HEAT TREATMENT OF Co-Cr-Mo-C SURGICAL IMPLANTS

by

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ABSTRACT

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Submitted to the Department of Metallurgy and Materials Science on May 10, 1974 in partial fulfillment of the requirements for the degree of Bachelor of Science and the degree of Master of Science.

Investment cast Co-Cr-Mo-C surgical implant alloy (Vitallium and H.S.21) tensile test specimens from three different industrial sources were subjected to heat treatment at 1200°C under an argon pressure of 14.5 k.s.i. to ascertain what enhancement of tensile properties could be achieved by such processing. Improvements in ductility (percent elongation) were observed in all three cases. When this isostatic hot-pressing treatment was followed by a one hour solutionizing heat-treatment at 1230°C in purified hydrogen, water quenched, and aged for 20 hours at 650°C, a significant further improvement in tensile properties was attained.

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

Abstract. ......................................................... 2
List of Figures .................................................... 4
List of Tables .................................................... 5
Acknowledgements ............................................... 6
I. Introduction .................................................. 7
II. Experimental ............................................... 17
III. Experimental Results ..................................... 20
IV. Discussion .................................................. 23
V. Conclusions .................................................. 27
References ....................................................... 28
LIST OF FIGURES

1. Effect of Cobalt Content on Transformation Temperature of Co-Ni-20Cr-10Mo Alloys. 33
2. Hardness of Co-Cr-Mo Alloys After Heat Treating for 10 Hours at 700°C 34
3. As-Received Co-Cr-Mo-C Alloy From Source D. 5% HCl Electrolytic Etch. Original Magnification: 50X 35
4. As-Cast H.S.21 From Source A. 5% HCl Electrolytic Etch. Original Magnification: 50X 36
5. As-Cast H.S. 21 From Source B. 5% HCl Electrolytic Etch. Original Magnification: 50X 37
6. As-Cast H.S.21 From Source C. 5% HCl Electrolytic Etch. Original Magnification: 50X 38
7a. H.S.21 From Source A. Solutionized at 1230°C for One Hour. Water Quenched. 5% HCl Electrolytic Etch. Original Magnification: 50X 39
7b. H.S.21 From Source A. Solutionized at 1230°C for 24 Hours. Water Quenched. 5% HCl Electrolytic Etch. Original Magnification: 50X 40
8. H.S.21 From Source B. Solutionized at 1230°C for One Hour, Isothermally Transformed at 815°C for Two Hours. 5% HCl Electrolytic Etch. Original Magnification: 200X 41
9. H.S.21 From Source B. Hot Isostatically Pressed. 5% HCl Electrolytic Etch. Original Magnification: 200X 42
<table>
<thead>
<tr>
<th></th>
<th>Table Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nominal Composition of Surgical Implant Alloys.</td>
<td>43</td>
</tr>
<tr>
<td>2</td>
<td>Mechanical Properties of Surgical Implant Alloys.</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>Summary of Statistics Compiled by J.T. Scales</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>Mechanical Properties of HS21 Tensile Specimens —</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As Received</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>Mechanical Properties of HS21 From A &amp; C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solutionized at 1230°C</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>Mechanical Properties of HS21 from A &amp; C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solutionized and Aged at 650°C</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>Tensile Properties of HS21 From B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solutionized for 4 Hours; Aged at 815°C</td>
<td>49</td>
</tr>
<tr>
<td>8</td>
<td>Mechanical Properties of HS21 From A &amp; C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solutionized and Isothermally Transformed at 815°C</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>Mechanical Properties of Co-Cr-Mo-C Tensile Specimens — as HIP Processed</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Mechanical Properties of Co-Cr-Mo-C Tensile Specimens — HIP Processed and Heat Treated</td>
<td>52</td>
</tr>
</tbody>
</table>
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I. INTRODUCTION

The use of alloys for surgical implantation in the body is contingent upon the meeting of certain mechanical, chemical, and biochemical criteria. An implant material must be resistant to corrosion in the "angry environment" of body fluids, especially under the crevices found in many devices. Any ions released must not be harmful to bone, tissue, or fluids. Requirements for strength, ductility, and fatigue resistance must be strictly adhered to for multicomponent weight-bearing implants. In locations where the implant parts rub against one another, they should exhibit low friction and wear characteristics.¹

Surgical implant material currently used for the repair or replacement of damaged bone in patients is mainly wrought 316L stainless steel, cast Co-Cr-Mo base alloys (Vitallium, H.S.21, etc.), and wrought commercial titanium base alloys. The compositions and mechanical properties of these alloys are listed in Tables 1 and 2, respectively. However, none of the above alloys ideally satisfy all of the aforementioned implant criteria. The stainless steel, while displaying excellent mechanical properties, are susceptible to pit and crevice corrosion in body fluids.²⁻⁶ Although the precision-cast cobalt-chromium-molybdenum alloys have superior corrosion resistance, they possess insufficient torsional and fatigue strength for safe use in some weight-bearing implants.⁷⁻¹⁰ The latter alloys can only be hot worked with extreme care,¹¹ and yet thin sections are difficult to cast
without incurring harmful structural defects.\textsuperscript{12} For these reasons, the wrought alloy H.S. 25 is often used as a substitute in thin-section implants. Although it possesses admirable mechanical properties, H.S. 25 is susceptible to crevice corrosion pitting in body fluids.\textsuperscript{13-15} Commercially pure, wrought titanium and some of its alloys exhibit superior long time corrosion resistance compared to the other alloys generally used,\textsuperscript{16} yet show a high initial rate of corrosion in the first 24 or more hours after implantation in living tissue.\textsuperscript{17,18} The resulting tissue-staining corrosion product has not as yet been found harmful.\textsuperscript{16,19,20} Titanium alloys like Ti-6Al-4V have only been seriously faulted for use as rubbing members of total hip joint replacement prostheses of the McKee-Farrar type because of their poor wear resistance.\textsuperscript{21} Some of the shortcomings of the above mentioned alloy systems are statistically reinforced by Table 3. This table summarizes data collected by the British Ministry of Health on weight-bearing surgical implants inserted and removed from patients over a seven-year period.\textsuperscript{22} The high susceptibility of stainless steel to corrosion in body fluids, relative to the other two alloy systems is apparent in this table. It is also apparent that all of the implants show a rather high incidence of fretting corrosion at metal-metal contacts in multipart weight bearing implants. Wrought stainless steel implants appear, according to Table 3, to have greater fatigue strength than cast Co-Cr-Mo-C implants in spite of their tendency to pit corrode. What is needed according to most observers is an alloy whose
corrosion resistance in body fluids is equivalent to or better than cast Co-Cr-Mo-C and whose strength properties (especially torsional and fatigue strength) and fabricability are equivalent to those of stainless steel. Some of the wrought heat-treatable titanium alloys meet this specification and are currently being used abroad. The recent research and development efforts of Devine and Wulff\textsuperscript{23-25} have shown that cast Co-Cr-Mo-C alloys can be wrought (hot and cold worked) and heat treated to possess the superior properties required. They are somewhat more difficult to cold work and machine than stainless steel and have not as yet been adopted by implant fabricators and orthopedic surgeons in the U.S.A., although they are commercially available. There are, of course, certain implants of complex shape which cannot be as economically closed-die forged or machined from wrought Co-Cr-Mo-C as they can be shaped by investment casting. Since there will always be a need for such castings, Devine and Wulff\textsuperscript{23} explored methods by which torsional and fatigue strength could be improved by alloying. Age hardening alloy additions of Ti and Ta were tried, but gave only about a 25 per cent increase in tensile strength while reducing ductility and corrosion resistance. The ductility (\% elongation) could be improved by additions of over 5 per cent Ni but these lower the crevice corrosion resistance even further.

Measurement of the mechanical properties of as-cast Co-Cr-Mo-C tensile test specimens (0.25 inch in diameter and a one inch gauge length) obtained from custom foundries and implant fabricators, found them to meet ASTM property specifications
more than not. They do, however, show a broad scatter of tensile properties and considerable difference in microstructure and defect structure (inclusions, shrinkage cracks, and other voids). Study of the microstructure of excised cast Co-Cr-Mo-C implants in our laboratory at M.I.T. has revealed that at least two implant fabricators who produce superior products, heat-treat such castings. The ductility and implant strength of these castings were found to be superior to those of as-cast alloys of the same composition, according to measurements made at M.I.T. Although ample experimental data is available in the technical literature regarding the phase structure resulting from heat-treatment of Co-Cr-Mo-C alloys, reference to the resulting room temperature tensile properties is sparse. Since such information might be of value to implant fabricators who now only use as-cast alloys, it was decided to make such a study the prime focus of this thesis. We were also led by the work of Wasielewski and Lindblad\textsuperscript{26} to include tensile tests of as-cast Co-Cr-Mo-C specimens which had received a heat-treatment of elevated temperature (1200°C) in an atmosphere of argon at an isostatic pressure of 14.5 k.s.i.

To interpret the mechanical test results and the microstructures resulting from the different heat-treatments described in this study, a description of the phase structure of Co-Cr base alloys, as portrayed in the relevant technical literature, seems appropriate at this juncture.

Various observers\textsuperscript{27-30} have shown that the matrix phase of
cobalt rich alloys at high temperatures is FCC which transforms to an HCP structure at some lower temperature. In Co-Ni-Cr-Mo alloys, Smith and Yates\textsuperscript{27} have found that the transformation temperature varies with Co content as shown in Fig. 1. In pure Co the transformation temperature is $421^\circ$C.\textsuperscript{31} Alloy additions of Ni, Fe and C stabilize the FCC modification whereas additions of Cr, Mo, Ta, and W appear to stabilize the equilibrium HCP structure.\textsuperscript{32} Troiano and Trokich\textsuperscript{31} find that pure Co transforms martensitically during cooling. Weeton and Signorelli\textsuperscript{29} assume the same type of transformation in their discussion of Co-Cr-Mo-Ni alloys. Air cooled specimens of the Co-27Cr-5Mo-.32C alloy H.S. 21 air cooled from above $1180^\circ$C, were found to consist primarily of the FCC phase.\textsuperscript{33} Apparently the small amounts of Ni, Fe, and C in this alloy sufficiently stabilize the FCC phase to require much longer times at high temperatures to initiate the equilibrium transformation, or much lower cooling temperatures to reach the $M_s$ temperature.

Drapier et. al.\textsuperscript{30} found that a carbon free alloy containing Co-17Cr-13Mo when solutionized at $1200^\circ$C for 1,000 hours and water quenched, will upon aging from 20-100 hours at $800^\circ$C, precipitate a (Cr,Mo,Co) R phase. Aging of a Co-11Cr-14Mo solutionized alloy at $700^\circ$C for 2-20 hours was found to produce a needle-like precipitate of either Co$_3$Mo or Co$_7$Mo$_6$ by Drapier et. al.\textsuperscript{30} as well as by Lux and Bollman.\textsuperscript{34} Although the nature of the phases responsible for the hardening in cobalt-rich, chromium-molybdenum alloys has not been clearly established, Drapier and co-workers\textsuperscript{30} have demonstrated the significant increases in hardness produced
by aging treatments, as shown in Fig. 2.

The addition of small amounts of carbon to cobalt base Cr-Mo-Ni alloys such as H.S. 21, leads to much more complex precipitation behavior. A number of samples of H.S. 21 containing 0.29 C were solution treated by Weeton and Signorelli\textsuperscript{29} at 1230°C for 72 hours and then either water-quenched and aged or transferred to lower temperature furnaces for isothermal transformations. Microstructural and X-ray analyses were then done, and R\textsubscript{C} hardnesses determined. Isothermal transformations of the solution-treated material at 1065°C and 955°C resulted in the formation of a lamellar, pearlite type of precipitate, possibly of Cr\textsubscript{23}C\textsubscript{6} and/or M\textsubscript{6}C. There was also evidence of \(\sigma\) phase formation. For isothermal transformation at 815°C, the precipitate was almost entirely of a Widmanstätten type distributed throughout the grains. In sharp contrast to the precipitates formed during isothermal transformation, aging at 1065°C, 955°C, and 815°C resulted in precipitation along what the authors interpret as slip lines and twin boundaries formed during the quenching operation. Maximum hardness in the solution treated material was obtained by treatment in the temperature range between 760°C and 815°C. Aging for 72 hours in this range produced a hardness of R\textsubscript{C} 42. The maximum hardness for the isothermal transformation was R\textsubscript{C} 40 and was developed between 815°C and 870°C. The solutionizing at 1230°C reduced the hardness to 20-24 R\textsubscript{C}.\textsuperscript{29}

More recent studies by West and his co-workers\textsuperscript{35,36} have shed further light on the possibilities for property augmentation in Co-Cr base alloys. In looking at various superalloys, they
treated and tested one alloy of composition Co-25Cr-0.25C and another of Co-33Cr-0.18C. The latter alloy as shown in Table 1 is somewhat similar in composition to the implant alloy Vitallium (Co-27Cr-5Mo-.32C). They found that samples solutionized at 1300°C for 1 hour, water-quenched and then aged in the range 650°C - 800°C could be substantially strengthened by precipitation of Cr$_2$3C$_6$. Of the two aforementioned alloys, the one of lower chromium content aged to peak hardness after 500 hours at 700°C and showed a nearly three-fold increase in 0.2% proof stress (compression test) at room temperature. A four-fold increase in proof stress was observed in the higher chromium alloy after 100 hours of aging at 700°C. Precipitation in these alloys was found to occur largely along stacking faults and to be very fine. This type of stacking fault precipitation has also been found to occur in certain superalloys which have been solution heat-treated at high temperature, quenched and aged. Such a mechanism may provide an alternative explanation for the bands of precipitate observed by Weeton and Signorelli after aging solution treated samples of H.S. 21. West also determined by X-ray analysis that prolonged aging at 700°C and 800°C produced some σ phase.

In most of the above cited literature, the possible effect of σ phase formation is not dealt with in great detail. Indeed, up to 1957, the precipitation of σ was sought to improve the strength properties of Co-Cr alloys. Only recently have the deleterious effects of σ phase formation been so emphasized that an empirical method for predicting its formability in a given alloy system has been developed. The term "σ phase" is usually
associated with a hard, brittle, intermetallic compound. The crystal structure of the phase, (in a large number of binary and ternary systems) has been indexed on the basis of a tetragonal cell having at least 30 atoms.\textsuperscript{39} In the Co-base superalloys, precipitation of such an intermetallic phase is generally found to reduce room-temperature ductility and impact strength, though not always to a prohibitive extent.\textsuperscript{32} Working with a series of binary Co-Cr alloys, Acharya, Freise and Greener\textsuperscript{40} found that above 25\% Cr, a Cr-rich \(\sigma\) phase was precipitated in both as-cast structures and those homogenized at 1000\(^\circ\)C. Furnace cooling also favored the formation of \(\sigma\). Silverman and his co-workers\textsuperscript{39} studied the formation of \(\sigma\) in H.S. 21 by additions of 70-30 Cr-Mo to the melt. Small additions yielded, in a centrifugally cast structure, 20\% \(\sigma\). Aging produced oriented precipitation patterns similar to those observed by Weeton and Signorelli.\textsuperscript{29} However, Silverman\textsuperscript{39} found that this type of precipitation increased with increasing \(\sigma\) content and postulated that it was due to nucleation along common planes of the FCC and HCP structure or common planes between either of these and the \(\sigma\) phase. Again, the more recent literature suggests that this may simply be stacking fault precipitation.\textsuperscript{36,37} In the modified H.S. 21 most similar to the parent alloy, the \(\sigma\) was found to redissolve in 1/2 hour at a solutionizing temperature of 1250\(^\circ\)C.\textsuperscript{39} In general, where the embrittling effect of \(\sigma\) precipitation proves undesirable, resolution into the matrix seems to be possible by holding above 1205\(^\circ\)C.\textsuperscript{32} Aging treatments which produce \(\sigma\) precipitation yield
an increase in hardness but a decrease in impact resistance and ductility.\textsuperscript{39} In addition, the most recent studies suggest that the interface between $\sigma$ and the matrix is a more important factor in determining mechanical parameters, then the precipitation of $\sigma$ per se.\textsuperscript{38}

Finally, one recent development in the quest for property augmentation of cast superalloys has led to the application of a process known as Hot Isostatic Pressing (HIP). In this treatment, castings are heated to temperatures around 2,000 - 2,200°F, isostatically pressurized to from 5-30 ksi and held for various lengths of time. The purpose of the procedure is to close internal casting shrinkage and reduce porosity by a combined creep/diffusion mechanism. Wasielewski and Lindblad\textsuperscript{26} have determined the ranges for the temperature-time-pressure parameters and investigated the effects of the HIP process on certain investment-cast superalloys. Their tests indicate that HIP densification is a viable process for "healing" casting porosity and improving the quality of the Ni-base superalloy castings used. The common types of casting defects (macroshrink, hot tears, and microshrink) were completely eliminated in thick section investment castings. However, although the cast macrostructure was improved by HIP, the process tended to destroy the microstructure of the alloy, necessitating a post-HIP heat treatment to optimize microstructure and subsequent properties. While the tensile strengths of large castings were not significantly improved by HIP, densification was found to improve ductility by at least a factor of two.\textsuperscript{26} It must be
pointed out that the above results were primarily for large castings with known levels of porosity. The effects of HIP on small precision castings would not be expected to be as pronounced. However, the increased flexibility for designing superalloys for strength and oxidation/corrosion resistance with less concern for castability, is clear.

From the preceding discussion, several avenues of approach to the improvement of strength and ductility parameters in cast Co-Cr-Mo-C surgical implant alloys, such as H.S. 21, are indicated. Heat treatments to accomplish the above must seek to eliminate \( \sigma \) in the as-cast structure, or at least to render it more incoherent with the matrix, through solutionizing above 1180°C. Any aging to further increase strength must yield precipitates distributed within the grains, or ductility will suffer. Finally, the closing of casting defects through HIP may increase ductility, yet a post-HIP heat treatment appears necessary to optimize mechanical properties.
II. EXPERIMENTAL

For the purpose of the present study, as investment cast tensile specimens of Co-Cr-Mo-C alloy, compositions and dimensions as specified by Committee F-4 of the ASTM \(^{41}\), were obtained from three different custom foundries who supply implant fabricators. Specimens were procured in separate lots at different time intervals. Cast tensile specimens which had been heat-treated to optimize mechanical properties were also obtained from an implant fabricator which also makes its own castings. Earlier studies by Devine \(^{23}\) showed that the latter heat-treated material possessed appreciably better crevice corrosion resistance, impact strength, and ductility (percent elongation) than the as-cast material of essentially the same composition used by most other implant fabricators. The microstructure of the heat-treated castings, as can be seen in Fig. 3, exhibited a coarse-grained, cored structure of FCC material in which minor amounts of a secondary phase were found within the grains. The microstructure of all of the as-cast specimens was multiphase and consisted of a coarse-grained dendritic structure containing carbide and \(\sigma\) precipitates within and along the grain boundaries. The microstructures of the as-cast specimens are presented in Figs. 4, 5, and 6.

The tensile properties of the four types of as-received material were measured using an Instron testing machine with a 20,000 lb.-F load cell and a 0.02 in/min cross-head speed.
Hardness measurements were made with a Tykon Indentor. The specimens used for metallographic examination and exploratory heat-treatment studies were cut from the thread ends of the tensile test specimens. After metallographic polishing, these specimens were electrolytically etched in a 5 percent HCl solution. Photomicrographs were obtained at 50X and 200X.

Solutionizing, aging and isothermal heat treatments were carried out in a tubular electric resistance furnace in an atmosphere of purified hydrogen. The solutionizing temperature used in most cases was 1230°C. This temperature was selected based on previously cited references using solutionizing steps on similar alloys²⁹,³⁵,³⁶ and others aimed at eliminating the brittle σ phase.³²,³⁸,³⁹ All specimens were first heated to 1150°C for 30 minutes before raising the furnace to the solutionizing temperature, to avoid grain boundary melting of the as-cast material. Most solutionized samples were air cooled or water quenched. Those which were isothermally heat-treated were transferred from high temperature to a low temperature furnace. The air cooled or water quenched specimens were either tested directly, or further aged for various lengths of time at either 650°C or 815°C.

Tensile test specimens from all four sources were given HIP heat-treatments at the plant of Industrial Materials Technology Inc. in Woburn, Mass. These samples were put in a high pressure container, packed in ceramic pellets, cold-pressurized to 8 k.s.i., then heated and pressurized to treatment levels of 14.5 k.s.i. and 1200°C. Pressurization was done using purified argon gas.
After holding for four hours at 1200°C and 14.5 k.s.i., the apparatus was slowly cooled down to room temperature in approximately six hours. After removal from the depressurized chamber, the specimens were cleaned. Half of them were tensile tested after the above treatment, and half were further heat-treated, in a purified hydrogen atmosphere, to solutionize precipitated phases and then aged.
III. EXPERIMENTAL RESULTS

The measured tensile properties and hardness of the as-received tensile specimens are listed in Table 4 along with the minimum acceptable properties specified by Committee F-4 of the ASTM. From the table, it is evident that test specimens from sources B and D have properties which generally exceed the minimum, especially with regard to ultimate tensile strength. Moreover, specimens from source D, which were heat-treated by the supplier, exhibit twice the required percentage elongation and much lower hardness than the others. The microstructure of D, as seen in Fig. 3, is typical of solutionized cast material: a coarse-grained structure with only minor amounts of secondary phases and evidence of coring as in all cast materials of this kind.

The tensile properties and hardness of H.S. 21 specimens from lots A and C after solutionizing heat-treatment at 1230°C for different lengths of time, followed by water quenching, are shown in Table 5. It is interesting to note that the one hour treatment at this temperature significantly improved the ductility (percent elongation) of as-cast A and C, without lowering their yield or tensile strengths. As can be seen in Fig. 7a and 7b, the solutionizing treatment produced a structure somewhat similar to that of specimens from D.

Following a one hour solutionizing treatment at 1230°C with a 20 hour aging treatment at 650°C also showed improved properties
over the as-cast condition. Aging at this temperature should result in no increase in hardness, and only very fine stacking fault or matrix precipitate. The tensile data for specimens from A and C thus prepared, are listed in Table 6.

A longer, four hour solutionizing treatment followed by aging for various lengths of time at 815°C yielded no beneficial results. Table 7 lists the tensile properties of a series of specimens from B thus prepared.

Table 8 lists the tensile properties of specimens from A and C which were solution treated for one hour at 1230°C, followed by an isothermal transformation for one hour at 815°C. Precipitation in these specimens was shown to be of the Widmanstatten type reported by Weeton and Signorelli as seen in Fig. 8.

Table 9 gives the tensile properties of those specimens subjected to the hot isostatic pressing treatment in argon. In spite of the extremely coarse-grained structure and extensive precipitation produced by this treatment, the ultimate tensile strength of all specimens exceeds the minimum specified by ASTM. Only the yield strength of A and the percentage elongation of C depart from the minimum specifications. Fig. 9 shows the precipitate formed during HIP to be an oriented, perhaps stacking fault type.

The tensile properties of specimens which were given the HIP treatment, solutionized for one hour at 1230°C, quenched in water and aged for 20 hours at 650°C, are listed in Table 10. The
property augmentation over the as-cast condition can be quite pronounced as seen in the data for A, B, and D. Ductility (percent elongation) levels for specimens from these sources were well in excess of the minimum specification, and in B and A were over twice that measured in the as-cast condition. Yield and tensile strengths were also dramatically improved up to levels of 104,000 p.s.i. and 194,400 p.s.i., respectively. Strength characteristics of this magnitude are extraordinary for cast material of this type.
IV. DISCUSSION

The investment casting industry has undoubtedly made great progress in developing casting technology to produce high quality alloys of complex shapes, which generally meet the requirements of the aircraft industry no less than those of surgical implant fabricators and users. Investment castings of Co-Cr-Mo-C are nevertheless very sensitive to casting variables. These require meticulous control if such defects as microshrink, hot-tearing, alloy segregation, and foreign inclusions are to be avoided. These defects depend not only on casting variables, but also upon component size and shape. Surgical implant parts made of the Co-Cr-Mo-C alloys generally used (Vitallium, H.S. 21, etc.) have been successfully cast and used in many thousands of implants, but as the statistics of Scales\(^22\) show, some five or more percent used in weight-bearing surgical implants fail in implantation, use, or excision due to torsional or fatigue failure. This may be due to the inherently low tensile properties of such alloys for particular types of implants, or it may, according to some implant fabricators and materials engineers, be due to defective castings.

Metallographic examination of failed investment cast Co-Cr-Mo-C implants by Wulff and co-workers at M.I.T. during the last decade, has shown that most of the failed castings had a multi-phase dendritic structure indicative of as-cast material. Failed implants which exhibited a heat-treated structure were mostly long, thin implants of variable cross-section. It is well-known that thin sections of precision castings of this alloy have
extremely large grains and tensile properties which do not meet
the specifications of ASTM. Scanning electron microscope
examination of as-cast implants of larger cross section which had
suffered fatigue fracture were found to have shrinkage voids and
occasional inclusions.

The research and development work of Devine\textsuperscript{23} has shown
that Co-Cr-Mo-C alloys could be hot-cold-worked and heat-treated
in the wrought state to have tensile strength and ductility
nearly double that of as-cast material of the same composition.
He therefore recommends that fabricators use Co-Cr-Mo-C, thermo-
mechanically processed from wrought bar, rod, or stock in implants
capable of being shaped and finished to size. Some types of
complex shaped implants can be more economically shaped by
investment casting than by closed die-forging, machining or
grinding. For such castings, it appears from the results reported
in the previous section of this thesis that HIP processing of the
as-cast parts followed by a heat-treatment, would optimize their
mechanical properties and insure maximum crevice corrosion
resistance. Although implant fabricators could not afford to
have their own HIP processing facility, such castings could be
processed in a custom HIP processing plant, and receive final
heat-treatment in the plant of the fabricator.

In evaluating the results of the tensile tests on specimens
obtained from the three custom foundries designated A, B, and C,
it is necessary to point out that specimens of nearly identical
chemical composition obtained from source C in the past proved
to have higher ductility (percent elongation) than those used in
the present study. The very large grain size of the current lot
seemed to be primarily responsible for its lower strength and
ductility, an effect which could not be corrected by subsequent
heat-treatment. Analogously, some tensile specimens obtained from
foundry B had exhibited lower ductility in previous work.
Moreover, it is not uncommon to find in any large lot of specimens
from the same source, considerable scatter in the as-cast tensile
properties and less scatter in tensile properties when such cast
specimens are heat-treated at ~1230°C with or without subsequent
aging or isothermal transformation. This merely means that such
a preferred heat-treatment can be used to improve the as-cast
tensile properties of sound castings and not those which contain
casting defects such as shrinkage voids, non-metallic inclusions,
or excessive segregation. The limitations to property augmentation
imposed by very large as-cast grain size, are also nearly impossible
to circumvent. For that matter, HIP processing cannot eliminate
non-metallic inclusions or excessive segregation. In addition,
the time at temperature and the slow cooling required before the
HIP processed castings can be removed from the pressure chamber,
destroy the preferred microstructure of the casting. However, the
fact that HIP can heal shrinkage voids, and the ability to further
augment properties by post-HIP heat treatment, make the process of
considerable value in the fabrication of safe implants for specific
applications. Such easily accessible and relatively inexpensive
processes have been shown to sufficiently increase the mechanical
properties of cast Co-Cr-Mo-C alloys as to possibly broaden their range of applications and to increase their reliability in present uses.
V. CONCLUSIONS

1. The tensile properties of as-cast Co-Cr-Mo-C surgical implant alloys deemed acceptable by Committee F-4 of the ASTM, can be improved by a solutionizing heat-treatment at 1230°C for one hour, and further enhanced by following solution treatment by an aging heat-treatment of 20 hours at 650°C.

2. The tensile properties of as-cast Co-Cr-Mo-C alloys which meet ASTM specifications, or which fail to do so due to the presence of shrinkage voids, can be significantly improved by hot isostatic pressing in argon, followed by the heat treatment described in conclusion #1.
REFERENCES

4. J. Brettle, United Kingdom Atomic Energy Authority Report, No. GRO/44/83/13 (Ex), AWRE Metallurgy Division.
5. F.W. Bultitude and J.R. Morris, United Kingdom Atomic Energy Authority Report, No. GRP/44/83/22 (Ex).


17. R.W. Revie and N.D. Greene, "Comparison of the In Vivo and In Vitro Corrosion of 18-8 Stainless Steel and Titanium,"


Figure 1

Effect of Cobalt Content on Transformation Temperature
of Co-Ni-20Cr-10Mo Alloys
Figure 2

Hardness of Co-Cr-Mo Alloys After Heat Treating For
10 Hours at 700°C
WT° MOLYBDENUM
AGE FOR 10 HRS. AT 700°C

25%Cr

20%Cr

15%Cr

10%Cr

HARDNESS (HV)

700 500 300
Figure 3. As-Received Co-Cr-Mo-C Alloy from Source D. 5% HCl Electrolytic Etch. Original Magnification: 50X.
Figure 4. As-Cast H.S.21 From Source A. 5% HCl Electrolytic Etch. Original Magnification: 50X.
Figure 5. As-Cast H.S.21 From Source B. 5% HCl Electrolytic Etch. Original Magnification: 50X.
Figure 6. As-Cast H.S.21 From Source C. 5% HCl Electrolytic Etch. Original Magnification: 50X.
Figure 7a. H.S.21 From Source A. Solutionized at 1230°C for One Hour. Water Quenched. 5% HCl Electrolytic Etch. Original Magnification: 50X.
Figure 7b. H.S.21 From Source A. Solutionized at 1230°C for 24 Hours. Water Quenched. 5% HCl Electrolytic Etch. Original Magnification: 50X.
Figure 8. H.S.21 From Source B. Solutionized at One Hour, Isothermally Transformed at Two Hours. 5% HCl Electrolytic Etch. Magnification: 200X.
Figure 9. H.S.21 From Source 5% HCl Electrolyte 200X.
Table 1

NOMINAL COMPOSITIONS OF SURGICAL IMPLANT ALLOYS

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ni</th>
<th>C</th>
<th>Fe</th>
<th>Co</th>
<th>Ti</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>316</td>
<td>16 - 18</td>
<td>2 - 3</td>
<td>---</td>
<td>10 - 14</td>
<td>&lt;0.08</td>
<td>Bal</td>
<td>---</td>
<td>---</td>
<td>&lt;2Mn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;1Si</td>
</tr>
<tr>
<td>316L</td>
<td>17 - 20</td>
<td>2 - 4</td>
<td>---</td>
<td>10 - 14</td>
<td>&lt;0.03</td>
<td>Bal</td>
<td>---</td>
<td>---</td>
<td>&lt;2Mn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;.75Si</td>
</tr>
<tr>
<td>H.S.25</td>
<td>19 - 21</td>
<td>---</td>
<td>14 - 16</td>
<td>9 - 11</td>
<td>&lt;0.15</td>
<td>&lt;3</td>
<td>Bal</td>
<td>---</td>
<td>&lt;2Mn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;1Si</td>
</tr>
</tbody>
</table>
Table 2

MECHANICAL PROPERTIES OF SURGICAL IMPLANT ALLOYS

<table>
<thead>
<tr>
<th>Form</th>
<th>Yield Strength ksi</th>
<th>Ultimate Tensile Strength, ksi</th>
<th>Elongation, Percent</th>
<th>Reduction in Area, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>Annealed</td>
<td>35</td>
<td>80</td>
<td>45</td>
</tr>
<tr>
<td>316L</td>
<td>Cold Worked</td>
<td>125</td>
<td>145</td>
<td>15</td>
</tr>
<tr>
<td>H.S.25</td>
<td>Wrought</td>
<td>65 - 80</td>
<td>145 - 165</td>
<td>35</td>
</tr>
<tr>
<td>H.S.21</td>
<td>Precision Casting</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinertia</td>
<td>Cast</td>
<td>50</td>
<td>90</td>
<td>2.5</td>
</tr>
<tr>
<td>Titanium</td>
<td>Annealed</td>
<td>40</td>
<td>50</td>
<td>22</td>
</tr>
</tbody>
</table>
Table 3
Summary of Statistics Compiled by J. T. Scales

Percentage of Corroded Implants Among 667 Removed

<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></td>
<td>22.6</td>
</tr>
</tbody>
</table>

313 Multipiece Implants = 1,750 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>
Table 4

**Mechanical Properties of HS21**

**Tensile Specimens - As Received**

<table>
<thead>
<tr>
<th>Source</th>
<th>$R_c$</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>32</td>
<td>62,400</td>
<td>110,500</td>
<td>7.5</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>68,000</td>
<td>129,000</td>
<td>8.0</td>
</tr>
<tr>
<td>C</td>
<td>29</td>
<td>71,000</td>
<td>103,800</td>
<td>5.0</td>
</tr>
<tr>
<td>D</td>
<td>22</td>
<td>71,400</td>
<td>122,300</td>
<td>17.0</td>
</tr>
<tr>
<td>ASTM F-4 Specifications</td>
<td></td>
<td>65,000</td>
<td>95,000</td>
<td>8.0 Min.</td>
</tr>
</tbody>
</table>
Table 5
Mechanical Properties of HS21 From A & C
Solutionized at 1230°C

<table>
<thead>
<tr>
<th>Source</th>
<th>Time at 1230°C</th>
<th>$R_c$</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1/2 hour</td>
<td>25.5</td>
<td>56,000</td>
<td>108,700</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>1 hour</td>
<td>23.5</td>
<td>65,300</td>
<td>128,900</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>24 hours</td>
<td>15.6</td>
<td>34,200</td>
<td>86,000</td>
<td>11.0</td>
</tr>
<tr>
<td>C</td>
<td>1/2 hour</td>
<td>29.0</td>
<td>56,900</td>
<td>58,900</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1 hour</td>
<td>23.4</td>
<td>70.120</td>
<td>106,100</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>24 hours</td>
<td>20.5</td>
<td>42,800</td>
<td>76,000</td>
<td>17.0</td>
</tr>
</tbody>
</table>
Table 6

Mechanical Properties of HS21 From A & C Solutionized and Aged at 650°C

<table>
<thead>
<tr>
<th>Source</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>73,700</td>
<td>137,900</td>
<td>10.0</td>
</tr>
<tr>
<td>C</td>
<td>64,300</td>
<td>108,300</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Table 7

Tensile Properties of HS21 From B
Solutionized for 4 hours; Aged at 815°C

<table>
<thead>
<tr>
<th>Time At 815°C</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84,950</td>
<td>94,600</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>81,700</td>
<td>88,100</td>
<td>1.5</td>
</tr>
<tr>
<td>16</td>
<td>46,500</td>
<td>46,500</td>
<td>2.0</td>
</tr>
<tr>
<td>63</td>
<td>50,900</td>
<td>50,900</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Table 8

Mechanical Properties of H.S.21 From A & C Solutionized and Isothermally Transformed at 815°C

<table>
<thead>
<tr>
<th>Source</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>117,350</td>
<td>150,000</td>
<td>4.5</td>
</tr>
<tr>
<td>C</td>
<td>128,540</td>
<td>162,168</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Table 9

Mechanical Properties of Co-Cr-Mo-C
Tensile Specimens - As HIP Processed

<table>
<thead>
<tr>
<th>Source</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>55,300</td>
<td>103,000</td>
<td>12.3</td>
</tr>
<tr>
<td>B</td>
<td>72,000</td>
<td>135,000</td>
<td>10.0</td>
</tr>
<tr>
<td>C</td>
<td>87,000</td>
<td>98,500</td>
<td>4.0</td>
</tr>
<tr>
<td>D</td>
<td>63,000</td>
<td>119,000</td>
<td>11.0</td>
</tr>
</tbody>
</table>
### Table 10

**Mechanical Properties of Co-Cr-Mo-C**
**Tensile Specimens - HIP Processed and Heat Treated**

<table>
<thead>
<tr>
<th>Source</th>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>71,700</td>
<td>133,750</td>
<td>16.0</td>
</tr>
<tr>
<td>B</td>
<td>104,200</td>
<td>194,400</td>
<td>16.8</td>
</tr>
<tr>
<td>C</td>
<td>68,600</td>
<td>89,700</td>
<td>4.2</td>
</tr>
<tr>
<td>D</td>
<td>100,000</td>
<td>159,800</td>
<td>12.5</td>
</tr>
</tbody>
</table>
**Cr-Mo-C and Heat Treated**

<table>
<thead>
<tr>
<th>Strength</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>16.0</td>
</tr>
<tr>
<td>400</td>
<td>16.8</td>
</tr>
<tr>
<td>700</td>
<td>4.2</td>
</tr>
<tr>
<td>800</td>
<td>12.5</td>
</tr>
</tbody>
</table>