HEAT TREATMENT OF CAST Co-Cr-Mo-C SURGICAL IMPLANT ALLOYS

by

JAMES RICHARD COKE
S.B., M.I.T.
1971

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
June, 1975

Signature of Author .................................................

Department of Materials Science and Engineering

May 9, 1975

Certified by ...................................................

Tesis Supervisor

Accepted by ...................................................

Chairman, Departmental Committee on Graduate Students
ABSTRACT

HEAT TREATMENT OF CAST CO-CR-MO-C SURGICAL IMPLANT ALLOYS

by

JAMES RICHARD COKE

Submitted to the Department of Metallurgy and Materials Science on May 9, 1975 in partial fulfillment of the requirements for the degree of Master of Science.

The experiments reported in this thesis were undertaken to characterize the microstructures resulting in the improvement of room temperature tensile properties of Co-Cr-Mo-C surgical implants achieved by hot isostatic pressing and solutionizing and aging heat treatments. Optical metallography, microradiography, transmission electron microscopy, and tensile testing were used to study the microstructure and properties of investment cast tensile specimens. The most significant improvement in tensile properties was achieved by hot isostatic pressing of castings at 1200°C in an argon atmosphere at 15 ksi or higher pressure for four hours. Subsequent solutionizing and precipitation heat treatments provided further improvement. These treatments were found to enhance the corrosion resistance of the material studied.

Transmission electron microscopy was employed for extensive observations of the phase structure, precipitation behavior, and stacking fault phenomena occurring in both wrought and cast Co-Cr-Mo-C alloys. It has been attempted to rationalize tensile property modifications in terms of the microstructural features so observed.

Thesis Supervisor: John Wulff
Title: Professor Emeritus of Metallurgy
# TABLE OF CONTENTS

Abstract ................................................. 2

List of Figures .......................................... 4

List of Tables ........................................... 6

Acknowledgements ........................................ 7

I. Introduction ........................................... 8

II. Survey of the Literature ............................. 12

III. Organization of the Research ....................... 15

IV. Experimental Procedures and Materials .......... 16

V. Hot Isostatic Pressing and Heat Treatment of Cast
   Co-Cr-Mo-C Surgical Implant Alloys ............... 20
      V.1 Experimental Results .......................... 20
      V.2 Discussion and Conclusions .................. 22

VI. Transmission Electron Microscopic Studies of Wrought
    and Cast Co-Cr-Mo-C Surgical Implant Alloys .... 25
      VI.1 Experimental Results ....................... 25
         VI.1.1 Wrought and Cast Material, Solution Treated
                 and Quenched .............................. 25
         VI.1.2 Wrought Material Aged at 650°C .......... 26
         VI.1.3 Cast Material Aged at 650°C ............ 26
         VI.1.4 Wrought Material Aged at 750°C .......... 27
         VI.1.5 Stacking Fault Interaction ............... 28
      VI.2 Discussion and Conclusions .................. 28
         VI.2.1 Microstructures ......................... 28
         VI.2.2 Relation of Properties to the Microstructure . 31

VII. Conclusions ......................................... 33

VII. References .......................................... 34
LIST OF FIGURES

1. Comparison of microstructures resulting from casting by low superheat vacuum method and conventional technique ........ 41
2. Microstructure of as-wrought H.S.21 ................................. 43
3. Detail of grain boundary carbide formations typical of as-cast Co-Cr-Mo-C alloys ............................... 44
4. Microradiographs showing microporosity of as-cast specimens and absence of porosity in hot isostatic pressed specimens ... 45
5. Electron photomicrograph of cast solutionized H.S.21 showing fcc stacking faults and bands of martensitic hcp .... 47
6. Microstructure of cast specimen solutionized and aged at 650°C for 20 hours .................................................. 48
7. Electron photomicrograph showing dense stacking fault formations occurring in cast material following solution treatment and aging at 650°C for 20 hours ................. 49
8. Microstructure of solutionized cast H.S.21 showing particles of undissolved sigma phase ............................... 50
9. Microstructure of wrought solutionized modified H.S.21 showing intragranular transformation markings indicating presence of hcp ........................................ 51
10. Electron photomicrograph showing fcc stacking faults and bands of martensitic hcp in solutionized wrought modified H.S.21 ................................................ 52
11. Microstructure of wrought modified H.S.21 solutionized and aged at 650°C for 20 hours ........................................ 53

12. Electron photomicrograph showing typical hexagonal precipitate structure in cast H.S.21 solutionized and aged at 650°C for 50 hours ........................................ 54

13. Electron photomicrograph showing precipitates edge-on in cast H.S.21 solutionized and aged at 650°C for 50 hours ...... 56

14. Electron photomicrograph of large area of wrought modified H.S.21 solutionized and aged at 750°C for 20 hours ........ 58

15. Electron photomicrographs of large area of wrought modified H.S.21 solutionized and aged at 750°C for 50 hours .......... 60

16. Electron photomicrograph showing both blocked and successful intersections of fcc stacking faults ................. 62

17. Electron photomicrograph showing alignment of a row of precipitates in an hcp region with stacking faults in the adjacent fcc .................................................. 63
I. Summary of statistics compiled by J.T. Scales .............. 38

II. Compositions of alloys used or recommended for surgical
    implant applications  ________________________________ 39

III. Tensile properties of investment cast and wrought
    Co-Cr-Mo-C surgical implant alloys of A.S.T.M. composition
    Specification F75-67 ________________________________ 40
I am deeply indebted to Professor Emeritus John Wulff for suggesting the theme of this thesis, as well as the discussion and guidance he provided from its beginning to its completion, and to Associate Professor John Vander Sande for the great amount of time and effort he spent, and the guidance he provided in this work. To Mr. Guenter Arndt, I owe a special thanks for his technical assistance in the laboratory. The financial assistance provided by the National Science Foundation is also gratefully acknowledged.
I. Introduction

Some forty-five years ago, Erdel and Prang developed investment castings of Co-Cr-W-C alloys called Vitallium for dental applications. Somewhat later, they developed Co-Cr-Mo-C alloys, also called Vitallium, for the same purposes. In 1936, the latter were successfully used in orthopedic surgical implants by Venable and Stuck. In each case, the choice of these alloys was dictated by the earlier findings of Haynes that the similar Co-Cr alloys which he called Stellite exhibited excellent wear and corrosion resistance. Animal tests performed by Zierold in 1924 had shown Stellite to be compatible with living tissue. To date, only one serious case of crevice corrosion pitting of Vitallium in humans has been reported in the clinical literature, whereas of all stainless steel implants excised from patients, more than 80% of those examined have shown signs of crevice or pit corrosion. So far, Co-Cr-Mo-C implants have been faulted only for inadequate torsional and fatigue strength (Table I). According to Cahoon and Paxton, such failures of these implants can be attributed primarily to metallurgical defects incurred during casting. While most implant fabricators agree with this view, it is not uncommon for the stronger wrought Co-Cr-W-Ni (H.S.25) or wrought Co-Cr-Ni-Mo (M.P.35N) alloys to be substituted when possible for weight-bearing implant parts.

Committee F-4 (Surgical Materials) of the American Society of Testing and Materials has established chemical compositions and mechanical property specifications for surgical implants fabricated from as cast
Co-Cr-Mo-C alloys (e.g. H.S.25). Their composition specifications are listed in Table II along with compositions of other alloys not specified by A.S.T.M. for surgical implant uses, but which are used or recommended by others for such applications. The wrought alloys labelled M.I.T.No.7 and modified H.S.21 were developed at M.I.T. by Devine and others,9,10,11 and have been found to have crevice corrosion resistance in saline media superior to that of as cast H.S.21 and Vitallium.

Although it is not difficult to achieve the tensile property levels specified by A.S.T.M. for as cast Co-Cr-Mo-C alloys, a number of foundries engaged in the production of such castings do not consistently do so. They most often fail to meet the specification for minimum ductility (% elongation). This can be attributed not only to improper control of melting and casting variables but also to the basic investment casting technique employed. We have found that a number of methods of casting and post-casting treatment exist which can improve both strength and ductility of the product.

Foundries using grain-nucleating mold wash innoculants such as cobalt oxides or colbalt aluminate usually produce finer grained castings with somewhat higher ductility and tensile strength than those who do not use such innoculants. A greater reduction of grain size and improvement of tensile properties is achieved by a recently developed casting process 12 which uses no innoculants. In this process, the molten metal is not poured into the mold from above but is drawn by vacuum up into the mold from below. The mouth of the mold is held below the molten metal surface, and clean metal with very low superheat quick-
ly fills the mold. Figure 1 compares the microstructures of two castings of A.S.T.M. F75-67 composition. The material in Figure 1a was cast by this process; that in Figure 1b was produced by conventional methods.

Metallographic examination of commercially available Co-Cr-Mo-C cast implants shows that some fabricators use a solutionizing anneal on their products before finishing. Hollander and Wulff 13 have shown that solutionizing heat-treatments of approximately one hour at 1200°C - 1230°C can significantly raise the strength and ductility of H.S.21 or Vitallium implants. Treatment for more than one hour, however, can lead to losses of yield and tensile strengths which are difficult to recover. In addition, it was found that aging for 20 hours at 650°C following solutionizing provides further increase of UTS and YS.

The most effective method found by Hollander and Wulff for increasing ductility of as cast H.S.21 and Vitallium was to precede the solutionizing and aging heat treatments by hot isostatic pressing in argon for four hours at 1200°C and approximately 15,000 psi. As Wasielewski and Lindblad 14 and Basaran et al 15 have shown, and as seen in Chapter V of this thesis, this technique is capable of healing microvoids which can materially reduce the ductility and fatigue strength of as cast alloys.

Cyclic heat treatments have also been studied in our laboratory as a method of accomplishing grain refinement in Co-Cr-Mo-C castings. This is analogous to the process used in the grain refinement of carburized steels. It consists of isothermally cycling between a temperature where hcp is the dominant matrix phase and one where fcc is stable. Thus far,
it has been possible to achieve grain refinement by cycling between approximately 850°C and approximately 1050°C, but the original as cast grain boundaries and associated large quantities of minor phases remain. Cyclic heat treatments of this kind have not resulted in improved tensile properties.

The greatest grain size reduction and tensile property improvement in Co-Cr-Mo-C alloys to date has been accomplished by Devine by hot working either by extrusion at approximately 1200°C followed by hot rolling, or by multiple hot press forging. Figure 2 depicts the as wrought modified H.S.21 microstructure; the reduction of grain size is immediately evident when this structure is compared to the photomicrographs of Figure 1.
II. Survey of the Literature

The history of cobalt alloys has been presented in several publications.\textsuperscript{2,16,17,18} It is evident from the discussions of microstructure-property relationships in such surveys that more information is available regarding the high temperature behavior of these alloys than is available for their room temperature behavior. Definitive data on the phase structure of Co-Cr base alloys, including Co-Cr-Mo and Co-Cr-Mo-C alloys, has become available only since the early 1940's when it was found that these materials had considerable potential in turbosupercharger and other high temperature applications.\textsuperscript{19,20,21}

Of particular relevance to the present investigation are the studies of the microstructural constituents of heat treated wrought H.S.21 by Clauss and Weeton\textsuperscript{22} and Weeton and Signorelli.\textsuperscript{23} However, these authors present little data indicating the relation of microstructure and room temperature properties, their focus being high temperature behavior. Nevertheless, their determinations of matrix (fcc .vs. hcp) and minor phases (carbides, intermetallics, etc.) resulting from a wide range of heat treatments has been of great value in the development of the studies reported in this thesis.

Weeton and co-workers\textsuperscript{22,23} solutionized wrought H.S.21 for times from 16 hours to 72 hours at 1230\textdegree C, followed by water quench. This resulted in a coarse-grained single phase microstructure. The Weeton and Signorelli work does not present room temperature property data other than hardness curves. In the related study by Clauss and Weeton, some
room temperature tensile properties are presented for the heat treatments discussed by Weeton and Signorelli. It is clear in the Clauss and Weeton paper that in spite of the tremendous grain growth caused by solutionizing at 1230°C, aging treatments can greatly increase the room temperature tensile properties. The observation that aging at 650°C did not produce any change of hardness in wrought solutionized H.S.21 but did have a positive effect on tensile properties led Hollander and Wulff 13 to investigate the effect of this aging treatment on solutionized cast H.S.21. They found that the process provided significant improvement in the room temperature properties of their alloy.

More recently, transmission electron microscopy has been utilized in studying the microstructural response to heat treatment in related Co-Cr based alloys. 24,25,26 Ramaswamy et al. 24, using Co-25.3Cr-0.26C and Co-32.9Cr-0.18C alloys, found that solutionized specimens aged at 700°C to peak hardness exhibited 0.2% proof stress triple the levels determined for solutionized specimens. Based on their TEM studies, they attributed this increase to increased stacking fault density, precipitation in association with stacking faults, and precipitation in the matrix. Selected area electron diffraction and X-ray analysis identified the precipitate as Cr$_{23}$C$_6$. In addition, they observed a lamellar mode of precipitation resembling pearlite. This was visible both by electron and optical microscopy, and was identified as Cr$_{23}$C$_6$.

The above references (22 - 26) provided aid in interpreting the experimental studies reported in Chapters V and VI of this thesis. These sections were written to be more or less complete in themselves, but
complementary in subject range. Chapter V examines the microstructures and room temperature tensile properties of cast Co-Cr-Mo-C alloys resulting from hot isostatic pressing, solutionizing, and aging heat treatments. Chapter VI presents the results of the transmission electron microscopy studies of wrought and cast H.S.21 following solutionizing and aging for various times at 650°C and 750°C.
III. Organization of the Research

The work reported in this thesis began as a study of the effects of hot isostatic pressing (HIP) and the solutionizing plus aging heat treatments on the room temperature tensile properties of cast Co-Cr-Mo-C surgical implant alloys. Optical metallography, microradiography, and a limited amount of transmission electron microscopy were used to characterize the microstructures produced, in order to provide some understanding of the causes of properties modifications obtained. The results obtained in this part of the investigation (reported in Chapter V of this thesis), in particular the optical and electron microscopy observations, led to a more thorough investigation of the microstructures produced by heat treatment of both wrought and cast H.S.21. The wrought material was included because it had a significantly different carbon content than the cast material (0.29%C cast vs. 0.145%C wrought; see Table II). Heat treatments were selected to reveal the early stages of the microstructural changes previously observed in the cast HIP processed material, and to show the effects of longer times and higher temperatures on those microstructures. The results and discussions of the two parts of this investigation have been presented separately in Chapters V and VI. While the information in these chapters is complementary, clarity is best served by the separation.
IV. Experimental Procedures and Materials

The investment cast specimens used in this investigation were tensile test specimens made by five Co-Cr-Mo-C implant foundries to comply with A.S.T.M. specifications. The tensile specimens were made according to the dimensions of Figure 8 of the A.S.T.M. Methods E8-69 \(^{27}\) for small size specimens (0.250 inch gage diameter). Table II lists the A.S.T.M. chemical composition specification \(^{28}\) for cast Co-Cr-Mo-C surgical implant alloys along with the compositions of all alloys referred to in the text. The wrought specimens used were prepared from material which had been hot multiple press forged and hot rolled. The composition of this material is listed in Table II as modified H.S.21.

Tensile properties of the cast material were measured in the as-cast and heat treated conditions. Solution treatment of these specimens consisted of a 1130°C half hour preheat plus a one-half or one hour treatment at 1230°C in purified H\(_2\) atmosphere, followed by a water quench. Subsequent ageing was carried out at 650°C for 20 hours in an Ar atmosphere.

Hot isostatic pressing (HIP) preceded the solutionizing of a portion of the cast tensile specimens. This processing was carried out at 14.8 ksi and 30 ksi at approximately 1200°C in an Ar atmosphere. Maximum temperature and pressure were held for 4 hours and were followed by a 6 hour cool-down to room temperature.

Metallographic examinations were made with cast specimens cut from the ends of tensile specimens prior to heat treatment and tensile testing.
Wrought specimens were prepared from the forged and rolled wrought material. Following heat treatment, the specimens were polished first on abrasive papers, then with diamond paste. To distinguish sigma phase from carbides in the cast material, an electrolytic etchant of 10% NaCN in water followed by immersion staining with Murakami's Reagent (10g \( \text{K}_3\text{Fe(CN)}_6 \) + 10g KOH + 100m\( \text{H}_2\text{O} \)) was used. 29 Other etchants and stains were used to emphasize the microstructural features and they are indicated on each micrograph in the text.

Microradiography was performed with a simple camera constructed to hold a cassette containing the specimen and a photographic plate. X-ray beam collimation was provided by two \( \frac{1}{4} \) in. diameter lead apertures spaced approximately 4 in. apart in the camera. The specimens examined, cut from as-cast and as-HIP-processed tensile specimens, were carefully ground and polished to a thickness of approximately 0.002 in. (0.05 mm). They were placed in the camera in contact with the emulsion of a fine-grained photographic plate (Kodak High Resolution Plates) and were exposed to a beam of unfiltered Cr X-ray radiation (35kV, 15mA) for times ranging from 4 minutes to 15 minutes. After developing, the exposed plates were photographed at a magnification of 200x with a light microscope.

Transmission electron microscopy was used to investigate the microstructure of heat treated wrought material and heat treated, HIP processed cast material. Cast specimens were prepared from discs mechanically cut from the ends of HIP treated tensile specimens prior to heat treatment or tensile testing. These discs were ground to a thickness
of approximately 0.010 in. prior to a solution treatment consisting of a one-hour heat-up from room temperature to 1230°C, plus a dwell of one hour at 1230°C in H₂, followed by a water quench. Some of the discs were subsequently aged at 650°C in Ar for 5, 20, or 50 hours. After the heat treatment, discs of 3 mm diameter were removed from the larger discs by electric discharge machining. These 3 mm discs' surfaces were carefully polished on 600 mesh abrasive paper in preparation for electrochemical thinning. Wrought specimens were prepared from 3 mm diameter rods machined from a wrought strip. These rods were solutionized at 1230°C for 4 hours in H₂, water quenched, then aged in Ar at 650°C for 20, 100, or 200 hours, or at 750°C for 2.5, 5, 20, or 50 hours. One rod in the solution treated condition was examined. After heat treatment, discs approximately 0.012 in. thick were removed from the rods by electric discharge machining, and were prepared for electrochemical thinning in the manner of the cast specimens. Thinning was accomplished in a Fischione Jet Polisher using an electrolyte of 85% methanol and 15% H₂SO₄ by volume, maintained at a temperature of -50°C by means of methanol coolant circulating through a dry ice and acetone bath. Specimens thus prepared were examined at 100kV and photographed over a range of magnifications in either a Philips EM 300 or a Siemens 101 electron microscope. Electron diffraction patterns were recorded for purposes of phase and orientation identification.

Exploratory crevice corrosion tests of as-cast and HIP-processed and heat treated specimens were performed at 37°C in a 10% HCl - 1%FeCl₃ solution. These tests were terminated at four hour intervals up to
72 hours, and thereafter at 24 hour intervals up to a maximum of 28 days. Auxiliary open circuit potential, passive film corrosion, and breakdown potential measurements were carried out by T.M. Devine, and are to be reported elsewhere. Crevice corrosion specimens were force fitted with uniformly machined Teflon O-rings to provide equivalent crevice geometry for all specimens. After each test, the Teflon ring was cut away from the cylindrical metal specimen. The specimen surface was scrubbed with a bristle brush in running water, dried, and inspected for the presence of pits with a binocular microscope.
V. Hot Isostatic Pressing and Heat Treatment of Cast Co-Cr-Mo-C Surgical Implant Alloys

V.1 Experimental Results

Tensile properties and Rockwell C hardness of as-cast, HIP, and heat treated specimens are listed in Table III. The A.S.T.M. property specifications for the cast alloys and the tensile properties obtained with the wrought version of H.S.21 are also listed in Table III.

There is a considerable variation in both properties and microstructures observed in these alloys. Figure 1a represents the microstructure of the as-cast alloy cast by the low temperature vacuum method previously discussed. Figure 1b is a specimen which was cast by conventional methods. Those microstructures show intragranular sigma phase and grain boundary carbides. The carbides are shown more clearly in the higher magnification photomicrograph of Figure 3. Microporosity is difficult to distinguish metallographically, but it is apparent in the X-ray micrographs of Figure 4a and Figure 4b where isolated voids and larger areas of interdendritic porosity are both visible. The results of HIP processing at 1200°C and 14.5 ksi (4 hr) and 30 ksi (2 hr) are shown in Figures 4c and 4d, respectively. Neither form of porosity seen in Figure 4a or Figure 4b was found in any HIP-processed specimen, while one or both types of porosity were observed in every as-cast specimen examined.

The solution treatment used in this study (1130°C (1/2 hr) + 1230°C (1 hr) + water quench) was found to leave some intragranular sigma phase undissolved in the cast HIP-processed material. However, both metallography and electron microscopy indicated that neither intragranular nor
grain boundary carbides remained after solutionizing. The X-ray studies
of Devine \textsuperscript{11} indicated that a small amount (approximately 10%) of hcp
matrix exists after quenching from a temperature above the hcp-fcc tran-
sition temperature (\(\simeq 850^\circ\text{C}\)). The electron photomicrograph of Figure 5
confirms this finding. An area of matrix which has transformed martens-
tsitically to hcp is visible on the left edge of this photomicrograph and
numerous other similar areas were observed in solutionized specimens.
This transformation is believed to result from stresses induced by quench-
ing. The fcc stacking faults seen in Figure 5 are also typical of the
solutionized material; however, as will be seen in Figure 7, the density
of faulting here is much lower than that occurring in aged specimens.

The microstructure resulting from solutionizing and aging as-cast
material is depicted in Figure 6. Small particles of sigma phase undis-
solved by the 1230\(^\circ\text{C}\) solution treatment are visible within the grains.
The dark grain boundary formations are examples of the "pearlite" ob-
served in early studies by others. \textsuperscript{22,23} The etchant used here is respon-
sible for their dark coloring and for obscuring details of their morph-
ology. The intragranular transformation markings typical of aged
cobalt-base alloys are also evident in this photomicrograph. Electron
microscopic examination of the solutionized and aged HIP-processed cast
material revealed that these markings consist of dense clusters of fcc
stacking faults and bands of matrix which have transformed martensiti-
cally to the hcp structure. Figure 7 shows extensive faulting frequently
observed in fcc regions of the alloy. A few angular, plate-like precip-
itates, identified by electron diffraction as \(\text{M}_{23}\text{C}_6\), were evident in the
hcp bands. Such precipitation was observed only after the aging heat treatment and was always confined to hcp regions. The microstructure observed by electron microscopy will be more thoroughly discussed in Chapter VI.

The crevice corrosion tests carried out in 10% HCl - 1% FeCl₃ solution corroborated previous observations of Devine et al. ₃₀ which showed that crevice corrosion pitting of as-cast H.S.21 begins in the first 72 hours of immersion. In the present work, HIP-processed castings which were subsequently solution-treated and aged were found to resist crevice corrosion pitting for the full duration of the 28-day tests. This corrosion resistance was matched by H.S.21 specimens which had been hot-press forged and hot-rolled. These tests also confirm measurements of rest and breakdown potential made by Devine ₃₁ on H.S.21 at 37°C in the same corrodatant as well as in physiological and in isotonic salt solutions.

V.2 Discussion and Conclusions

As previously noted, the data in Table III show that all as-cast tensile specimens do not meet the relevant A.S.T.M. specifications; lack of ductility if the most frequent shortcoming. Though specimens received from the same foundries at other times meet all A.S.T.M. specifications, it is rare to find as-cast material in which the elongation exceeds 8%. In most as-cast specimens it is not difficult to increase ductility by a solutionizing anneal of an hour or less at 1190-1250°C followed by a gas or water quench. While not all fabricators utilize such heat treatment, those who do, according to our results, increase
their ductility by as much as a factor of two without serious losses in
yield or ultimate tensile strength. We have tested some specimens heat-
treated in this way which showed elongations of up to 17% with ultimate
tensile strength and yield stress of 137 ksi and 74 ksi, respectively.
These specimens were cast in vacuum or inert atmosphere from master alloy
melts without scrap additions from previous melts. However, the products
from these fabricators do not consistently show such excellent properties.
That HIP treatment can further improve the tensile properties of castings
is indicated by the data of Table III. Although the mechanism of HIP
densification is not rigorously understood, it is reasonable to believe
that the collapse and sealing of voids takes place by a combined diffu-
sion and creep process which can be accelerated by increasing the temp-
erature and pressure applied.

As previously noted, hot extruded or multipress-forged and hot
rolled H.S.21 has a much finer grain size and finer distribution of sec-
ondary phases than the as-cast alloy. Hence, wrought alloy properties
should be superior to the cast. In addition, this explains the superior
corrosion resistance shown by the wrought alloy in 10% HCl + 1% FeCl₃ ,
and in physiological and isotonic salt solutions.31 However, HIP-treated
solutionized, and aged cast material shows, in the best instances, ulti-
mate tensile strength and yield strength close to the levels found in
wrought material similarly solutionized and aged, and its crevice corro-
sion resistance in the 10% HCl - 1% FeCl₃ solution is comparable. The
significantly higher ductility observed in the wrought material can be
attributed to its higher degree of chemical and structural homogeneity.
In the cast material, the increase of tensile strength and yield strength produced by aging at 650°C for 20 hours is primarily caused by the generation of dense networks of fcc stacking faults and by the martensitic transformation of regions of the matrix to the heavily faulted hcp structure. The precipitate density produced by this treatment is so low that it probably does not contribute significantly to the strength increase, but should restrict slip in the hcp somewhat. A more detailed study of the microstructures produced by solutionizing and aging the wrought and cast material will be presented in Chapter VI of this thesis.

In view of studies by Devine and by Devine et al. showing wrought H.S.21 to have crevice corrosion resistance far superior to the wrought alloys H.S.25 and MP35N while exhibiting equivalent tensile properties, it appears that wrought H.S.21 should be preferred when cast Co-Cr-Mo-C alloys are inadequate. Where implants cannot be readily shaped from wrought stock and investment casting is mandatory, patients and surgeons would be best served by the use of Co-Cr-Mo-C castings which have been HIP-processed and subsequently heat-treated to obtain optimum properties.
VI. Transmission Electron Microscopic Studies of Wrought and Cast Co-Cr-Mo-C Surgical Implant Alloys

VI.1 Experimental Results

The wrought and cast specimens observed in this study, although showing significant differences in their response to aging, had a number of general features in common. Following solutionizing and quenching, both were predominantly fcc and contained a low density of stacking faults. About 5% of the areas observed had martensitically transformed to bands of the hcp phase. Aging heat treatments increased the density of fcc stacking faults and promoted transformation of the fcc to the hcp phase, with the longest aging times yielding ~95% transformation. Precipitation occurred in the wrought material aged at 750°C and in the aged (650°C) cast material. In both, the precipitation morphology exhibited a strong dependence on the structure and orientation of the surrounding matrix. In all specimens, precipitation was confined to the hcp regions. The specifics of the responses of the two materials to heat treatment are presented in the following sections.

VI.1.1 Wrought and Cast Material, Solution Treated and Quenched

In both wrought and cast solution-treated material, the dominant phase was fcc, although there were numerous bands of heavily faulted, martensitically transformed hcp phase which were up to 5 - 7 μ in width in the wrought material and 10 - 15 μ in width in the cast material. A low density of stacking faults was found in the fcc regions. No secondary phases were found by transmission microscopy in either the fcc or the hcp regions. Metallographic examination of the cast material, however,
revealed fairly large islands of undissolved sigma phase (Figure 8). The presence of the hcp bands observed by electron microscopy had been indicated by the occurrence of intragrannular transformation markings in the metallography specimens. Figure 9 shows an optical photomicrograph of wrought solutionized material. In the electron photomicrographs of Figures 5 and 10, fcc stacking faults and regions of martensitic hcp are visible.

VI.1.2 Wrought Material Aged at 650°C

As aging time at 650°C was increased from 20 hours through 200 hours the wrought specimens developed increasingly dense arrays of fcc stacking faults on all \{111\} planes. The martensitic transformation of hcp also progressed with aging time, with hcp becoming the dominant phase after 100 hours and 200 hours of aging. The progress of the transformation can be inferred by comparing the density of the transformation markings in the aged material of Figure 11 with the solution treated material in Figure 9. No precipitation in any form was observed by electron microscopy in any wrought specimen aged at 650°C, within the aging times used.

VI.1.3 Cast Material Aged at 650°C

TEM observations of cast material aged 5 hours at 650°C following solutionizing and quenching showed that these specimens had a higher density of fcc faults and a higher proportion of martensitically transformed hcp than were observed in cast solutionized material. A number of hcp bands greater than 10 μ in width were observed.

The proportion of martensitically transformed hcp continued to increase with aging time, reaching approximately 90% in the specimens aged
50 hours. Profuse precipitation was observed in the 50 hour specimens and a smaller amount in the 20 hour specimens. In both, the precipitates were roughly hexagonal, plate-like structures of fcc $M_{23}C_6$ aligned with the basal planes of the hcp regions. A typical precipitate microstructure is shown in Figure 12. An observation of the precipitates edge-on is shown in Figure 13. The precipitates and their hcp surroundings exhibited the orientation relationship $\{111\}_{\text{fcc}} \parallel \{0001\}_{\text{hcp}}$ and $\langle 110 \rangle_{\text{fcc}} \parallel \langle 11\bar{2}0 \rangle_{\text{hcp}}$. Although cellular grain boundary precipitation and undissolved sigma phase are both visible in metallographic specimens (Figure 6), neither was observed by electron microscopy. The most notable features in this group of specimens were the extremely dense stacking fault formations in the 20 hour specimens (Figure 7) and the occurrence of extensive precipitation in the longer-aged specimens.

VI.1.4 Wrought Material Aged at 750°C

Aging of solutionized and quenched wrought material for 2.5 hours and 5 hours at 750°C produced extensive transformation to martensitic hcp and yielded a density of fcc stacking faults greater than existed in wrought solutionized specimens. Aging at 750°C for 20 hours and 50 hours produced the transformation to hcp in up to approximately 75% of the areas observed. Much of this hcp had a structure which differed from the previously observed martensitic hcp. Unlike the heavily faulted martensitic structure, this hcp had a very low stacking fault density and numerous undissociated dislocations were observed (Figure 14). Extensive precipitation of $M_{23}C_6$ occurred in these regions yielding block-like precipitates, frequently arranged in rows, which coarsened
considerably as aging time increased from 20 hours to 50 hours (Figure 15). The rows were sometimes, but not always, aligned with the basal planes of their hcp region. Rows which were not aligned with surrounding hcp basal planes were sometimes observed to be aligned with stacking faults in adjacent fcc regions. More often, there was no clear relationship between the orientations of the precipitate rows and the remaining observable fcc regions.

VI.1.5 Stacking Fault Interaction

Stacking fault interaction is believed to play an important role in the mechanical behavior of these alloys. The stacking faults formed were intrinsic faults on \{111\} planes of the fcc matrix and were bound by Shockley partial dislocations of the type $\frac{a}{6} <112>$. Careful observations were made of instances where stacking fault intersections had occurred and of instances where a pre-existing stacking fault had apparently obstructed the motion of a partial dislocation on another plane. Figure 16 contains examples both of completed and blocked intersections. It is obvious from the micrographs previously shown that such interactions are forced to occur with greater frequency. The fcc faults played no direct role in precipitate formation, all precipitation in these alloys having occurred in hcp regions.

VI.2 Discussion and Conclusions

VI.2.1 Microstructures

The most conspicuous features of the specimens observed were the formation of extensive fcc stacking faults and the formation of heavily
faulted hcp bands. The production of fcc faults and hcp bands are closely related. As is well known, the hcp stacking sequence can be produced by introducing an intrinsic stacking fault on every second \{111\} plane of an fcc lattice. Further, this can be accomplished by a shearing process if the intrinsic faults are bounded by Shockley $\frac{a}{6}$ <112> partial dislocations. If this process were imperfectly executed, it would result in retention of the fcc stacking sequence for at least a few atomic planes. It has been shown by use of dark-field techniques $^{26}$ that the hcp regions of a similar alloy retain narrow plates of fcc. The driving force for the fcc + hcp transformation during aging is the fact that the equilibrium crystal structure for this alloy is hcp below approximately 850°C. The exact temperature for this transformation is not established, but other work $^{11}$ has indicated that it is in this vicinity. Clearly, slip will be restricted if the fcc phase is intersected on its \{111\} planes by bands of hcp.

The presence of large numbers of stacking faults in the fcc phase also restricts slip on intersecting planes. In a study of intersecting intrinsic stacking faults in fcc lattices, $^{32}$ it was determined that two results were possible, depending on the signs of the existing fault vector and the Burgers vector of the intersecting partial dislocation. Either a partial row of vacancies or interstitials must be formed. The energies required are $\frac{2}{9} E_v$ per atomic plane (i.e., two atoms in nine are missing, and $E_v$ is the energy for the formation of a vacancy) in the former case, and $\frac{1}{9} E_I$ in the latter, where $E_I$ is the energy for the formation of an interstitial and there is an excess of one atom in nine. This
becomes a significant energy barrier considering the density of stacking faults common to the alloys studied here. Successful and unsuccessful intersections of partial dislocations and stacking faults must be associated with the availability of sufficient energy, in whatever form, to complete the intersection process and produce the point defect partial row.

The same intersection process would occur if a region of hcp formed by intrinsic faulting on every second plane was growing in an area already traversed by stacking faults on other planes. The resulting hcp region would have partial rows of vacancies or interstitials. Because of formation energies, intersections producing vacancies are more likely to be successfully completed while those which would produce interstitials would be expected less frequently. Partial vacancy rows would facilitate diffusion and could accommodate part of the mismatch strain between lattice and precipitate. Thus they would provide likely sites for precipitate formation and could explain certain observed alignments between fcc stacking faults and precipitate rows in adjacent hcp regions (Figure 17).

This model, however, does not satisfactorily explain all cases of precipitate row alignment observed. In the wrought specimen aged at 750°C (20 hr) of Figure 14, the orientation of the hcp stacking faults show that the precipitate rows are not aligned with the basal plane, while inspection of electron diffraction patterns and stacking faults proved they were not aligned with fcc stacking faults either. The spacing of the precipitate rows and their orientation in relation to the fcc-hcp interface suggest that the precipitates may, in fact, be associated with
this interface.

The structure of the hcp phase tends to change considerably with elevated temperature aging. After aging at 650°C in both wrought and cast material, the hcp phase has an extremely high stacking fault density. In contrast to this, the wrought material aged at 750°C for 20 hours or more exhibits an hcp phase with a very low stacking fault density and a large number of non-planar precipitates. Short aging times at 750°C produce the heavily faulted hcp structure, so it appears that simultaneously with the formation of the blocky precipitates, the hcp "equilibrates" or "recrystallizes".

VI.2.2 The Relation of Properties to the Microstructure

It has been observed that hot isostatic pressing of cast Co-Cr-Mo-C alloys improves the room temperature strength and ductility of these alloys. Certainly a substantial segment of this improvement results from the elimination of casting microporosity. In addition, further improvements in strength and ductility can be achieved by a solutionizing treatment followed by an aging at 650°C for 20 hours. Typical values for alloys so treated would be a yield strength of 75 ksi, ultimate tensile strength of 120 ksi, and 15% elongation to fracture.

The room-temperature mechanical properties observed for these alloys in the HIP-solutionized and aged condition are related to the phase distribution (hcp, fcc, carbides) and the dislocation and stacking fault densities as well as to the elimination of microporosity. Slip in the fcc phase will be restricted by the presence of the hcp bands and by the existence of stacking faults in the fcc phase. As the amount of the
hcp phase and the number of stacking faults increase, the mean free slip path available will decrease and a higher strength is expected. The results presented document the fact that with increased aging time, the proportion of hcp phase in the matrix and the density of fcc stacking faults is increased. Thus, the correlation of aging time with improved mechanical properties is explained from the standpoint of slip in the fcc phase.

Slip in the hcp phase is expected to be limited after the shorter aging times used here, since the hcp phase is very heavily faulted, and additional slip is unlikely to occur. After longer aging times the precipitates observed in this study form and will strengthen the hcp phase.
VII. Conclusions

1. Cast H.S.21, if hot isostatic pressed at at least 15 ksi and 1230°C for 4 hours, solutionized at 1230°C for 1/2 to 1 hour, and aged at 650°C for 20 hours, consistently exceeds the A.S.T.M. specifications for mechanical properties of cast Co-Cr-Mo-C implant alloys.

2. The above treatment provides superior resistance to crevice corrosion pitting in a number of media relevant to judging physiological performance.

3. The benefits of hot isostatic pressing are due to the closure of casting microporosity.

4. Castings produced by vacuum filling of the mold, with both mold temperature and melt superheat held to a minimum, provide finer grain size and superior properties than most conventional castings.

5. The improvement in tensile properties provided by aging at 650°C can be attributed to the limitation of slip caused by the profuse generation of fcc stacking faults and the interruption of fcc slip planes by bands of hcp. Slip in the hcp is restricted by the presence of precipitates of $M_{23}C_6$.

6. Precipitation at the aging times and temperatures observed is restricted to regions which have transformed to the hcp structure.
VIII. REFERENCES


May 14, 1971.


31. T. M. Devine and J. Wulff, to be published in Journal of Biomedical
Materials Research.

TABLE I

Summary of Statistics Compiled by J. T. Scales

<table>
<thead>
<tr>
<th></th>
<th>S. S.</th>
<th>Co-Cr-Mo</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number and percent of total number of implants</td>
<td>478 (71.6%)</td>
<td>83 (12.4%)</td>
<td>106 (15.8%)</td>
</tr>
<tr>
<td>Percentage corrosion and/or fretting</td>
<td>62.6</td>
<td>21.7</td>
<td>22.6</td>
</tr>
</tbody>
</table>

313 Multiplace Implants = 1,759 Components Used in Weight-Bearing Alloys

<table>
<thead>
<tr>
<th></th>
<th>S. S.</th>
<th>Co-Cr-Mo</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage with contact crevice corrosion and/or fretting</td>
<td>87</td>
<td>59.3</td>
<td>65.4</td>
</tr>
<tr>
<td>Percentage with fatigue or torsion failure</td>
<td>0.5</td>
<td>6.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>

1,232 Screws Used with Intertrochanteric and Bone Plates in Weight-Bearing Bone

<table>
<thead>
<tr>
<th></th>
<th>S. S.</th>
<th>Co-Cr-Mo</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage with contact crevice corrosion and/or fretting</td>
<td>55</td>
<td>41.9</td>
<td>43.2</td>
</tr>
<tr>
<td>Percentage with fatigue or torsion failure</td>
<td>0.2</td>
<td>8.03</td>
<td>4.2</td>
</tr>
</tbody>
</table>
Compositions of alloys used or recommended for surgical implants

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>H.S.21</td>
<td>Co - 28.75 Cr - 3.01 Ni - 5.52 Mo - 0.33 Fe - 0.44Si -</td>
</tr>
<tr>
<td></td>
<td>0.56 Mn - 0.29 C</td>
</tr>
<tr>
<td>Vitallium</td>
<td>Co - 27.81 Cr - 0.23 Ni - 5.85 Mo - 0.29 Fe - 0.65 Si -</td>
</tr>
<tr>
<td></td>
<td>0.66 Mn - 0.80 W - 0.25 C</td>
</tr>
<tr>
<td>MP35N</td>
<td>35 Co - 20 Cr - 35 Ni - 10 Mo</td>
</tr>
<tr>
<td>H.S.25</td>
<td>Co - 19-21 Cr - 9-11 Ni - 3 Fe - 14-16 W - 0.15 C</td>
</tr>
<tr>
<td>Mod H.S.21</td>
<td>Co - 26.7 Cr - 5.46 Mo - 0.01 Ni - 0.10 Fe - 0.145 C</td>
</tr>
<tr>
<td>F75-67 ASTM</td>
<td>Co - 27-30 Cr - 2.5 Ni max - 5-7 Mo - 0.75 Fe max -</td>
</tr>
<tr>
<td></td>
<td>1.0 Si max - 1.0 Mn max - 0.35 C max</td>
</tr>
<tr>
<td>Set</td>
<td>Condition</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>As-investment cast</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>As-investment cast plus</td>
</tr>
<tr>
<td></td>
<td>Solution heat-treated at</td>
</tr>
<tr>
<td></td>
<td>1230ºC 1 hr plus quench</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>As-investment cast plus</td>
</tr>
<tr>
<td></td>
<td>1 hr at 1230ºC plus 20 hr at 650ºC</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>HIP (15 ksi at 1200ºC 4 hr) plus 1230ºC in H_2</td>
</tr>
<tr>
<td></td>
<td>quench plus 650ºC 20 hr</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Same as 4 but HIP at 30 ksi 4 hr</td>
</tr>
<tr>
<td>6</td>
<td>Hot press-forged and hot-rolled</td>
</tr>
<tr>
<td>7</td>
<td>Same as 6 but solutionized</td>
</tr>
<tr>
<td></td>
<td>1 hr at 1230ºC plus quench plus 650ºC 20 hr</td>
</tr>
<tr>
<td>8</td>
<td>Same as 6 plus cold-rolled to 15.1% reduction in area. Heat-treated at 1065ºC for 30 min air cooled</td>
</tr>
<tr>
<td>9</td>
<td>A.S.T.M. specification for Co-Cr-Mo-C castings</td>
</tr>
</tbody>
</table>
Figure 1:
Comparison of microstructures resulting from casting by low superheat, vacuum method and conventional technique. (a) Cast with minimal superheat with molten metal drawn by vacuum up into the mold from below the surface of the melt. (b) Casting produced by conventional pouring with higher superheat (Etchant: 5% HCl, electrolytic; 100x)
Figure 2:

Microstructure of as wrought modified H.S. 21 (Etchant: 5% HCl, electrolytic; 100x)
Figure 3:
Detail of grain boundary carbide formations typical of as cast Co-Cr-Mo-C alloys. (Etchant: 2% CrO₃ in H₂O, electrolytic: Stain: Murakami's Reagent; 1100x)
Microradiographs showing microporosity of as-cast specimens and absence of porosity in hot isostatic pressed specimens. (a) Isolated voids such as occur in all as cast specimens observed. (b) Interdendritic porosity occurring in specimens showing the greatest degree of casting segregation. (c) Specimen following hot isostatic pressing at 14.5 ksi and 1200°C for 4 hours. (d) Specimen following hot isostatic pressing at 30 ksi and 1200°C for 4 hours.
Electron photomicrograph of cast solutionized H.S.21 showing fcc stacking faults and band of martensitic hcp (i.e. along A - A). Beam direction $\bar{Z} = h00_{\text{fcc}}$, operating reflection $\bar{G} = 002_{\text{fcc}}$. 
Microstructure of cast specimen solutionized and aged at 650°C for 20 hours. Cellular precipitation along grain boundaries, undissolved sigma phase, and intragranular transformation markings are visible. (Etchant: 4 parts HCl + 1 part acetic acid, electrolytic; 100x).
Figure 7:

Electron photomicrograph showing dense stacking fault formations occurring in cast material solution treated and aged at 650°C for 20 hours. Beam direction $\bar{Z} \sim [100]_{\text{fcc}}$, operating reflection $\bar{g} = 002_{\text{fcc}}$. 
Figure 8:

Microstructure of solutionized cast specimen showing particles of undissolved sigma phase. (Etchant: 2% CrO₃ in H₂O, electrolytic; Stain: Murakami's Reagent; 100x).
Microstructure of wrought solutionized modified H.S.21 showing intragranular transformation markings indicating the presence of hcp.

(Etchant: 4 parts HCl + 1 part acetic acid, electrolytic; 100x)
Figure 10:

Electron photomicrograph showing fcc stacking faults and a band of martensitic hcp (along A - A) in solutionized wrought modified H.S.21. Beam direction $\mathbf{z} \sim \{211\}_{fcc}$, operating reflection $\mathbf{g} = \{\overline{1}11\}_{fcc}$.
Figure 11:

Microstructure of wrought modified H.S.21 solutionized and aged at 450°C for 20 hours. (Etchant: 4 parts HCl + 1 part acetic acid, electrolytic; 100x)
Figure 12:

Electron Photomicrograph showing typical hexagonal precipitate structure in cast H.S.21 solutionized and aged at 650°C for 50 hours. (a) Micrograph (b) Electron diffraction pattern. Beam direction $\bar{Z} \sim \{0001\}_{hcp}$
Electron photomicrograph showing precipitates edge-on in cast H.S.21, solutionized and aged at 650°C for 50 hours. (a) Micrograph; (b) Electron diffraction pattern; (c) Interpretation of diffraction pattern. Beam direction \( \mathbf{z} \parallel 10 \bar{1} 0 \text{hcp} \), operating reflection \( \mathbf{q} = 0002 \text{hcp} \).

Note that the diffraction pattern includes the patterns for the hcp and fcc matrix phases (10\(\bar{1}0\) and 110, respectively) and for a precipitate with the same orientation as the fcc matrix and a lattice parameter three times as large, i.e. \( M_{23}C_6 \).
Figure 13:

Electron photomicrograph showing precipitates edge-on in cast H.S.21, solutionized and aged at 650°C for 50 hours. (a) Micrograph  (b) Electron diffraction pattern  (c) Interpretation of diffraction pattern. Beam direction \( \vec{Z} \sim (10\bar{1}0)_{\text{hcp}} \), operating reflection \( \vec{g} = \{0002\}_{\text{hcp}} \). (Note that the diffraction pattern includes the patterns for the hcp and fcc matrix phases [(10\bar{1}0) and (110), respectively] and for a precipitate with the same orientation as the fcc matrix and a lattice parameter three times as large, i.e. \( M_{23}C_6 \).)
Figure 4:

Electron photomicrographs of large area of wrought modified H.S.21, solutionized and aged at 750°C for 20 hours. Note orientation of precipitate rows in relation to hcp-fcc interface (arrow). Beam direction $\bar{Z} \sim (01\bar{1}1)_{\text{hcp}}$, operating reflection $\bar{q} = (1\bar{1}01)_{\text{hcp}}$. 
Figure 15:

Electron photomicrographs of large area of wrought modified H.S.21, solutionized and aged at 750°C for 50 hours. Notice coarsening of precipitates relative to Figure 14. Beam direction $\bar{Z} \sim (10\bar{1}0)_{hcp}$, operating reflection $\bar{g} = \{01\bar{1}1\}$.
Electron photomicrograph showing both blocked (A) and successful (B) intersections of fcc stacking faults. Beam direction $\bar{Z} \sim [111]_{\text{fcc}}$, operating reflection $\bar{\gamma} = \{220\}_{\text{fcc}}$. 

Figure 16:
Figure 17:

Electron photomicrograph showing alignment of a row of precipitates in an hcp region with stacking faults in the adjacent fcc. Beam direction $\bar{Z} \sim [1\bar{2}30]_{hcp}$, operating reflection $\bar{g} = (2\bar{1}2)_{hcp}$. 