S_M$. Assume the intermetallic compound is FeM.

Thus, $S_M \equiv 1 - C_{\gamma\beta} \to 0$;

$S_{Fe} \equiv C_{\alpha\beta} \to 0$;

$C_{\beta} = 0.5$.

The following simplified expression for the growth of FeM intermetallic compound with limited primary solid solution is then obtained:

$$W_{\beta} = 2\left(\sqrt{S_M^2 D_{M} t} + \sqrt{S_{Fe}^2 D_{Fe} t}\right)$$  \hspace{1cm} \text{Eqn. C.5}

The growth of the intermetallic compound is suppressed by the solubility limit when compared to a type 1 diffusion barrier in Eqn. C.2. For example, a 10% solubility results in an effective diffusivity 2 orders of magnitudes smaller. The thickness of the
diffusion barrier is calculated by the complete consumption of the barrier by the growth of the compound. Assuming all the barrier material ends up in the compound:

$$ h = C_B \times W_B $$  \hspace{1cm} \text{Eqn. C.6} \\

In addition, since the primary solid solution has very limited solubility, we can approximate it as dilute solution and the interdiffusion coefficient can be replaced by impurity tracer diffusion coefficient, which can be readily obtained from diffusion data book. The diffusivity data\textsuperscript{[1, 6]} and the expected barrier thickness for the candidates in Table B.3 are computed in Table C.2. Here, diffusivities are evaluated at 1200 °C and $h$ is calculated for a time of 30 min with the formation of intermetallic compound FeM according to Eqn. C.5 and Eqn. C.6.

<table>
<thead>
<tr>
<th>Diffusion Barrier Element (M)</th>
<th>Hf</th>
<th>Nb</th>
<th>Sc</th>
<th>Ta</th>
<th>W</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility of M in Fe, $S_{Fe}$, at%</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Solubility of Fe in M, $S_M$, at%</td>
<td>0.1</td>
<td>6</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>Diffusivity of M in Fe, $D_{Fe}$, $10^{-16}$ m$^2$/s</td>
<td>13</td>
<td>2900</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Diffusivity of Fe in M, $D_M$, $10^{-16}$ m$^2$/s</td>
<td>*10$^6$</td>
<td>**5.1</td>
<td>10$^7$</td>
<td>13</td>
<td>2.2</td>
<td>10$^7$</td>
<td>10$^6$</td>
</tr>
<tr>
<td>Barrier thickness, $h$, μm</td>
<td>0.88</td>
<td>0.57</td>
<td>2.77</td>
<td>0.09</td>
<td>0.34</td>
<td>2.77</td>
<td>42.5</td>
</tr>
</tbody>
</table>

* Diffusivity of Fe in Hf is an assumed value in reference to Fe diffusion in Zr.
** Diffusivity of Fe in Nb is extrapolated from high temperature measurement.
† Estimated diffusivities from diffusion of other transition metals in Fe in Figure C.1

Table C.2 Required thicknesses of type 2 diffusion barrier candidates.

It should be pointed out that the above analysis is for the formation of compound of FeM type. Other compound such as Fe$_2$M or FeM$_2$ can be formed first, depending on the materials system. In that case, there is only a minor change of the factor 2 in Eqn. C.5. The prediction of the first phase formation and the formation of a series of compounds at the interface can be found in other texts\textsuperscript{[4, 5]} Besides, the calculation is very sensitive to
the accuracy of actual solubility values and diffusivities. For example, a change of $S_{Re}$ from 1% to 0.1% results in an order-of-magnitude decrease in barrier thickness. Nevertheless, it is safe to say that a diffusion barrier made of refractory metal (Ta, W, Nb, and Hf) with a thickness of the order of 1 µm is possible for the protection of steel substrate against reaction of molten infiltrant at 1200 °C for 30 min.
C.3 REFERENCES


### APPENDIX D  COMPOSITIONS OF STEELS

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Ni</th>
<th>W</th>
<th>Cu</th>
<th>V</th>
<th>Ta</th>
<th>Al</th>
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</thead>
<tbody>
<tr>
<td>316L</td>
<td>0.02</td>
<td>16.42</td>
<td>1.66</td>
<td>0.61</td>
<td>2.08</td>
<td>10.44</td>
<td>0.32</td>
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<td></td>
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<tr>
<td>17-4PH</td>
<td>0.04</td>
<td>15.73</td>
<td>0.29</td>
<td>0.39</td>
<td>0.09</td>
<td>4.17</td>
<td>3.30</td>
<td></td>
<td></td>
<td>0.26</td>
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</tr>
<tr>
<td>420</td>
<td>0.15</td>
<td>12.85</td>
<td>0.81</td>
<td>0.26</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>1018</td>
<td>0.18</td>
<td>0.70</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H13</td>
<td>0.40</td>
<td>5.22</td>
<td>0.34</td>
<td>1.08</td>
<td>1.32</td>
<td>0.19</td>
<td>0.10</td>
<td>0.96</td>
<td>0.01</td>
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</tr>
<tr>
<td>4142</td>
<td>0.42</td>
<td>1.00</td>
<td>0.90</td>
<td>0.15</td>
<td>0.20</td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>S7</td>
<td>0.50</td>
<td>3.25</td>
<td>0.75</td>
<td>0.25</td>
<td>1.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>0.85</td>
<td>4.15</td>
<td>0.25</td>
<td>0.30</td>
<td>5.00</td>
<td>6.30</td>
<td>1.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.95</td>
<td>0.50</td>
<td>1.20</td>
<td>0.30</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>1.00</td>
<td>5.25</td>
<td>0.60</td>
<td>0.40</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>440C</td>
<td>1.03</td>
<td>16.41</td>
<td>0.67</td>
<td>0.47</td>
<td>0.46</td>
<td>0.34</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>1.50</td>
<td>12.00</td>
<td>0.30</td>
<td>0.30</td>
<td>0.75</td>
<td>0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data source: Alliant Metals Inc. for 316L, 17-4PH, 420 and 440C.  
Carpenter Technology Corp. for H13.  
MSC (Starrett) for 1018 and A2.  
Burgon Tool Steel Co. Inc. for 4142, S7, M2, O1 and D2.

Table D.1  Composition of steel bars in weight percent (Fe balance).
<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Ni</th>
<th>W</th>
<th>Cu</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-4PH</td>
<td>0.07</td>
<td>15-17.5</td>
<td>1</td>
<td>1</td>
<td>3-5</td>
<td></td>
<td>3-5</td>
<td>0.15-0.45 Nb</td>
<td></td>
</tr>
<tr>
<td>H13</td>
<td>0.35</td>
<td>5</td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>420</td>
<td>0.47</td>
<td>14</td>
<td>0.29</td>
<td>0.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>0.98</td>
<td>4.2</td>
<td>0.28</td>
<td>0.44</td>
<td>5.1</td>
<td>5.8</td>
<td></td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>440C</td>
<td>0.95-1.2</td>
<td>16-18</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>1.51</td>
<td>11.7</td>
<td>0.36</td>
<td>0.3</td>
<td>0.77</td>
<td>0.1</td>
<td>0.03</td>
<td>0.03</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Data source: Ultrafine Powder Technology M2. UFC, Inc. for 174PH and 440C. Anval (now Carpenter Technology Corp.) for 420, H13, and D2.

Table D.2 Composition of steel powders in weight percent (Fe balance).
APPENDIX E  THERMO-CALC RESULTS ON THE
INTERACTIONS OF TiN WITH STEELS

Figure E.1  Phase mole fraction vs. temperature of TiN/316L stainless steel.

Figure E.2  Major elements in TiN phase of TiN/316L stainless steel.
Figure E.3  Phase mole fraction vs. temperature of TiN/17-4PH stainless steel.

Figure E.4  Major elements in TiN phase of TiN/17-4PH stainless steel.
Figure E.5  Phase mole fraction vs. temperature of TiN/420 stainless steel.

Figure E.6  Major elements in TiN phase of TiN/420 stainless steel.
Figure E.7  Phase mole fraction vs. temperature of TiN/1018 low carbon steel.

Figure E.8  Major elements in TiN phase of TiN/1018 low carbon steel.
Figure E.9  Phase mole fraction vs. temperature of TiN/H13 tool steel.

Figure E.10  Major elements in TiN phase of TiN/H13 tool steel.
Figure E.11  Phase mole fraction vs. temperature of TiN/4142 standard alloy steel.

Figure E.12  Major elements in TiN phase of TiN/4142 standard alloy steel.
Figure E.13  Phase mole fraction vs. temperature of TiN/S7 tool steel.

Figure E.14  Major elements in TiN phase of TiN/S7 tool steel.
Figure E.15  Phase mole fraction vs. temperature of TiN/M2 tool steel.

Figure E.16  Major elements in TiN phase of TiN/M2 tool steel.
Figure E.17  Phase mole fraction vs. temperature of TiN/O1 tool steel.

Figure E.18  Major elements in TiN phase of TiN/O1 tool steel.
Figure E.19  Phase mole fraction vs. temperature of TiN/A2 tool steel.

Figure E.20  Major elements in TiN phase of TiN/A2 tool steel.
Figure E.21  Phase mole fraction vs. temperature of TiN/440C stainless steel.

Figure E.22  Major elements in TiN phase of TiN/440C stainless steel.
Figure E.23  Phase mole fraction vs. temperature of TiN/D2 tool steel.

Figure E.24  Major elements in TiN phase of TiN/D2 tool steel.
APPENDIX F  EFFECT OF THERMAL-MISMATCH STRESS

Since there is a difference in the coefficient of thermal expansion (CTE) between the steel substrate and the TiN coating, thermal residual stress in the TiN coating is expected after the coating process. In order to estimate the effect of this thermal stress mismatch to the fracture strength measurement, the thermal residual stress in the TiN coating is estimated according to the following equation.

\[
\sigma_{TN} = \frac{E_{TN} (\alpha_{steel} - \alpha_{TN}) \Delta T}{(1 - v_{TN})}
\]

Eqn. F.1

where \( E_{TN} = 590 \, \text{GPa} \) is the Young’s modulus of TiN;
\( v_{TN} = 0.24 \) is the Poisson’s ratio of TiN;
\( \alpha_{steel} \approx 11 \times 10^{-6} \, \text{°C}^{-1} \) is the average CTE of steel;
\( \alpha_{TN} = 9.35 \times 10^{-6} \, \text{°C}^{-1} \) is the CTE of TiN;
\( \Delta T = 1000 \, \text{°C} \) is the difference between the depositing temperature and room temperature.

(Data from reference 1)

Assuming that there is no stress at the deposition temperature, the thermal residual stress is estimated to be 1.3 GPa in compression according to Eqn. F.1. It is believed that the residual stress in the TiN coating originates solely from the thermal residual stress.\(^2\)

F.1 REFERENCES
