INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI[®]

**The Influence of Chemical Composition and Heat Treatment
on Microstructure and Mechanical/Tribological Properties
of Cobalt-based Triballoy Alloys**

by
Wei Xu
B. Eng.

A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of

Master of Applied Science

Department of Mechanical and Aerospace Engineering
Ottawa-Carleton Institute for
Mechanical and Aerospace Engineering

Carleton University
Ottawa, Ontario
Canada
August, 2005

© Copyright
2005, Wei Xu

Library and
Archives Canada

Bibliothèque et
Archives Canada

0-494-08391-3

Published Heritage
Branch

Direction du
Patrimoine de l'édition

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file *Votre référence*

ISBN:

Our file *Notre référence*

ISBN:

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protègent cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

The undersigned recommend to the faculty of Graduate Studies and Research
acceptance of the thesis

**The Influence of Chemical Composition and Heat Treatment on
Microstructure and Mechanical Properties of Tribaloy Alloys**

Submitted by Wei Xu

In partial fulfillment of the requirements for the degree of
Master of Applied Science

Thesis Supervisor

Chair, Department of Mechanical and Aerospace Engineering

Carleton University

September 1, 2005

To my parents

ABSTRACT

Wear and corrosion are two major factors that cause machinery failure in engineering. Development of advanced materials to combat these damages is a constant trend. Tribaloy alloys are an important group of cobalt-based alloys, which exhibit excellent wear and corrosion resistances.

This study compared the microstructures and properties of five Tribaloy alloys with different chemical compositions, T-400, T-401, T-400C, T-800 and T-200. Among them, T-401, T-400C and T-200, are newly developed alloys; T-400 and T-800 are traditional Triballoys, which exist in a hypereutectic state containing intermetallic Laves phases (the primary) and eutectic phase (the secondary). T-400C is still a hypereutectic alloy but with higher Cr content for increased corrosion resistance. T-401 and T-200, on the other hand, were cast in a hypoeutectic state with the Co solid solution as the primary phase and the Laves phase contained eutectic as the secondary phase. In this study, the nanoindentation technique has been used to assess the mechanical properties of each constituent phase in these alloys, and their macroscopic properties including hardness, tensile and fatigue strength, wear resistance and corrosion resistance have also been evaluated, in accordance with the ASTM standards for the use of respective testing methods.

The study has found that the strength/hardness and wear resistance of the Tribaloy alloys are controlled by the volume fraction of the Laves phase, which either exists as the primary phase or in the eutectic, such that they increase with the

increasing volume fraction of the Laves phase. Therefore, hypoeutectic alloys with Co solid solution as the primary phase are generally not as hard as the hypereutectic alloys but more ductile. The corrosion resistance of the alloys, on the other hand, is controlled by the Cr content.

In addition, two different heat treatments have been conducted on T-400 and T-200 respectively. It has been found that T-400 was softened slightly by the heat treatment while T-200 was hardened.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis supervisor, Professor R. Liu, for her guidance throughout this research and for her help whenever needed.

I am grateful to Dr. P. Patnaik, Dr. X. J. Wu and Dr. M. X. Yao for their generous help. I also wish to thank Dr. Q. Yang, D. Morphy and D. Chow for their assistance in my laboratory work at National Research Council Canada (NRC).

Thanks to my parents who are a source of unwavering encouragement and my friends for their energetic support.

TABLE OF CONTENTS

ABSTRACT.....	iv
ACKNOWLEDGEMENTS.....	vi
TABLE OF CONTENTS.....	vii
LIST OF TABLES	x
LIST OF FIGURES.....	xi
NOMENCLATURE.....	xvii
 CHAPTER 1: INTRODUCTION	 1
1.1 Background and Significance.....	1
1.2 Objectives and Methods	4
1.3 Construction of the Thesis.....	6
 CHAPTER 2: LITERARATURE REVIEW	 7
2.1 The Wear Mechanisms.....	7
2.2 Wear-resistant Materials.....	9
2.3 Cobalt-based Alloys	9
2.3.1 Basic Properties	10
2.3.2 History of Co-based Alloy Development.....	11

2.4	Stellite alloys	12
2.5	Tribaloy alloys	14
2.5.1	Microstructures	15
2.5.2	Effects of Alloying Elements.....	16
2.5.3	Wear Resistance	17
2.5.4	Hardness	19
2.5.5	Cracking and Ductility	20
2.5.6	Cracking and Ductility	20
2.5.7	Heat Treatment.....	21
2.5.8	Fabrication methods	22
2.5.9	Applications	22
2.6	Summary	23
CHAPTER 3: EXPERIMENTAL DETAILS		25
3.1	Alloy Fabrication	25
3.2	Differential Scanning Calorimetry (DSC) Test	26
3.3	Microstructure Examination and Phase Analysis	26
3.4	Nano Indentation Test	27
3.5	Tensile Test.....	28
3.6	Rotation Bending Fatigue Test	28
3.7	Hardness Test.....	29
3.8	Wear Test.....	30
3.9	Corrosion Test	31
3.10	Heat Treatments	32
CHAPTER 4: RESULTS AND DISCUSSION		34
4.1	Microstructures	34
4.1.1	Microstructure of T-400	34
4.1.2	Microstructure of T-401	35
4.1.3	Microstructure of T-401	35

4.1.4	Microstructure of T-800	36
4.1.5	Microstructure of T-200	36
4.2	Calorimetric Results.....	37
4.3	Nano Mechanical Properties of Constituent Phases	38
4.4	Hardness	40
4.5	Wear Resistance.....	40
4.6	Tensile Strength and Elongation.....	41
4.7	Fatigue Strength	42
4.8	Corrosion Resistance.....	43
4.9	Effects of Heat Treatment	43
4.9.1	Microstructures	43
4.9.2	Nano mechanical properties	44
4.9.3	Macro hardness and wear resistance	45
4.10	Discussion.....	46
4.10.1	Relationship between chemical composition and microstructure.....	46
4.10.2	Microstructure ~ Property Relationships.....	47
4.10.3	Effects of Heat Treatment.....	49
CHAPTER 5: CONCLUSIONS AND FUTURE WORK		52
5.1	Conclusions	52
5.2	Future Work.....	56
REFERENCES.....		57
TABLES		64
FIGURES		72

LIST OF TABLES

- Table 2.1 Chemical compositions (wt.%) of various Co-based alloys
- Table 2.2 Chemical compositions (wt.%) of Tribaloy alloys
- Table 2.3 Microstructure of as-cast T-400 and T-800 Tribaloy alloys
- Table 2.4 Alpha wear test results in naphtha, a poor lubricant
- Table 2.5 Rider/Drum corrosion-wear test results
- Table 2.6 Corrosion rates for T-400, T-800 and selected commercial compositions
in several environments
- Table 3.1 Chemical compositions (wt.%) of tested Tribaloy alloys
- Table 4.1 DSC results (Temperature in °C) of tested Tribaloy alloys
- Table 4.2 Nano mechanical properties of individual phases in the tested alloys
- Table 4.3 Nano mechanical properties of individual phases in the as-cast and
heat-treated alloys

LIST OF FIGURES

Figure 2.1 SEM backscatter images of microstructures:

(a) Stellite HS4 HIP'ed at 1200°C

(b) Stellite HS6 HIP'ed at 1200°C

(c) Stellite HS7 HIP'ed at 1200°C

Figure 2.2 Macro hardness of various Stellite alloys

Figure 2.3 SEM microstructure of PTA T-400:

(a) 500X

(b) 1500X

Figure 2.4 Macro hardness of various Tribaloy alloys

Figure 3.1 Centrifugal casting technique:

(a) operating model

(b) front side view

(c) back side view

Figure 3.2 Differential scanning calorimetry (DSC) device

Figure 3.3 DSC heating/cooling cycle

Figure 3.4 Nano mechanical testing machine

Figure 3.5 Typical loading/unloading curve under indentation

Figure 3.6 Tensile testing machine

Figure 3.7 Rotating-bending fatigue machine

Figure 3.8 Wilson Rockwell hardness tester

Figure 3.9 Pin-on-disc tribometer

Figure 3.10 Schematic drawing of the wear track and the pin

Figure 3.11 Profiler used to simulate the wear track

Figure 4.1 SEM microstructure of T-400:

(a) 500X

(b) 1500X

(c) EDX spectrum of primary Laves phase

(d) EDX spectrum of eutectic mixture

Figure 4.2 SEM microstructure of T-401:

(a) 500X

(b) 1500X

(c) EDX spectrum of primary Co solid solution

(d) EDX spectrum of eutectic mixture

Figure 4.3 SEM microstructure of T-400C:

(a) 500X

(b) 1500X

(c) EDX spectrum of primary Laves phase

(d) EDX spectrum of eutectic mixture

Figure 4.4 SEM microstructure of T-800:

(a) 500X

(b) 1500X

(c) EDX spectrum of primary Laves phase

(d) EDX spectrum of eutectic mixture

Figure 4.5 SEM microstructure of T-200:

(a) 500X

(b) 1500X

(c) EDX spectrum of primary Co solid solution

(d) EDX spectrum of eutectic mixture

Figure 4.6 X-ray diffraction pattern of T-400

Figure 4.7 X-ray diffraction pattern of T-401

Figure 4.8 X-ray diffraction pattern of T-400C

Figure 4.9 X-ray diffraction pattern of T-800

Figure 4.10 X-ray diffraction pattern of T-200

Figure 4.11 DSC heating and cooling curves:

(a) T-400

(b) T-401

(c) T-400C

(d) T-800

(e) T-200

Figure 4.12 Loading/unloading curves of T-400 under indentation:

(a) primary Laves phase

(b) eutectic mixture

Figure 4.13 Loading/unloading curves of T-401 under indentation:

(a) primary Co solid solution

(b) eutectic mixture

Figure 4.14 Loading/unloading curves of T-400C under indentation:

(a) primary Laves phase

(b) eutectic mixture

Figure 4.15 Loading/unloading curves of T-800 under indentation:

(a) primary Laves phase

(b) eutectic mixture

Figure 4.16 Loading/unloading curves of T-200 under indentation:

(a) primary Co solid solution

(b) eutectic mixture

Figure 4.17 Macro hardness of the tested alloys

Figure 4.18 Wear loss of the tested alloys

Figure 4.19 Stress - Strain curve of T-401 under tension

Figure 4.20 Stress - life (S - N) curve of T-401 under rotating bending

Figure 4.21 Fractured surfaces of T-401 under rotating bending:

(a) an enlarged view of the fracture surface

letter A indicates the fatigue region

letter B indicates the overload (tensile mode) region

(b) the detailed feature of fatigue fracture

(c) the alveolate structure of the tensile fracture mode

Figure 4.22 Corrosion resistances of T-400, T-401 and T-400C:

(a) in H_2SO_4

(b) in HNO_3

(c) in HCl

Figure 4.23 SEM microstructures of the as-cast and the heat-treated T-400 specimens:

- (a) as-cast
- (b) heat-treated at 1232°C
- (c) heat-treated at 1257 °C
- (d) heat-treated at 1282°C

Figure 4.24 X-ray patterns of the as-cast and the heat-treated T-400 specimens

Figure 4.25 SEM microstructures of the as-cast and the heat-treated T-200 specimens:

- (a) as-cast
- (b) heat-treated for 16 h
- (c) heat-treated for 48 h

Figure 4.26 X-ray patterns of the as-cast and the heat-treated T-200 specimens

Figure 4.27 Loading/unloading curves of the heat-treated T-400 at 1282°C under indentation:

- (a) primary Laves phase
- (b) eutectic mixture

Figure 4.28 Loading/unloading curves of the heat-treated T-200 for 48 h under indentation:

- (a) primary Co solid solution
- (b) eutectic matrix

Figure 4.29 Macro hardness of the as-cast and heat-treated alloys:

- (a) T-400
- (b) T-200

Figure 4.30 Wear loss of the as-cast and heat-treated alloys:

(a) T-400

(b) T-200

Figure 4.31 Relationships between Laves phase volume fraction, hardness
and wear loss

Figure 4.32 Relationships between Cr content and corrosion resistance

Figure 4.33 SEM images of indentation surface of T-400:

(a) 100X

(b) 500X

Figure 4.34 SEM images of indentation surface of T-401:

(a) 100X

(b) 500X

Figure 4.35 SEM images of indentation surface of T-400C:

(a) 100X

(b) 500X

NOMENCLATURE

<i>DSC</i>	Differential scanning calorimetry
<i>SEM</i>	Scanning electron microscope
<i>EDX</i>	Energy dispersive X-ray diffraction
<i>PTA</i>	Plasma transferred arc
<i>PM</i>	Powder metallurgy
<i>HIP</i>	Hot isostatic pressing
<i>FCC</i>	Face-centered-cubic
<i>HCP</i>	Hexagonal-close-packed
<i>E</i>	Young's modulus
<i>UTS</i>	Ultimate tensile strength
<i>ASTM</i>	American Society for Testing and Materials

CHAPTER 1 INTRODUCTION

1.1 Background and Significance

Wear of materials occurs in almost every field of engineering, which is one of main causes of machinery failure in terms of material loss. When exposed to a corrosive environment, the synergy of corrosion and wear can render the total material loss much greater than those caused by corrosion and wear respectively [1–4]. In recent years, material designers have developed several classes of alloys to combat corrosion wear. Cobalt-based superalloys are one of them, which are especially targeted for high-temperature applications to resist corrosion and wear because they retain good properties over a wide temperature range [5]. These alloys can be classified into three categories: carbide-strengthened alloys (Stellite alloys), intermetallic Laves phase alloys (Tribaloy alloys) and solid solution-strengthened alloys, depending on the chemical composition, mainly the content of carbon in the alloys. Stellite alloys gain their strength and hardness primarily by combining solid-solution-strengthening with carbide precipitation, while Tribaloy alloys contain a large volume fraction of a hard, intermetallic Laves phase dispersed in a eutectic

matrix. The carbon content in Triballoy alloys is kept low to prevent carbides forming in preference to Laves phase. The main alloying elements in the alloys are chromium (Cr), molybdenum (Mo), tungsten (W), carbon (C) and silicon (Si). Chromium is used to enhance corrosion resistance and strengthen the solid solution in cobalt-based alloys. It also provides wear resistance to Stellite alloys by forming, with C, carbides during alloy solidification. The main functions of molybdenum and tungsten in cobalt-based alloys are to strengthen the solid solution matrix due to their large atomic size impeding dislocation flow when present as solute atoms [6]. In Triballoy alloys molybdenum is also used to impart wear resistance by forming Laves phase. The role of carbon in Stellite alloys is to control the carbide volume fraction. Alloys with a low carbon content offer better corrosion resistance. Silicon is an important element in Triballoy alloys to form Laves phase, thus providing wear resistance of the alloys. Solid solution-strengthened alloys are primarily designed for resisting erosion-corrosion and galling, which are enriched with Cr, Mo and W to provide resistance to various corrosive media [7].

The major difference between Stellite alloys and Triballoy alloys is that the former gains wear resistance from carbides and the latter from Laves phases. The hardness of the carbides is in the range above Vickers 2000 (HV) and that of the Laves phase is between 1000 ~ 1300 (HV). The Laves phase is hard enough to resist wear, but is not so hard that it becomes a cutting tool to wear away a mating surface. Therefore Triballoy alloys are mostly used to resist wear under poorly lubricated or unlubricated conditions [8].

Triballoy alloy family consists of a series of alloy categories, designated as T-400, T-700, T-800 and T-900. Among them, T-400 and T-800 are the most popular

ones. Because the Laves phase is so abundant in Triballoy alloys (35 ~ 70 vol.%), its presence governs all the material properties. Accordingly, the effects of the matrix composition in these alloys are less pronounced than in the case for the cobalt-based carbide-type alloys (Stellite alloys) [6]. As a result of the hard brittle nature of the Laves phase, Triballoy alloys possess a relatively low resistance to brittle crack propagation and little capacity for plastic flow [9, 10]. Although wear resistance is a necessity for Triballoy alloys, other properties such as ductility, fracture toughness and high-temperature oxidation resistance are also important for some specific applications. In recent years, alloy designers have developed several groups of alloys that address this issue. Although certain compromises in properties still had to be made, for example, improving wear resistance of a material often results in reduction of fracture toughness and ductility; the new alloys have met the needs in some applications [11].

Heat treatment, in general, has some effects on material properties of most engineering alloys. However, heat treatment effect on Triballoy alloys is arguable. Some research found that the microstructures of Triballoy alloys could not be modified by subsequent heat treatment after casting because these alloys were believed to be stable up to at least 1230°C [8], but it was also reported that the cast alloys could be softened or hardened by heat treatment, which was mainly a result of precipitation within the cobalt solid solution also with some contribution from the face centered cubic (fcc) → hexagonal close packed (hcp) allotropic transformation [5]. Therefore the effects of heat treatment on Triballoy alloys need further investigation.

1.2 Objectives and Methods

This project is a joint research between Carleton University, Deloro Stellite Inc. and NRC, sponsored by a NSERC Collaborative Research and Development Grant (CRD), with aim at developing advanced cobalt-based Tribaloy alloys for specific applications. Three new alloys, designated as T-401, T-400C and T-200, were designed and fabricated. Material characterization was conducted on these alloys. T-401 is a Co-Mo-Cr-Si Tribaloy alloy, designed for increasing ductility and corrosion resistance by modifying the chemical composition, mainly adjusting the silicon and chromium contents. T-400C is also a Co-Mo-Cr-Si Tribaloy alloy, with improved corrosion resistance by increasing the content of chromium. T-200 is a totally new alloy; it is a Co-Mo-Ni-Nb Tribaloy alloy, with the Laves phase formed by Co and Nb. Strength, ductility, wear and corrosion resistances are the major properties of concern in application of these new alloys.

The objective of this thesis was to study relationships between chemical composition, microstructure and properties of Tribaloy alloys, in order to verify the new alloy design.

The following tests/methods were used to achieve the objectives:

1. A combination of metallurgical techniques, including scanning electron microscope (SEM) with backscatter electron imaging, energy dispersive X-ray (EDX) spectrum and X-ray with Cu K_{α} radiation, would be used to examine the microstructures of the new Tribaloy alloys as well as conventional Tribaloy alloys for comparison.

2. Differential scanning calorimetry (DSC) technique would be used to study the solidus/liquidus properties of the constituent phases in the Tribaloy alloys.

3. Nanoindentation technology would be used to assess the mechanical properties of each individual phase in the alloys, in order to understand the contribution of each constituent to the macroscopic properties of the alloys.

4. The hardness would be assessed using a Wilson Rockwell machine.

5. Wear resistance would be evaluated on a pin-on-disc tribometer.

6. The tensile properties of T-401, as a representative of hypoeutectic alloys, would be obtained using an MTS system (capacity 1000 kg), in accordance with the ASTM standard test method for tension testing of metallic materials (E8-96).

7. Fatigue properties, in terms of S-N data, of T-401 would be assessed using a rotating-bending fatigue machine (RBF-200 with capacity 200 in-lb).

8. Corrosion resistance of T-401 and T-400C would be evaluated in an immersion corrosion test, in accordance with ASTM standard test designations G 1, G 28 and G 31, in comparison with T-400.

9. Heat treatments would be done to T-400 and T-200 to study their effects on microstructural modification and properties.

1.3 Construction of the Thesis

This thesis consists of five chapters as described below:

Chapter 1 is an introduction to this research, which states the background and significance, and the objectives and methods of the research.

Chapter 2 is a literature review of the previous research related to the current project.

Chapter 3 describes the details of the experimental work.

Chapter 4 presents the experimental results with extensive discussion.

Finally, the conclusions of this study and future work recommended are summarized in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

2.1 The Wear Mechanisms

Wear is the mechanical interaction between two materials that leads to a progressive modification of the contacting surfaces with material loss. The forms of wear damage can be deformation, pitting, cracking and material transfer. It is one of the major causes of machinery failure, part retirement/replacement and machine downtime, resulting in economic waste.

Wear mechanisms may be classified into three categories, as described in the following [12]:

- 1) Sliding wear: it occurs when two solid surfaces are rubbing together with no abrasive particles present.
- 2) Abrasive wear: it happens when hard particles are forced against and move relative to a surface, by which the material is cut away via either plowing or chipping depending on the material's surface properties (ductile or brittle).
- 3) Erosive wear: it occurs as the result of mechanical interactions between a

material surface and a gas or a liquid that may or may not carry solid particles impacting on the surface.

The common characteristic of these wear mechanisms is that the real contact area between the two solid surfaces is much smaller than what it appears to be, since both surfaces cannot be perfectly smooth. Therefore, the contacting force is actually borne by a few material spikes at the surface, and hence the local force will be large enough to knock off those material spikes. Thus, wear progressively occurs.

Wear is a very complex process wherein the dominant mechanism may change across the life span of the component. The wear performance of a material is influenced by its inherent properties such as hardness, strength, ductility and environmental factors such as lubrication conditions, pressure, corrosion, and temperature. There are a number of ways to reduce wear damage, such as (1) using lubricants, (2) optimizing material properties such as hardness and ductility, (3) employing hard coatings on the surfaces, and (4) optimizing the contact conditions, for example, minimize surface contact area, and so on [13, 14].

In practice, lubricant is usually applied to reduce wear damage or some tribological techniques are used to improve contact conditions. However, these technologies are not applicable in every situation. For example, in food or textile machinery, lubricant can not be allowed as a contaminant. Some pump parts must use the processing fluid alone otherwise they will dissolve away oil. Some seals or bearings must operate at high temperature level exceeding the functional range of lubricants. Even in the lubricated condition, sometimes due to eccentricity and vibration of the parts, the lubricant film may be damaged, resulting in contact of surfaces in relative motion [15].

The present study is focused on the development and investigation of wear-resistant materials to combat wear.

2.2 Wear-resistant Materials

Industrial wear in production processes constantly demands materials with high wear resistance. A wide range of wear-resistant materials have been developed and employed in various fields of engineering, which include cast iron, steels, copper alloys, polymers, composites and superalloys [14].

2.3 Cobalt-based Alloys

Among the above mentioned wear resistant materials, cobalt-based alloys are a special class of materials that find their applications under high temperature level and highly corrosive conditions. Generally, Cobalt-based alloys can be classified into three groups [16]:

- (1) carbide-strengthened alloys
- (2) intermetallic Laves phase alloys
- (3) solid solution-strengthened alloys

The alloy properties depend on the crystallographic nature of cobalt; the solid-solution strengthening contents such as chromium, tungsten and molybdenum; the metal carbides and intermetallic Laves phase. Generally, the solid solution strengthened cobalt alloys are softer and tougher which are often used for high-temperature corrosion and oxidation resistance applications while the carbides

and Laves phase contained alloys are harder, which are usually used for wear resistance. Table 2.1 shows the compositions of various Co-based alloys in terms of different applications.

2.3.1 Basic Properties

Metallic cobalt (Co) has a atomic number of 27. It locates between iron (Fe) and Nickel (Ni) in the first long period of the periodic table. The density of cobalt is 8.85 g/cm^3 , which is similar to that of nickel (8.902 g/cm^3) [17]. The melting point of cobalt is 1493°C (2719°F), and the Vickers hardness is 1043 HV. Its thermal expansion coefficient lies between those of iron and nickel.

Cobalt has a hexagonal close-packed (hcp) crystal form at room temperature, which will transform to a face-centered cubic (fcc) form at higher temperatures (above 417°C). The nature of this transformation is martensitic. Naturally, most alloys contain both phases at ambient temperature. The stacking fault energy of these crystal forms can be influenced by alloying components. Chromium, tungsten, and molybdenum, are hcp stabilizers and can lower the stacking fault energy. On the contrary, elements such as carbon (within the soluble range) nickel, iron, zirconium, and tantalum are known as fcc stabilizers, which increase the stacking fault energy and lower the transformation temperature [6]. Because of the sluggish nature of the transformation, the structure of the Co-rich matrix of the alloys is generally fcc at ambient temperature, which implies that the alloys are in a metastable state [18]. Addition of Cr and W increase the transformation temperature so that in most cobalt alloys the transformation temperature is somewhat higher. The relationship between

stacking-fault energy and the allotropic transformation is that as the stacking fault energy becomes vanishingly small the fcc will transform to hcp as the partial dislocations constituting the fault boundaries become independent [9].

2.3.2 History of Co-based Alloy Development

Historically, commercial cobalt-based alloys were derived from the Co-Cr-W and Co-Cr-Mo ternaries which were first studied by E. Haynes in 1907. He discovered the high strength and stainless nature of the binary cobalt-chromium alloy, and later identified tungsten and molybdenum as powerful strengthening agents within the cobalt-chromium system [6]. These alloys, named Stellites, were investigated to retain their hardness up to 800°C (1472°F).

Stellite alloys were first used for commercial purpose in 1917 and then were used from about 1922 in weld overlay form to protect surfaces from wear. These early Co-based “hardfacing” alloys were used on plowshares, oil well drilling bits, dredging cutters, hot trimming dies, and combustion engine valves and valve seats [19].

Later in the 1930s, Co-based alloys for corrosion and high-temperature applications were developed in a series of related events involving the Austenal Laboratories and Hayes Stellite Division of Union Carbide [6]. The cobalt-chromium-based dental alloy called Vitallium, developed in 1936, was found to have unusual high temperature properties; it was used successfully during World War II in buckets for turbochargers blades of aircraft engines.

Current Co-based alloys are little changed from the early alloys. The major differences among Stellite alloy grades today relate to the control of carbon and

tungsten contents [20]. The 700 series (Stellite 703, 706, 712, and 720) are the most recently developed alloys in the Stellite family. The tungsten in these alloys has been replaced by molybdenum (Mo content ranges from 5~18 wt.%). The 700 series alloys have excellent corrosion resistance in reducing acid environments.

Tribaloy alloys, which are intermetallic Laves phase containing alloys, came around 1980. They contain Co, Mo, and Si to form a close-packed structure to obtain excellent wear resistance. Compared with the carbides in Stellite alloys, the Laves phase is relatively soft but hard enough for wear resistance. Therefore, Tribaloy alloys are not as suitable for cutting tools as Stellite alloys. However, owing to their special properties, Tribaloy alloys are mostly used to resist wear when lubrication is a problem.

2.4 Stellite Alloys

Stellite alloys typically contain (in weight percent) about 50-60% Co, 20-30% Cr, 5-20% W, and 0.1-1% C with the balance made up mostly by nickel, molybdenum, niobium, tantalum and iron. For example, wrought Co-based Stellite alloys contain about 40% Co and 20% Ni for increased workability [21].

Co-based Stellite alloys are mainly strengthened by a combination of solid solution and precipitation of carbides in an fcc matrix [22]. There are two basic families of carbide phases in Co-based Stellite alloys:

- (1) M_7C_3 and $M_{23}C_6$ carbides, where “M” represents basically Cr but can be substituted by W and Mo. The most common carbide in Co-based Stellite alloys is the

M_7C_3 type although the Cr-rich carbide $M_{23}C_6$ is abundant in low carbon alloys such as Stellite 21. M_7C_3 can be dissolved during solution treating and in some cases transforms to $M_{23}C_6$ during aging [6, 23].

(2) M_6C and MC carbides. M_6C carbide is generally found in low Cr alloys with the molybdenum or tungsten content exceeding about 5 wt.% [6, 23].

Figure 2.1 shows typical microstructures in Stellite alloys, which are composed of dendritic Co solid solution and various carbides [24]. Regarding the carbides, there are two ways to strengthen Co-based Stellite alloys. One is that carbides precipitate at the grain boundaries to decrease the grain boundary sliding, thus prolonging rupture life; the other is that some carbide particles precipitate in the stacking faults to impede dislocation movement, thus strengthening the material [25].

Cobalt-based Stellite alloys can be divided into two groups: 1) high-carbon alloys and 2) low carbon alloys. High carbon Stellite alloys have superior wear and corrosion resistance. Their wear rates, as characterized by the pin-on-disc wear test (ASTM G 99), are typically in the order of 10^{-6} mm³/s [6]. In particular, the wear resistance tends to increase with the volume fraction of carbides, while the corrosion resistance increases with the Cr content. A number of studies [26-32] have been carried out on Stellite alloys with regards to their various properties, and in comparison with stainless steels. Low-carbon alloys, on the hand, are mostly designed with good ductility and corrosion/oxidation resistance for high temperature applications such as in gas turbine engines.

In addition, Stellite alloys also provide good tensile strength (UTS), in the range of 800 to 1200 MPa, and hardness ~50 HRC (as shown in Figure 2.2), which

makes them attractive as structural alloys too [7].

2.5 Tribaloy Alloys

Tribaloy designates a group of wear and corrosion-resistant Co- or Ni- based alloys that are primarily strengthened by intermetallic Laves phases dispersed in a eutectic matrix. It is the presence of a high-volume fraction of Laves phase that enables Tribaloy alloys to resist wear under poorly lubricated or unlubricated conditions, although Laves phase is traditionally not desirable for high temperature alloys because it has a deleterious effect on ductility [6]. Generally, in these two-phase alloys the solid solution offers high mechanical strength, fracture toughness and ductility while the Laves phase provides wear resistance.

Traditional Tribaloy alloys are named as T-400, T-800, T-700 and T-900 with the chemical compositions given in Table 2.2. T-400 and T-800 are Co-based Triballoys which contain (in weight percent) 8.5%-17.5% Cr, and 2.6%-3.4% Si, respectively, and the same amount of Mo, 28.5%. T-400 and T-800 have excellent high-temperature wear and corrosion resistance and they are the most commonly used commercial Tribaloy alloys in the industry. T-900 is also Co-based Tribaloy which contains (in weight) 18% Cr, 23% Mo, 16% Ni, and 2.7% Si with improved ductility. T-900 offers good high-temperature wear resistance, and good localized corrosion resistance.

The most commonly used Ni-based Tribaloy alloy is T-700 which possesses high corrosion and oxidation resistance. It contains (in weight) 15.5% Cr, 32.5% Mo and 3.4% Si. The absence of cobalt makes T-700 an outstanding candidate in nuclear

industry for corrosion, oxidation and radiation resistance applications (replacing Co-Cr-W alloys), because cobalt is one of the most important elements in nuclear reactions [17].

2.5.1 Microstructures

Tribaloy alloys are usually hypereutectic with 35 ~ 70 vol.% primary intermetallic phase evenly dispersed in a softer eutectic matrix [33]. The hard primary phase is a ternary Laves phase of the C-14 (MgZn_2) type and its composition is typically between CoMoSi and its isomorph $\text{Co}_3\text{Mo}_2\text{Si}$ because the atom ratios are continuously variable between these two stoichiometric limits. The melting point of the primary Laves phase is about 1595°C and that of eutectic matrix is approximately 1230°C . The primary dendrites of the hard intermetallic phase are in a matrix consisting of areas of lamellar eutectic mixture, which are smaller intermetallic particles embedded in a Co solid solution, and regions of cobalt solid solution, which are free from the secondary Laves phase [34]. Because the Laves intermetallic phase is so abundant in these alloys, its presence governs all the material properties. Accordingly, the effects of the matrix composition in these alloys are less pronounced than in the case for the Co-based Stellite alloys [35].

The allotropic nature of cobalt can cause either the fcc or hcp crystal structures or both to be presented in Tribaloy alloys depending on the thermal treatment. This allotropic transformation increases the work hardening rate, thus benefiting the abrasive and metal to metal wear resistance of the alloys [36]. Halstead and Rawlings [5] demonstrated by X-ray diffraction study that the cobalt solid

solution constituent of Tribaloy alloys in the cast condition had both hcp and metastable fcc crystal structure, with the hcp form being more prevalent than fcc form.

T-400 exhibits a large proportion of fine lamellar eutectic which is composed of the secondary Laves phase and cobalt solid solution. In addition to the primary Laves phase and the lamellar eutectic, this alloy contains areas of solid solution which are essentially free from secondary Laves phase particles [9]. The typical microstructure of T-400 is shown in Figure 2.3.

The features of microstructure in T-800 are also primary dendrites of Laves phase in a eutectic matrix, same as that in T-400. As shown in Table 2.3, the main difference between T-400 and T-800 is that T-400 has a finer eutectic mixture, a smaller volume fraction of primary Laves phase, and a smaller proportion of Laves free cobalt solid solution [5]. The other difference is that T-800 contains higher content of Cr than T-400. It follows that T-800 has greater proportion of hcp phase due to the nature of Cr to increase the likelihood of the fcc form transforming to hcp at room temperature. In addition, T-800 has better oxidation and corrosion resistance also owing to higher Cr content.

2.5.2 Effects of Alloying Elements

The main alloying elements in Co-based Tribaloy alloys are Cr, Mo and Si. Addition of alloying elements changes the temperature at which the martensitic transformation occurs and alters the range of thermodynamic stability of the fcc and hcp phases [9]. Cobalt can be alloyed with these elements and tends to form a tough

matrix.

Chromium (Cr): The major effect of Cr in Tribaloy alloys is to impart corrosion resistance. Generally, Chromium partitions itself about 1/3 in the Laves phase and 2/3 in the solid solution imparting corrosion resistance to both phases and thus to the material as a whole [5]. In addition, the addition of Cr can increase the likelihood of cobalt transforming from the high temperature fcc to hcp at room temperature by decreasing the stacking fault energy in the Tribaloy alloys.

Silicon (Si): Silicon is an important alloying element in Tribaloy alloys and is added at levels in excess of its solubility limit with the purpose of inducing the precipitation of the hard Laves phase, thus imparting wear resistance to Tribaloy alloys.

Molybdenum (Mo): Molybdenum is used to impart wear resistance by forming the Laves phase and strengthening the solid solution [37]. Moreover, the addition of Mo will favor the retention of fcc cobalt at room temperature.

Carbon (C): Carbon is not a significant alloying element in Tribaloy alloys and its content is held as low as possible (less than 0.08 wt.%) so that carbide forming elements are free to form the hard Laves phase.

2.5.3 Wear Resistance

In Tribaloy alloys, wear resistance is mainly gained by the hard intermetallic Laves phase. They exhibit outstanding resistance to galling and corrosion, and are particularly suitable for applications where lubrication is a problem [38]. T-800 contains more Cr offering T-800 higher corrosion resistance than T-400.

General laboratory wear tests are not satisfactory to predict wear resistance in specific applications. However, the relative performance of materials system in simplified tests is useful to provide guidelines for materials selection [8]. Many wear testing methods have been used to investigate the tribological properties of T-400 and T-800. The Alpha wear tests [8] have been used extensively to demonstrate the superior wear resistance of Tribaloy alloys under a 'poorly lubricated' condition. The results indicate that these alloys possess better performance in resisting adhesive wear under high local loads than commonly specified alloys. The Alpha wear test results are presented in Table 2.4.

The oscillating slider test was another testing method used to determine the friction and wear resistance of Tribaloy alloys up to a temperature nearly 1000°C. In this test, the 7.1 mm diameter superalloy pin moved back and forth 25 mm at up to 30 mm/s under a load on the test flat of Tribaloy T-120. The conclusion was obtained that the oxides of Tribaloy alloys had the non-galling properties at high temperatures as the clean Tribaloy alloys at room temperature. Therefore, Tribaloy alloys surfaces can be pre-oxidized for service at a lower temperature range, for high temperature applications [5].

Above two methods are not applicable for investigating the wear resistance of Tribaloy alloys in corrosive environments. A non-commercial rider-on-drum machine, similar in principle to the Alpha tester, was therefore adapted for the wear-corrosion tests. The 7.1 mm wide-face of a rectangular test block was loaded under 6.8 kg in contact with an 89 mm diameter drum rotating at 400 r.p.m. in a pool of 5% (absolute) hydrochloric acid [11]. The results of this test are presented in Table 2.5. It is shown that Co-based Tribaloy alloys have superior resistance to a wear-corrosion

combination environment. There were no signs of corrosion on the tested surfaces and the weight loss was low or moderate. These data are valid to predict their performance only in the medium of 5% (absolute) hydrochloric acid.

2.5.4 Hardness

Overall bulk hardness of Co-based Tribaloy alloys varies with the chemical composition and the method of manufacturing. Moreover, the hardness of Tribaloy alloys is determined by the hardness and proportions of the primary Laves phase and the matrix. The hardness of Laves phase is approximately 1000 to 1300 on the Vickers scale (HV) while that of cobalt solid solution is about 300 to 800 HV [7, 39]. Bulk hardness of the hardest available tool steel and commercial TiC strengthened composite are about 950 HV and 1800 HV, respectively [10]. Apparently, Laves phase is harder than the hardest tool steel but much softer than the carbide compounds generally identified as wear resistant. This hardness difference between carbide-strengthened composites and Co-based Tribaloy alloys contributes that the latter can be machined by TiC tools which are much cheaper than traditional diamond grinding tools.

The macro hardness of various Tribaloy alloys is summarized in Figure 2.4. It is illustrated that the hardness of T-400 and T-800 are approximately 55 HRC and 56 HRC, respectively. T-800 was harder because of the greater volume fraction of the primary Laves phase and the slightly higher hardness of the matrix.

2.5.5 Cracking and Ductility

Due to the presence of the large volume fraction of Laves phase, Triballoy alloys are hard and have a relatively low resistance to brittle crack propagation, with a fracture toughness of about $20 \text{ MN m}^{-3/2}$ [9].

The recent work [10] has shown that the resistance to crack initiation and growth of Triballoy alloys is considerably influenced by the microstructures which may be varied due to the allotropic nature of the cobalt solid solution and a precipitation phenomenon that occurs on annealing in the temperature range 600 to 1100°C [10].

2.5.6 Corrosion Resistance

T-400 and T-800 have excellent resistance to a combined corrosion and wear environment, such as oil production and refining, over a wide temperature range mainly due to the Cr addition. Corrosion resistance is one of the major differences among Triballoy alloys. Table 2.6 shows corrosion rates of Triballoys *versus* those of some common commercial alloys which are designed for corrosion resistance and have low wear resistance [11].

2.5.7 Heat Treatment

Heat treatment is often used to manipulate alloy's microstructure to achieve the desired properties. Some previous [11,18] studies reported that the microstructures

of Triballoy alloys could hardly be modified by heat treatment after casting; because the constituents of these alloys, Laves phase and the eutectic phase, would stay stable up to 1230°C (the melting point of the Laves phase is even higher, about 1595°C). The study by Schmidt and Ferriss reported that the structure of Triballoy T-400 was stable from cryogenic temperatures to just below the eutectic temperature, at which some grain growth and phase coarsening would occur. Therefore, the alloy was not believed to be heat treatable [11]. On the other hand, Halstead and Rawlings demonstrated that the cast T-400 and T-800 could be softened or hardened by heat treatment, which lead to a change in the precipitate morphology within the eutectic phase and also some allotropic transformation from fcc to hcp [5]. It was also found that by heat treatment in the range 600 to 1100°C it was possible to obtain precipitation within the Co solid solution in either a spheroidal or a Widmanstätten form [6] and when T-400 and T-800 were heat treated in the range 600 to 900°C the regions of metastable fcc transformed to hcp and a Widmanstätten precipitate, whereas the regions of hcp present at room temperature showed evidence of a spherical precipitate [5].

The effect of heat treatment on the hardness of the as-cast T-400 and T-800 was investigated by Halstead and Rawlings [5]. One heat treatment was conducted at temperatures in the range of 700 - 900°C in order to examine its effect on hardness in terms of different temperatures and aging time. It was found that there was a hardness increment which started as about 600°C, reached to the maximum value of 80 - 150 HV (depending on the material concerned) at approximately 800°C and then decreased at higher temperatures. Another heat treatment was also carried out on T-400 and T-800 at 1250°C for 2 hours. A drop of hardness of about 40 HV occurred for both Triballoy alloys. It was observed from X-ray data that the solid solution

became fcc, but not the same as the fcc and hcp mixture in the as-cast states and this was the main reason for the softening during the heat treatment although coarsening and spheroidization of the lamellar eutectic may also contribute to the hardness decrease.

2.5.8 Fabrication Methods

Co-based Tribaloy alloy parts can be fabricated by casting, hardfacing, plasma spraying or powder metallurgy. Small components of Tribaloy alloys can be cast by investment and centrifugal methods. Tribaloy alloys can also be used for hardfacing softer base metals using oxyacetylene or gas-tungsten arc welding processes [7]. However, Co-based Tribaloy alloys are not available in wrought form because they are not easily workable, either in cold or hot temperatures.

Powders of Tribaloy alloys are not easily compacted by themselves owing to their refractory nature under pressure. However, blends with up to 25% Tribaloy alloys are compatible; therefore, parts can be made by plasma spraying or compacted by conventional powder metallurgy (P/M) [11,39]. The wear resistances of P/M products of bronze, stainless and alloy steel have been improved significantly by the addition of 15% or 20% T-400.

2.5.9 Applications

Wear and corrosion resistance properties make Co-based Tribaloy alloys most suitable for antiwear surfaces and bearings used in air or in low lubricity liquids such

as gasoline, benzene, hydraulic fluids, and refrigerants under sliding and rolling contact, boundary lubrication conditions [34]. Typical applications include diverter valve bushing, tappet inserts, magnetic tape heads, screw flights, chemical and automotive valves pump parts, thrust washers, and copier assembly, bushing in food blender, calibrated ratchet, and high temperature control device.

Tribaloy alloy powders are also used to fabricate components used in a variety of industries including automotive, business machines, aircraft and garden equipments under higher speed; high temperatures, in high stress, poorly or none lubricated conditions [6].

2.6 Summary

Cobalt based alloys, with addition of Cr, W, Mo, maintains a high melting point that is particularly suitable for high temperature applications in corrosive environment. Depending on the chemical composition, with precipitation of carbides (in Stellite alloys) or Laves phase (in Tribaloy alloys), their wear resistance is greatly increased. These properties can even be enhanced with increasing volume fraction of the precipitation or the content of particular elements. For example, increasing the volume fraction of carbides or Laves phase will increase the alloys' strength, hardness and wear resistance, whereas increasing the Cr content increases their corrosion resistance. However, high wear resistance is often compromised with poor ductility. For some special applications, such as, casting dies, blanking dies and deep drawing dies, alloys with balanced properties are required. Therefore, it is important to study the properties of each constituent phase in these alloys and their influence on the

macroscopic properties such as tensile strength, hardness, wear/corrosion resistances, and ductility of the alloys.

The focus of the present study is to investigate the properties of three new Tribaloy alloys and their relationships with the phase/microstructure of the alloys.

CHAPTER 3 EXPERIMENTAL DETAILS

Three new Co-based Triballoy alloys, designated as, T-401, T-400C and T-200, respectively, were selected as the subject of study to investigate the influence of chemical composition and heat treatment on their properties. To obtain a comprehensive understanding, the following experiments/tests have been conducted: (1) differential scanning calorimetry (DSC) analysis, (2) microstructure examination and phase analysis, (3) nano indentation test, (4) tensile test, (5) rotation bending fatigue test, (6) hardness test, (7) wear test, (8) corrosion test, and (9) heat treatment.

3.1 Alloy Fabrication

The samples of Co-based Triballoy alloys T-400, T-401, T-400C, T-800, and T-200 were fabricated using a centrifugal casting technique at Deloro Stellite Inc.. Their chemical compositions are given in Table 3.1. The schematic drawing of the device are shown in Figure 3.1. Centrifugal casting is a casting process specifically suitable for producing cylindrical parts. In this casting process, a mould is spinning around its axis at high speeds (300 to 3000 r.p.m.) as the molten metal is poured in. The molten metal is centrifugally thrown to the inside walls of the mould and then solidified after cooling.

3.2 Differential Scanning Calorimetry (DSC) Test

The (DSC) tests were conducted to determine thermodynamic properties of the tested alloys, such as melting ranges, phase transition temperatures, and heat capacity, using the instrument DSC 404 C, as shown in Figure 3.2. DSC is a thermodynamic analysis technique that measures the amount of transition energy, in terms of heat, absorbed or dissipated by the tested samples as a function of temperature, to characterize the endothermic (heat absorption) and exothermic (heat release) processes. The solidification transition temperatures were taken as the onset temperatures of the exothermic peaks on cooling process and that of liquidation were taken as the onset temperatures of the endothermic peaks on melting process [6, 7].

The temperature range of DSC 404C is from -120°C to 1650°C. All the tested samples went through the same heating/cooling cycle at the same heating/cooling rate (20°C/min). The maximum temperature in the cycle was determined in terms of the melting point of Co (1495°C), as shown in Figure 3.3, it is 1500°C.

3.3 Microstructure Examination and Phase Analysis

The alloys samples were sectioned into small pieces and ground with grit papers from #180 to 1200 and then polished with abrasive cloth plus 1 μm alumina powders before being etched in the solution mixture of 15 ml HNO_3 , 15 ml acetic acid, 60 ml HCl and 15 ml H_2O . The microstructures were studied by means of a Hitachi Model S-570 Scanning Electron Microscope (SEM) in the back scattered mode

presenting contrast between phases due to differences in average atomic number. Energy dispersive X-ray analysis (EDX) of the phases was carried out using images formed by the back scattered atomic number contrast mode for location [7]. A Philips diffractometer, utilizing Cu K_α radiation and scanning at 1°min^{-1} , was used to obtain diffraction traces from rotating bulk specimens of the test alloys. These traces were then used to determine the crystal structure and the lattice parameters of the phases present in the alloys [6].

3.4 Nano Indentation Test

The mechanical behavior and nano hardness of individual phases in the alloys were investigated using a load and displacement sensing indentation technique on a CSM machine (see Figure 3.4). This technique uses a new nano technology allowing precise measurement and control of the indenting forces and precise measurement of the indentation depths, thus enabling determination of mechanical properties of individual phases in a material. The range of Poisson ratio for metallic materials is about 0.3. The values of effective Young's modulus $E^* = \frac{E}{(1-\nu^2)}$ and hardness H are calculated by the computer automatically based on the loading/unloading curves measured with a Berkovich indenter using the Oliver-Pharr method [41], where E and ν are the Young's modulus and Poisson ratio of the tested materials respectively. The load - depth curves of loading and unloading were recorded automatically during the indentation. A typical loading/unloading curve is shown in Figure 3.5. The area I between the loading and unloading curve represents the energy dissipated in the

material due to plastic deformation, and the area II under the unloading curve represents the elastic recovery [42,43]. D_{max} and L_{max} are the maximum deformation and maximum load, respectively, with the L_{max} being 50 mN in each indentation of the present study. An average of three indentations in every phase was taken as the results.

3.5 Tensile Test

Tensile tests of T-401 were conducted on a MTS 810 material testing machine (capacity 10 Mg, shown in Figure 3.6), according to the ASTM standard test method for tension testing of metallic materials (E8-96), in order to compare its tensile properties with those of T-400 which have already been reported in previous research. The dimensions of the specimens were $150 \times 30 \times 5$ mm. The test was performed in a strain-rate-controlled mode, at the rate of 6×10^{-4} /s. An extensometer was used to determine the elongation and the stress-strain diagram was finally produced to determine the tensile properties.

3.6 Rotation Bending Fatigue Test

For further investigation, the fatigue strength of T-401 was evaluated on a rotating-bending (the stress ratio r was -1) fatigue machine (RBF-200 with capacity 200 in-lb, shown in Figure 3.7) at a rotational speed of 3000 to 3600 r.p.m., in stress-controlled mode, in room temperature. The tests were started at 60% to 80% of

the tensile strength of T-401 and the load (stress) level was then adjusted either higher or lower than the starting stress in order to obtain fatigue life points locating between 10^4 to 10^7 cycles. The data from the first pair of specimens were discarded for the vibration problem of the test machine. Fifteen specimens were tested but only twelve were valid.

The applicable pound-inch moment setting for the poise weight was determined on the basis of desired bending stress level in the specimen. This moment may be determined from the equation [44]:

$$M = 3.1416SD^3 / 32 = 0.0982SD^3$$

Where

M — moment selected to applied on the test machine according to different stress level requirements (in-lb)

S — desired bending stress in the specimen at minimum cross section (lb/in²)

D — diameter of the specimen at minimum cross section (in)

3.7 Hardness Test

The macro hardness of the specimens was measured on a Wilson Rockwell machine (shown in Figure 3.8). The hardness was measured by the size or depth of

the indentation made under a constant load impressed upon an indenter [45]. Five measurements were made on each specimen and the average was taken as the result.

3.8 Wear Test

A TEER-POD-2 pin-on-disc tribometer, as shown in Figure 3.9, was used to measure the wear resistance of the specimens. The POD-2 wear tester is a computer-controlled device creating wear tracks to provide a measurement of tribological properties of materials. Basically, the device consists of a 'pin' in contact with a rotating disc. The relative motion between them creates a circumferential wear path on the disk surface. The pin is made of 94% WC and 6% Co, with the hardness of HV 1534. It is loaded under a normal force, in contact with the specimen surface rotating at 319 r.p.m.. Frictional force is monitored continuously by load cell and recorded by the computer during the wear process and the corresponding friction coefficient can be calculated afterward by the ratio of the friction force to the applied normal load. The material loss is determined by measuring the profile of the resulting wear track and then evaluating its volume after the specimen surface is worn for a set time. The diameters of the ball and wear track are 5 mm and 6 mm, respectively, as illustrated in Figure 3.10. All the specimens were tested under a normal load of 10 N and the wear loss was evaluated after the surfaces were worn for 10^4 s except for T-200. Since T-200 is much softer than common Tribaloy alloys, it was only worn for 2×10^3 s.

Wear resistance of each tested alloy was evaluated by calculating the volume loss of the material, that is, the volume of the wear track. To evaluate the volume loss,

the cross-sections at least at three positions along each wear track were simulated using a surface profiler, as shown in Figure 3.11. The cross-sectional areas of three positions along each wear track were taken and averaged. The volume of the wear track was calculated using the average cross-sectional area multiplied by the periphery of the circular wear track, with the formula expressed below:

$$VolumeLoss(mm^3) = 2\pi RA$$

Where

R — the wear track radius (mm)

A — the average of the cross-sectional area of the each wear track (mm²)

3.9 Corrosion Test

Immersion corrosion test was conducted on T-401, T-400C and T-400, in terms of ASTM standard test designations G 1, G 28 and G 31. Strip coupons had the dimensions of approximately 50×25×3 mm³. The surfaces of each specimen were ground to 0.41μm finish, cleaned in acetone and air-dried. The geometric area calculation was accurate to 1% and the mass of each specimen was measured to an accuracy of 1 mg. The specimens were supported in glass cradles (reference ASTM G 28-97) in the test solutions. The test media were oxidizing acid 65% HNO₃ at 66°C, reducing acids 10% H₂SO₄ at 102°C and 5% HCl at 66°C. After exposed to the test solutions for 3 days, the specimens were cleaned by brushing under warm tap water and dried with ethanol and a blow dryer. The mass of each corrosion coupon was

measured and the weight loss was expressed as mil/year (thousandths of an inch). Corrosion rate was calculated assuming uniform corrosion over the entire surface of

the coupon and the formula is described as following:

$$\text{CorrosionRate} = \frac{W \times 22,300}{Adt}$$

Where

W — weight loss (g)

A — area of coupon (in²)

d — metal density of coupon (g/cm³)

t — time of exposure in corrosive environment (day)

3.10 Heat Treatments

The effects of heat treatment on mechanical and tribological properties of T-400 and T-200 were investigated. Different heat treatment processes were performed according to the following description:

I. For T-400, the specimens were given a solution treatment, which consisted of heating the specimens to 1232°C, 1257°C and 1280°C respectively, and holding for 2 hours, followed by rapid water quenching.

II. For T-200, the heat treatment consisted of two steps: firstly, the specimens were homogenized at 1100°C for 8 hours followed by air cooling, and then aged at 800°C for 16 and 48 hours respectively, followed by air cooling.

CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Microstructures

The microstructures of Tribaloy alloys T-400, T-401, T-400C, T-800, and T-200, together with the EDX spectra, are shown in Figures 4.1–4.5, respectively. In the SEM backscatter images of the tested Tribaloy alloys, the Laves phase appears much lighter than the matrix due to the concentration of Mo in the Laves phase, because Mo has large atomic number and SEM images can show marked atomic number contrast between phases.

4.1.1 Microstructure of T-400

It is seen that T-400 consists of primary Laves phase and an eutectic mixture. Accordingly, the EDX spectrum of the primary Laves phase shows high level of Si and Mo, while that of the eutectic shows high level of Co and Cr. The X-ray diffraction pattern in Figure 4.6 shows the primary Laves phase and eutectic phases present in the alloy. The Laves phase in T-400 is an intermetallic compound of

$\text{Co}_3\text{Mo}_2\text{Si}$ and the Co solid solution is a mixture of fcc and hcp phases. T-400 typically contains about 55% Laves phase in volume fraction.

4.1.2 Microstructure of T-401

As shown in Figure 4.2, the microstructure of T-401 can be clearly divided into two regions: one is eutectic solid solution plus Laves phase, and the other is Co solid solution. It is totally different from T-400 in that the primary phase is no longer Laves phase. Therefore, it is a hypoeutectic microstructure. Similar to T-400, as shown by the EDX spectra in Figures 4.2 (c) and (d), the primary solid solution contains high Co and Cr but low Si and Mo, and the eutectic contains high Si and Mo because of the presence of the 25 vol.% Laves phase, which is also the intermetallic compound of $\text{Co}_3\text{Mo}_2\text{Si}$. The Co solid solution in T-401 is also the mixture of fcc and hcp phases. But T-401 has more hcp phase than T-400, comparing the hcp/fcc peaks in the X-ray patterns for the two alloys (see Figure 4.6 and 4.7).

4.1.3 Microstructure of T-400C

As shown in Figure 4.3, T-400C has a similar microstructure to T-400, which is comprised of the primary Laves phase and the eutectic phase. Compared to T-400, T-400C contains less amount of Laves phase, with a volume fraction of ~ 45 vol.%. This may be attributed to the lower Mo content in T-400C, as Mo is a participating element to form Laves phase. Again, as shown in the EDX spectra, Figures 4.3 (c) and (d), the primary Laves phase contains high contents of Si and Mo, but high

contents of Co and Cr are in the eutectic phase. The Laves phase in T-400C is also the intermetallic compound, $\text{Co}_3\text{Mo}_2\text{Si}$; the Co solid solution is also a mixture of fcc and hcp phases, as revealed by the X-ray diffraction in Figure 4.8.

4.1.4 Microstructure of T-800

T-800 has a similar microstructure to T-400, but due to higher content of Si, T-800 contains a larger volume fraction of Laves phase than T-400, at about 70 vol.%, as seen in Figures 4.4 (a) and (b). Another difference is that the Laves phase in T-800 is the intermetallic compound of CoMoSi rather than $\text{Co}_3\text{Mo}_2\text{Si}$, as in T-400, as shown by the X-ray pattern in Figure 4.9. The EDX spectra in Figures 4.4 (c) and (d) show that high contents of Si and Mo are in the primary Laves phase and high contents of Co and Cr in the eutectic. It is also noticed that much higher Cr level is found in the eutectic of T-800 than in T-400, because T-800 has a higher content of Cr in chemical composition (see Table 3.1). The Co solid solution in T-800 is also a mixture of fcc and hcp phases, as known from the X-ray pattern in Figure 4.9.

4.1.5 Microstructure of T-200

Similar to T-401, T-200 is also hypoeutectic, with the primary phase being Co solid solution, as shown by the micrographs in Figures 4.5 (a) and (b). The eutectic is a mixture of solid solution and the intermetallic compound of Co_2Nb , as shown by the X-ray pattern in Figure 4.10. However, the volume fraction of Laves phase in T-200 is 14 vol.% and much less compared to T-401. Both the primary solid solution and the

eutectic contain high Co, as Co is one of the forming elements of the Laves phase, Co_2Nb . The former also contains high Cr, while the latter contains high Nb. These can be evidenced by the EDX spectra in Figures 4.5 (c) and (d).

4.2 Calorimetric Results

The DSC curves of the tested alloys are presented in Figure 4.11. In each plot, the upper curve represents the material responses during heating, with a rate of $20^\circ\text{C}/\text{min}$, whereas the lower trace represents the solidification transition behavior during cooling. The melting ranges of endothermic processes and solidification range of exothermic processes could be defined from these DSC plots. The DSC data for all the tested alloys are accordingly obtained and shown in Table 4.1.

It can be seen that the hypereutectic alloys, T-400, T-400C and T-800, exhibited only one endothermic peak occurred in the heating process, as shown in Figures 4.11 (a), (c) and (d), which implied that the dissolution of the primary Laves phase and the eutectic phase occurred at almost the same temperature, that is, Laves phase and the eutectic have similar dissolution points. The hypoeutectic alloys, T-401 and T-200, on the other hand, exhibited two peaks in the heating process, these two peaks occurred closely in T-401 but well separated in T-200, as shown in Figures 4.11 (b) and (e). The first peak represents the dissolution of the eutectic phase and the second indicates the dissolution of the primary phase, which is Co solid solution. This demonstrates that the Co solid solution and the eutectic have different phase transition temperatures, especially for T-200, the difference in dissolution temperatures between the two phases is about 100°C ; as shown in Figure 4.11 (e). Therefore, it can be

concluded that the hypereutectic Co-based Triballoy alloys have nearly the same dissolution temperature for both Laves phase and eutectic phase, whereas the hypoeutectic Co-based Triballoy alloys have two dissolution temperatures for Co solid solution and the eutectic. In the cooling process, however, solidification of the primary phase and the eutectic phase in all the tested alloys occurred at different temperature, as shown in Figure 4.11.

With regards to the primary phase, according to the DSC data as shown in Figure 4.11, T-200 can be ranked #1 with the highest bulk dissolution temperature (the temperature corresponding to endothermic peak, 1420°C), followed by #2) T-800 (1349°C), #3) T-400 (1338°C), #4) T-400C (1328°C) and #5) T-401 (1303°C) successively. Moreover, T-200 also has the largest dissolution range, followed by T-401. T-400, T-400C and T-800 have similar melting ranges which are smaller than that of T-401 (See Table 4.1). Thus it can be concluded that hypoeutectic Triballoy alloys have larger melting range than hypereutectic alloys.

4.3 Nano Mechanical Properties of Constituent Phases

The loading/unloading curves of each individual phase in the tested alloys, obtained from the nano indentation test, are presented in Figures 4.12 – 4.16. In the load-displacement plot, the total energy is equal to the area under the loading curve (see Figure 3.5). The dissipated energy is evaluated from the area between the loading and unloading curves. The elastic energy is evaluated from a differential energy between total energy and the dissipated energy. An energy dissipation ratio η_p can be defined as the ratio of the dissipated energy to the total applied energy, which

indicates the degree of plastic deformation during the indentation process. In the content of this study, this parameter is used as an indicator to the ductility. Similarly, an elastic energy ratio η_e can be defined as the ratio of the elastic deformation energy to the total deformation energy. Then, $\eta_e + \eta_p = 1$. For evaluation of the mechanical properties of the constituent phases, the hardness, Young's modulus, η_e and η_p values for each alloy are summarized in Table 4.2.

The results show that, among the hypereutectic alloys, the primary Laves phases in T-400 and T-400C have a similar hardness and it is higher than that of the primary Laves phase in T-800. The difference can be attributed to the different crystal structures of the Laves phases. According to the X-ray analyses as described above, the Laves phase in T-800 is CoMoSi, whereas that in T-400 and T-400C is Co₃Mo₂Si. Therefore the comparison seems to indicate that Co₃Mo₂Si is harder than CoMoSi. On the other hand, the Young's moduli of the primary Laves phase in T-400 and T-400C are also similar, and they are also higher than T-800. This is consistent with the conclusion that Co₃Mo₂Si is a harder phase than CoMoSi. As of plasticity, the primary Laves phases in all the hypereutectic alloys have similar η_p values; as shown in Table 4.2. As far as the eutectic phases are concerned, that in T-400 was found to be the hardest, that in T-800 was the second and that in T-400C was the third. However, the ranking may not mean anything because the eutectic phase is a mixture of Laves phase and Co solid solution and their volume fraction ratio varies from alloy to alloy. As of the plasticity of the eutectic mixture, T-400 and T-400C has the lowest η_p and the highest η_e , respectively, with T-800 falling in the middle.

In hypoeutectic alloys, T-401 and T-200, the primary phases have much lower hardness and Young's modulus than those of the hypereutectic alloys, T-400, T-400C

and T-800, because the primary phases in T-401 and T-200 are Co solid solutions which are much softer than Laves phases. As it is well-known, solid solution is, in general, ductile and tough. As shown in Table 4.2, the η_p values of the primary solid solution phase in T-401 and T-200 are very high, as compared to the Laves phase, which may indicate good ductility. The eutectic mixtures of T-401 and T-200 have comparable hardness and Young's modulus to those of T-400, T-400C and T-800 and also similar η_p values.

4.4 Hardness

The macro hardness results of the tested alloys, which were taken as the averages of five measurements on each specimen, are presented in Figure 4.17. It is shown that T-800 exhibits the highest hardness, followed by T-400, and then T-400C and T-401. T-200 is much softer than other alloys. The high hardness of T-800 is due to the large volume fraction of Laves phase compared with the other alloys, although the Laves phase (CoMoSi) of T-800 itself is softer than the Laves phase (Co₃Mo₂Si) of T-400 and T-400C. The main reason for the low hardness of T-200 is the small volume fraction of Laves phase contained. This alloy is designed for increasing ductility; therefore, hardness is not the main concern

4.5 Wear Resistance

Figure 4.18 illustrates the wear volume losses of the tested alloys. It can be seen obviously that T-800 has the highest wear resistance, which is attributed to the

large volume fraction of Laves phase, compared with T-400 and T-400C. T-400C has lower wear resistance than T-400, although they contain the same Si content. The possible reason is the reduction of Mo content in T-400C, which may result in the decrease of Laves phase volume fraction. T-401 has much less Laves phase so that it exhibits much lower wear resistance. Similar to T-401, due to the small volume fraction of Laves phase contained, T-200 also has low wear resistance. Note that T-200 should have more wear loss than that shown in Figure 4.18 under equivalent wear condition; because the wear loss for T-200 in that figure was evaluated after the specimen surface was worn for 2×10^3 s, but for the other alloys the surfaces were worn for 10^4 s. The reason for the different time is that T-200 has too low wear resistance to be worn for 10^4 s.

4.6 Tensile Strength and Elongation

As a representative of hypoeutectic alloy, T-401 was evaluated via tensile testing to compare tensile strength with that of a representative hypereutectic alloy T-400. The stress - strain curve of T-401 under tension is shown in Figure 4.19. There was not obvious yielding for the stress - strain behavior which indicated that T-401 had almost no plastic deformation. T-401 exhibited the characteristics of brittle materials. The tensile strength of T-401 was read from the maximum point on the curve as 697 MPa. The ductility was estimated by back-extrapolation of the elastic recovery of the total elongation, which left a residual elongation of 0.1%. In comparison, T-400 has a tensile strength of 690 MPa with almost zero elongation [10]. The tensile tests have shown that T-401 has a comparable strength to T-400 but has

higher ductility than T-400. This is expected because the primary phase in the hypoeutectic alloy is Co solid solution, which is a soft and ductile phase, as shown by nano-indentation tests.

4.7 Fatigue Strength

The fatigue behavior of T-401 was investigated on a rotating-bending fatigue machine and its fatigue strength was characterized by using a plot of stress range against the number of fatigue cycles to failure, N_f . As presented in Figure 4.20, under a constant amplitude loading condition, T-401 exhibits a plateau in the stress ~ lives ($S \sim N$) curve typically beyond about 10^6 fatigue cycles. Below this plateau level, the specimen may be cycled indefinitely without causing failure. This stress amplitude is known as the fatigue limit or endurance limit, σ_e , which was evaluated to be 400 MPa for T-401.

The fracture surfaces of T-401 specimens under the fatigue test were examined using SEM. As shown in Figure 4.21, the fracture surface can be divided into two regions, marked A and B on the micrograph in Figure 4.20 (a): one (A) is truly the fatigue cracking region and the other (B) is the overload tensile fracture region. Region B had a rough alveolate structural pattern, which was somewhat like a ductile fracture. Region A, on the other hand, contains more complicated features. First of all, plenty of striations could be found in the lower areas, which are typical evidence of fatigue crack propagation. The high areas, however, appeared to be smeared, with local plateaus formed. This was due to the pounding of two mating

surfaces during the compression of the rotation cycle. The exhibition of these features also corroborates the finding that T-401 has certain ductility.

4.8 Corrosion Resistance

Immersion corrosion tests were conducted on T-400, T-401 and T-400C in three different corrosive media, respectively. The experimental results are illustrated in Figure 4.22. According to the corrosion rates, it is evident that both T-401 and T-400C offer a corrosion resistance superior to T-400 in the three acids. Between T-401 and T-400C, T-400C has higher corrosion resistance than T-401 in the H_2SO_4 and HNO_3 solutions but lower corrosion resistance in HCl , see Figure 4.22. The higher corrosion resistance of T-401 and T-400C can be attributed to the higher Cr contents in the alloys, compared with T-400.

4.9 Effects of Heat Treatment

Different heat treatment processes were performed on T-400 and T-200, respectively, as described in Chapter 3. The microstructures, mechanical and tribological behaviors of the tested specimens, before and after the heat treatments, were studied.

4.9.1 Microstructures

The SEM backscatter images of the microstructures of the as-cast T-400 and the heat-treated T-400 at different temperatures are shown in Figure 4.23. It was observed that the morphology of the primary phase — Laves phase — did not change much by the heat treatments, except the phase boundaries in the heat-treated alloys became a little blur and rounded, as a result of inter-diffusion. It is also noticed that the Laves phase in the eutectic matrix has changed to a more spherical morphology, as opposed to a fine laminar structure in the as-cast T-400, as a result of heat treatment. The microstructural sphericalization tended to be coarsened as the heat treatment temperature increased from 1232°C to 1282°C. The X-ray patterns of the as-cast and the heat-treated T-400 specimens are presented in Figure 4.24. It is shown that the Laves phase in the heat-treated T-400 is the intermetallic compound of $\text{Co}_3\text{Mo}_2\text{Si}$ which is the same as in the as-cast alloy. The Co solid solution in the heat-treated T-400, on the other hand, has totally transformed into fcc structure, while the as-cast T-400 contains both fcc and hcp phases.

For T-200, it was found that the heat-treated alloy had a similar microstructure to the as-cast alloy, that is, the microstructure containing the eutectic phase and the Co solid solution, except that the volume fractions of the eutectic phase has increased with the aging time. The volume fractions of the eutectic phase in the as-cast specimen was 14%. After aging for 16 h and 48 h, the volume fraction of the eutectic phase increased to 21% and 26%, respectively. The X-ray patterns of the as-cast and the heat-treated T-200 specimens are presented in Figure 4.26. It is shown that there is no difference in phase between the as-cast and heat-treated specimens. The Laves phase in the alloys is the intermetallic compound of Co_2Nb with a C-15 structure and the Co solid solution is mainly the fcc phase.

4.9.2 Nano Mechanical Properties

The nano indentation test was performed on the primary Laves phase and the eutectic mixture of the as-cast and heat-treated T-400 specimens, respectively. The loading and unloading curves were obtained from the indentation. Figure 4.27 presents the loading and unloading curves of the heat-treated T-400 at 1282°C. For T-200, the test was conducted on the primary Co solid solution and the eutectic mixture respectively. Figure 4.28 presents the loading and unloading curves of the heat-treated T-200 for 48 h. The hardness, Young's modulus, η_e and η_p values, which are calculated from the loading and unloading curves of the as-cast and heat-treated specimens, are summarized in Table 4.3.

Firstly, comparing the as-cast and the heat-treated T-400, the primary Laves phase was softened greatly by the heat treatment, but the eutectic was not changed as much, the hardness was increased only slightly. There was a slight decrease in the Young's modulus and slight increase in the η_p value of the primary Laves phase, but no significant change in both parameters for the eutectic, see Table 4.3. Secondly, comparing the as-cast and the heat-treated T-200, both the solid solution and the eutectic were hardened significantly by the heat treatment. The Young's modulus of the solid solution was decreased and that of the eutectic was not changed. With the increase in the hardness, the plasticity (η_p value) of both the solid solution and the eutectic was reduced greatly, see Table 4.3.

4.9.3 Macro Hardness and Wear Resistance

The macro hardness test and pin-on-disc wear test were also conducted on the as-cast and heat-treated T-400 and T-200 specimens, respectively. Again five tests of macro hardness were carried out on each specimen and the average was taken as the result. The wear loss of each specimen was obtained by calculating the volume of the wear track, which represents the material removed from the surface due to the wear. The average hardness and wear loss of the tested specimens are illustrated in Figures 4.29 and 4.30, respectively.

It is shown that the heat treatment had little effect on the hardness and wear resistance of T-400. The hardness of T-400 was decreased slightly by the heat treatment with the increasing temperature up to 1282°C, but the wear resistance of T-400 was not changed by the heat treatment. Regarding T-200, it is evident from Figures 4.29 and 4.30 that both the hardness and the wear resistance of the alloy were enhanced by the heat treatment significantly, and the aging time affected the hardness but not the wear resistance.

4.10 Discussion

4.10.1 Relationship between Chemical Composition and Microstructure

Triballoy alloys are two-phase intermetallic materials. The chemical composition is a major factor that not only determines the amount and properties of the Laves phase precipitated in the alloys, but also the hypereutectic/hypoeutectic state of the alloy. In addition, the chemical composition also influences the Co solid

solution which plays an indispensable role in the functions of the Triballoys, for example, providing the binder for the Laves phase and enhancing the overall fracture toughness of the alloys.

In particular, the amount of Si and Mo contents in the Co-Mo-Cr-Si Triballoy alloys play a controlling role. As seen in Figures 4.1 - 4.4, due to the different amount of Si and Mo, the primary phase changed from Laves phase in T-400 to Co solid solution in T-401. In this transformation, the reduction in Si and Mo contents changed the solidification process from hypereutectic to hypoeutectic, because both elements are key elements in the formation of the intermetallic Laves phase, $\text{Co}_3\text{Mo}_2\text{Si}$. Modification of Cr content would not change the microstructure very much, because the main effect of Cr in Triballoy alloys is solid solution strengthening and corrosion resistance. T-800 contains very high Si and Cr contents so that it has a high volume fraction of Laves phase and an outstanding corrosion resistance.

T-200 has a significant different chemical composition from conventional Triballoy alloys in that it does not contain Si and Mo at all. Consequently, the Laves phase precipitated in the alloy is not $\text{Co}_3\text{Mo}_2\text{Si}$ or CoMoSi , but, owing to the presence of Nb, it is a new intermetallic compound, Co_2Nb , in a cubic or hexagonal C-15 structure.

4.10.2 Microstructure ~ Property Relationships

As discussed above, compositional variations among Triballoy alloys resulted in various microstructures with different amount of Laves phases, where the Laves phases were present either as the primary phase or in the eutectic. This had a profound

influence on the alloys properties. Comparing the hardness and wear loss of the five Triballoy alloys, T-400, T-401, T400C, T-800 and T-200, as a function of the volume fraction of the Laves phase, as shown in Figure 4.31, it clearly shows the trend that hardness increased with the volume fraction of the Laves phase, but vice versa for the wear loss.

The corrosion rate, on the other hand, was more controlled by the Cr content than any other features of the microstructure in the Triballoy alloys evaluated. Figure 4.32 shows that the corrosion resistance increased greatly from T-400 with increasing of Cr content in T-400C, T-401 and T800.

The effect of microstructure on ductility was not systematically evaluated by tensile testing in this study because one of the main purposes of this research was to investigate the ductility of T-401, which was expected to be better than conventional Triballoy alloys as it is a hypoeutectic alloy. One case is shown for T-401 that, with changing the primary phase from Laves phase to cobalt solid solution, the ductility of T-401 has been improved. The results of nanoindentation tests can further verify this issue. Nanoindentation has shown that Co solid solution phase has much lower hardness and Young's modulus but better ductility than Laves phase. Therefore the hypoeutectic alloy, T-401, exhibits lower macro hardness and wear resistance than the hypereutectic alloys, T-400, T-400C and T-800, but the hypereutectic to hypoeutectic transformation has provided the alloy with better ductility, due to the reduction of the brittle Laves phase.

The indentation surfaces of T-400, T-401 and T-400C under the macro hardness test condition were examined using SEM. The images of the indentation surfaces are shown in Figures 4.33-4.35. Almost no cracking can be seen in the T-401

surface, but many cracks can be obviously seen along the edges of the indents in the T-400 and T-400C specimen surfaces. This indicates that T-401 has a higher resistance to cracking than T-400 and T-400C, that is, T-401 has a higher fracture toughness.

Generally speaking, increasing hardness and wear resistance is compromised by loss in corrosion resistance [17]. For Triballoy alloys, the wear resistance is mainly attributed to the presence of the Laves phase and the corrosion resistance to the high content of Cr. By proper alloy design, the two desired properties can co-exist in one alloy, which is the biggest advantage of Triballoy alloys. Owing to their superior high-temperature properties, Triballoy alloys are probably the best materials available for high-temperature wear/corrosion applications.

4.10.3 Effects of Heat Treatment

Comparing the microstructures in Figure 4.23, it was found that the high-temperature treatment conducted on T-400 has increased the proportion of the Laves-free solid solution regions and produced coarsening and sphericalization of the eutectic structure. This phenomenon was also observed by Halstead and Rawlings in the investigation of heat treatment effects on T-400 and T-800 [5]. During the treatment at 1282°C the structure of the Laves phase was homogenized, strains and dislocations at the grain boundaries were removed, which caused softening of the Laves phase. The homogeneous Laves phase had higher ductility and thus provided the alloy with high rupture strength. The strengthening of the eutectic matrix resulted from the dissolution of the Laves phase into the Co solid solution, which contributed

to the increase in the hardness of the eutectic matrix. In the meanwhile, from the X-ray pattern in Figure 4.24, it is seen that the eutectic mixture changed to fcc structure and the hcp form disappeared. The co-contribution of the dissolution of the Laves phase and the hcp $\rightarrow$ fcc transformation led to the slight increase in hardness of the eutectic. However, the ductility of the eutectic was increased by the heat treatment (Table 4.3), which was attributed to the hcp $\rightarrow$ fcc transformation. This result was also obtained by Halstead and Rawlings [10]. The small particles of the dissolved Laves phase dispersed uniformly in the Co solid solution, functioning as precipitates, which strengthened the matrix without detriment to the ductility. As seen in Figure 4.29, the overall hardness was reduced slightly by the solution treatment. As far as the constituents were concerned, the Laves phase was softened significantly and the eutectic mixture was hardened slightly, as seen in Table 4.3, which resulted in the little reduction of the overall hardness and nearly invariable wear resistance of the alloy.

Regarding T-200, as a result of the heat treatment, there was an increase in the volume fraction of the eutectic mixture due to the increased content of the Lave phase. This might be attributed to the aging process, which caused second precipitation of the Laves phase. The increase in the volume fraction of the Laves phase enhanced the hardness and the wear resistance of the alloy, as presented in Figures 4.29 and 4.30. The nano indentation test demonstrated that both the primary Co solid solution and the eutectic mixture were hardened by the heat treatment. The eutectic mixture was hardened due to the precipitation of the additional volume of Laves phase. The hardening of the primary Co solid solution might be caused by dissolution of the Laves phase into the Co solid solution when the alloy was heated to 1100°C. The

X-ray pattern shows that there was no fcc $\rightarrow$ hcp transformation occurring during the air cooling. In addition, the secondary precipitation of the Laves phase during the heat treating greatly contributed to the increase of the hardness, but it severely deteriorated the ductility, as seen in Table 4.3.

CHAPTER 5 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

This study compared the microstructures , mechanical properties, wear and corrosion resistances of five (three hypereutectic and two hypoeutectic) Tribaloy alloys, with the emphasis on the relationships between chemical compositions, microstructures and properties. The conclusions from this research are summarized below:

1. Chemical composition has significant effects on the microstructures and material properties of the alloys. Due to the large reduction of Si content, as compared with T-400 and T-800, T-401 becomes hypoeutectic, that is, the primary phase is Co solid solution, rather than Laves phase. T-400C has similar microstructure to T-400 because their chemical compositions are similar, except that T-400C contains higher Cr for increasing corrosion resistance.
2. The Co solid solutions of both T-401 and T-400C are a mixture of fcc phase and hcp phase, and the Laves phase is $\text{Co}_3\text{Mo}_2\text{Si}$.

3. T-200 differs from conventional Triballoy alloys in chemical composition, so does the microstructure. It is hypoeutectic, with the primary phase being Co solid solution, and the eutectic Laves phase is Co_2Nb . The solid solution is entirely fcc phase.

4. T-401 has lower phase dissolution temperature than T-400, T-800 and T-400C. The dissolution temperature of T-400C is slightly below those of T-400 and T-800. The primary Laves phase and the eutectic phase of the hypereutectic alloy, T-400C, have close melting points, thus resulting in smaller melting range, compared with the hypoeutectic alloys, T-401 and T-200, of which the primary Co solid solution and the eutectic have different dissolution temperatures.

5. Nano indentation technique provides effective approach to evaluate mechanical properties of individual phases in Triballoy alloys. The Co solid solution in Triballoy alloys is not as hard as the Laves phase, and it has a lower Young's modulus but better ductility than the Laves phase.

6. The Laves phase of T-400C has comparable hardness and deformation resistance to that of T-400; and both Laves phase have similar ductility. The eutectic phase of T-400C is not as hard as but more ductile than that of T-400.

7. Since the primary phase of T-401 is Co solid solution, the volume fraction of the Laves phase in this alloy is much less than that in conventional Triballoy alloys. Therefore T-401 has better ductility.

8. T-401 and T-200 are hypoeutectic, but due to the difference in chemical composition, they exhibit different mechanical properties in individual phases. Both the Co solid solution and the eutectic phase of T-401 are harder than those of T-200, respectively, but the deformation resistance and ductility are similar. T-200 possesses better ductility owing to the primary solid solution.

9. Due to the significant reduction in Laves phase, T-401 and T-200 have lower overall (macro) hardness than T-400 and T-800. T-400C is harder than T-401 and T-200 but not as hard as T-400 and T-800.

10. Consistent with the hardness results, T-401 and T-200 have lower wear resistance than T-400 and T-800; and T-400C is more wear-resistant than T-401 and T-200 but less than T-400 and T-800.

11. Between T-401 and T-200, the former is harder and more wear-resistant than the latter. This may be attributed to the relatively large volume fraction of Laves phase in T-401 while smaller volume fraction in T-200.

12. T-401 and T-400C exhibit much higher corrosion resistance in various corrosive media than T-400. There is no significant difference in the corrosion resistance between T-401 and T-400C.

13. With the increase in ductility, T-401 and T-200 have lost wear resistance, but they are still superior to most of wear-resistant materials. For an application condition that requires both wear resistance and ductility, T-401 and T-200 are good candidates for the material selection.

14. Heat treatment has influence on the microstructure and material properties of Tribaloy alloys, for example, T-400 and T-200. For T-400, the solution treatment softened the primary phases, accompanied with an increase in ductility, and hardened the eutectic. The overall hardness of this alloy was reduced slightly by the heat treatment but the wear resistance was not changed, which was not expected, because normally wear resistance increases with the hardness of a material.

16. The solution treatment on T-200 caused dissolution of the Laves phase into the Co solid solution, which hardened the solution matrix. The following aging treatment resulted in second precipitation of the Laves phase in the alloys. All these contributed to the increase of the overall hardness and wear resistance of the alloy.

5.2 Future Work

The advantages of Co-based Tribaloy alloys over common wear-resistant materials are the superior high-temperature properties due to the high melting point of Co. Also the presence of the high content of Cr provides the alloys with high-temperature corrosion/oxidation resistance. Therefore, these alloys are commonly used in high-temperature wear/corrosion environments. However, due to the limitation of available testing facilities, many useful high-temperature experiments could not be realized, for example, high-temperature hardness test, erosion test, sliding wear test, etc. The attempt to achieve these goals has been made. A couple of high-temperature testers will be available shortly in the NRC research labs. Consequently, the planned experiments will be completed in the next step of this project.

References

- [1] M. F. Ashby, and D. R. H. Jones (1980), *Engineering Materials 1*, Butterworth-Heinemann, Oxford.

- [2] F. A. A. Crane, and J. A. Charles (1984), *Selection and Use of Engineering Materials*, Butterworths, London.

- [3] R. Liu, and D. Y. Li (1999), Protective Effect of Yttrium Additive in Lubricants on Corrosive Wear, *Wear*, 225-229 (11), 968-974.

- [4] R. Liu, and D. Y. Li (2000), Effects of Yttrium and Cerium Additives in Lubricants on Corrosive Wear of Stainless Steel 304 and Al Alloy 6061, *Journal of Materials Science*, 35 (3), 633-641.

- [5] A. Halstead, and R. D. Rawlings (1984), Structure and Hardness of Co-Mo-Cr-Si Wear Resistant Alloys (Triballoys), *Metal Science*, 18 (10), 491-500.

- [6] J. R. Davis (2000), *Nickel, Cobalt, and Their Alloys*, ASM International, Materials Park, OH.

- [7] W. Betteridge (1982), *Cobalt and Its Alloys*, Halsted Press, Chichester.

- [8] C. B. Cameron, R. A. Hoffman, and R.W. Poskitt (1975), Tribaloy Intermetallic Alloy Compositions-New Materials or Additives for Wear Resistant Applications, *Progress in Powder Metallurgy*, 31, 41-51.
- [9] A. Halstead and R. D. Rawlings (1985), Effect of Iron Additions on the Microstructure and Properties of the “Tribaloy” Co-Mo-Cr-Si Wear Resistant Alloys, *Journal of Materials Science*, 20 (5), 1693-1704.
- [10] A. Halstead, and R. D. Rawlings (1985), Fracture Behavior of Two Co-Mo-Cr-Si Wear Resistant Alloys (“Tribaloys”), *Journal of Materials Science*, 20 (4), 1248-1256.
- [11] R. D. Schmidt, and D. P. Ferriss (1975), New Materials Resistant to Wear and Corrosion to 1000°C, *Wear*, 32 (3), 279-289.
- [12] A. R. Lansdown, and A. L. Price (1986), *Materials to Resist Wear*, Pergamon Press, Oxford, New York.
- [13] R. G. Bayer (1994), *Mechanical Wear Prediction and Prevention*, M. Dekker, New York.
- [14] M. B. Peterson, and W. O. Winer (1980), *Wear Control Handbook*, American Society of Mechanical Engineers, New York.

- [15] I. M. Hutchings (1992), *Tribology: Friction and Wear of Engineering Materials*, CRC Press, Boca Raton.
- [16] P. Crook, and S. Grainger (1985), *Proceedings of Second Congress: Cobalt Metallurgy and Uses*, Cobalt Development Institute, Barnes, London.
- [17] R. S. Young (1960), *Cobalt: Its Chemistry, Metallurgy, and Uses*, Reinhold Publication Corporation, New York.
- [18] D. Raghu, J. B. C. Wu (1997), Recent developments in wear-and corrosion-resistant alloys for the oil industry, *Materials Performance*, 36 (11), 27-36.
- [19] C. T. Sims, N. S. Stoloff and W. C. Hagel (1987), *Superalloys II*, Wiley, New York.
- [20] R. Tanaka (2000), Research and Development of Ultra-high Temperature Materials in Japan, *Materials at High Temperatures*, 17 (4), 457-464.
- [21] H. So, C. T. Chen, and Y. A. Chen (1996), Wear Behaviours of Laser-Clad Stellite Alloy 6, *Wear*, 192 (1-2), 78-84.
- [22] P. S. Liu, and K. M. Liang (2000), New Way to Evaluate the High-Temperature Oxidation Life of Aluminide Coatings On Co-Base Superalloys in Air, *Surface & Coatings Technology*, 126 (1), 64-68.

- [23] T. Garvare (1988), *Hot Isostatic Pressing-Theories and Application*, Centek Publishers, Sweden.
- [24] Centre D'information du Cobalt (1960), *Cobalt Monograph*, Brussels, Columbus.
- [25] G. H. Gessinger (1984), *Powder Metallurgy of Superalloys*, Butterworth & Co., London.
- [26] M. A. Ashwarth, J. C. Bryar, M. H. Jacobs, and S. Davies (1999), Microstructure and Property Relationships in HIPped Stellite Powders, *Powder Metallurgy*, 42 (3), 243.
- [27] Z. M. Fu, and K. J. Song (1989), Microstructure and Mechanical Properties of P/M Co-Cr-W-C Alloy, *Kexue Tongbao/Science Bulletin*, 34 (9), 784-787.
- [28] V. Kuzucu, M. Ceylan, H. Celik, and I. Aksoy (1997), Microstructure and Phase Analyses of Stellite 6 plus 6 wt.% Mo Alloy, *Journal of Materials Technology*, 69 (1-3), 257- 263.
- [29] W. L. Karlsen (1998), The Influence of Microstructure on the Mechanical Properties of Wrought, Heat-treated, High-Nitrogen Stellite 21, *ASM Proceedings: Heat Treating*, 447-453.

- [30] P. Kumar (1986), Properties of P/M Stellite Alloy No. 6, *Progress in Powder Metallurgy*, 41, 415-437.
- [31] R. I. Blombery and C. M. Perrott (1974), Adhesive Wear Processes Occurring During Abrasion of Stellite Type Alloys, *Journal of the Australian Institute of Metals*, 19 (4), 254-258.
- [32] U. Malayoglu and A. Neville (2003), Comparing the Performance of HIPed and Cast Stellite 6 Alloy in Liquid-solid Slurries. *Wear*, 255 (1-6), 181-194.
- [33] J. Przybylowicz and J. Kusinski (2000), Laser Cladding and Erosive Wear of Co-Mo-Cr-Si Coatings, *Surface and Coatings Technology*, 125 (1), 13-18.
- [34] Anon (1975), Unique Intermetallics Combat Wear and Corrosion, *Metal progress*, 107 (5), 90-92.
- [35] L. B. Vul'f, N. V. Menushenkova, and V. S. Shubakov (1987), Laves Phases in Fe-Cr-Co Alloys Containing Molybdenum and Niobium, *Metal Science and Heat Treatment (English Translation of Metallovedenie i Termicheskaya Obrabotka)*, 29 (1-2), 76-77.

- [36] Y. Ning, P. C. Patnaik, R. Liu, M. X. Yao, and X. J. Wu (2005), Effects of Fabrication Process and Coating of Reinforcements on the Microstructure and Wear Performance of Stellite Alloy Composites, *Materials Science and Engineering A*, 391 (1-2), 313-324.
- [37] M. Riddihough (1970), Stellite as a Wear- Resistant Material, *Tribology (London)*, 3 (4), 211-15.
- [38] J. E. Shigley and C. R. Mischke (1986), *Corrosion and Wear*, McGraw-Hill Inc., New York, NY.
- [39] G. Dowson (1990), *Powder Metallurgy: the Process and its Products*, A. Hilger, Bristol [England], New York.
- [40] T. Sahraoui, H. I. Feraoun, N. Fenineche, G. Montavon, H. Aourag, and C. Coddet (2004), HVOF-Sprayed Tribaloy©-400: Microstructure and First Principle Calculations, *Materials Letters*, 58 (19), 2433-2436.
- [41] W. C. Oliver. and G. M. Pharr (1992), Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments, *Journal of Materials Research*, 7 (6), 1564-1580.

[42] J. Musil, F. Kunc, H. Zeman, and H. Polakova (2002), Relationships between Hardness, Young's Modulus and Elastic Recovery in Hard Nanocomposite Coatings, *Surface and Coatings Technology*, 154 (2-3), 304-313.

[43] N. Kikuchi, M. Kitagawa, A. Sato, E. Kusano, H. Nanto, and A. Kinbara (2000), Elastic and Plastic Energies in Sputtered Multilayered Ti-TiN Films Estimated by Nanoindentation, *Surface and Coatings Technology*, 126 (2-3), 131-135.

[44] E. J. Hearn (1997), *An introduction to the Mechanics of Elastic and Plastic deformation of Solids and Structural Materials*, Third Edition, Butterworth Heinemann, Oxford.

[45] B. W. Mott (1956), *Micro-Indentation Hardness Testing*, Butterworths Publications Ltd., London.

Table 2.1 Chemical compositions (wt.%) of various Co-based alloys

Alloy Tradename	Chemical composition								
	Co	Cr	W	Mo	C	Fe	Ni	Si	Mn
Wear resistant alloys									
Stellite 1	Bal.	30	13	0.5	2.5	3	1.5	1.3	0.5
Stellite 3 (P/M)	Bal.	31	12.5	...	2.4	5(max)	3(max)	2(max)	2(max)
Stellite 6	Bal.	29	4.5	1.5(max)	1.2	3(max)	3(max)	1.5(max)	1(max)
Stellite 12	Bal.	30	8.3	...	1.4	3(min)	1.5	0.7	2.5
Stellite 21	Bal.	27	...	5.5	0.25	3(max)	2.75	1(max)	1(max)
Stellite 706	Bal.	29	...	5	1.2	3(max)	3(max)	1.5(max)	1.5(max)
Stellite 712	Bal.	29	...	8.5	2	3(max)	3(max)	1.5(max)	1.5(max)
Tantung G	Bal.	29.5	16.5	...	3	3.5	7(max)	...	2(max)
Tantung 144	Bal.	27.5	18.5		3	3.5	7(max)	...	2(max)
Stellite 6B	Bal.	30	4	1.5(max)	1	3(max)	2.5	0.7	1.4
Stellite 6K	Bal.	30	4.5	1.5(max)	1.6	3(max)	3(max)	2(max)	2(max)
Corrosion resistant alloys									
Ultimet	Bal.	26	2	5	0.06	3	9	0.3	0.8
MP 159	Bal.	19	...	7	...	9	25.5	...	...
Wrought heat resistant alloys									
Haynes 25	Bal.	20	15	...	0.1	3(max)	10	0.4(max)	1.5
Haynes188	Bal.	22	14	...	0.1	3(max)	22	0.35	1.25

Table 2.2 Chemical compositions (wt.%) of Tribaloy alloys

Alloy Element	Co	Cr	Mo	Si	Ni	Fe	C
T-400	Bal.	8.5	28.5	2.6	1.5(max)	1.5(max)	0.08(max)
T-700	1.5	15.5	32.5	3.4	Bal.	1.5(max)	0.08(max)
T-800	Bal.	17.5	28.5	3.4	1.5(max)	1.5(max)	0.08(max)
T-900	Bal.	18	23	2.7	16	3.0(max)	0.08(max)

Table 2.3 Microstructure of as-cast T-400 and T-800 Tribaloy alloys

Specimen	Proportion, vol. %		
	Primary Laves phase	Eutectic structure	Balance*
T-400			
Components	33 ± 4	47 ± 5	20 ± 5
Tapered (1)**	30 ± 3	...	...
Tapered (2)	32 ± 3	...	...
T-800			
Components	59 ± 8	16 ± 5	25 ± 5
Tapered (1)	50 ± 7	...	...
Tapered (2)	50 ± 6	...	...

* Balance refers to the Laves phase free solid solution plus regions containing secondary Laves phase not in the lamellar, eutectic form;

** The numbers refer to position in the tapered ingot

Table 2.4 Alpha wear test results in naphtha, a poor lubricant*

Test block material	Coefficient of friction	Weight loss, mg		Surface rating**	
		Block	Ring	Block	Ring
T-400	0.13	0.0	0.7	E	E
T-700	0.13	0.7	0.8	E	E
T-800	0.13	0.0	0.4	E	E
Stellite 6B	Shut off-high friction/galling			P	P

* Test conditions: test ring, AISI 4620, Rc 60; velocity, 26 ft/min (7.9 m/min); normal load, 600 lbf (2669 N);

Naphtha, Stoddard Solvent; 1 h test.

** E, excellent, no visible score marks at 10X, no galling, weight loss less than 10 mg;

P, poor, scoring and galling or transverse microcracks visible, or weight loss more than 100 mg.

Table 2.5 Rider/Drum corrosion-wear test results*

Test block material	Drum material	Weight loss, mg		Surface rating**	
		Block	Drum	Block	Drum
Cast T-400	Cast T-400	12.6	28	G	G
Cast T-400	Plasma sprayed and sintered T-400	2.0	92.6	E	G ⁺
Cast T-800	Cast T-800	86.5	7.3	G	G
Cast T-700	Cast T-700	77.8	23	F	F
Cast Stellite 6B	Cast Stellite 6B	81.5	93.5	P	P

* Test conditions-velocity, 400 ft/min (120 m/min); normal load, 15 lbf (67 N);
5% (absolute) HCl; 1h test.

** Ratings similar to those for Alpha Wear test (Table 2.3).

E and G, no corrosion visible;

F, evidence of incipient corrosion;

P, severe corrosion.

+ Surface quality was good. High weight loss attributed to corrosion of uncoated portions of the mild steel drum.

Table 2.6 Corrosion rates* for T-400, T-800 and selected commercial compositions
in several environments
Mil/year (1 mil = 0,001 in. =0.0254 mm)

	Oxidizing		Reducing		Oxidizing	
	Chloride 10% Ferric** chloride (Rm. Temp.)	No Chloride 65% Nitric acid (150°F (66°C))	3.5% Sodium chloride (250°F (121°C))	50% Acetic acid (212°F (100°C) ***)	Chlorides 5% Hydro- chloric acid (150°F (66°C) ***)	10% Sulfuric acid (215°F (102°C) ***)
T-400	101	1365	0.2	N	194	218
T-800	9.0	39	N	N	1.5	34
SS 316	>1000	11	-	2.0	>500	900
Stellite 6B	80	8.0	0.3	N	4100	240
WC/ 6% Co	-		-	-	82	160

N: Nil corrosion < 0.1 mil/year

* Average of 3 to 5 24-hour periods

** 5 to 7 days exposure

*** Boiling

Table 3.1 Chemical compositions (wt.%) of tested Tribaloy alloys

Element Alloy	Co	Cr	Mo	Si	Ni	Nb
T-400	Bal.	8.5	28.5	2.6		
T-401	Bal.	17	22	1.2		
T-400C	Bal.	14	26	2.6		
T-800	Bal.	17.5	28.5	3.4		
T-200	Bal.	11		0.75	20	6.5

Table 4.1 DSC results (Temperature in °C) of tested Tribaloy alloys

	Melting (endothermic) process			Solidifying (exothermic) process		
	Solidus	Liquidus	Melting range	Liquidus	Solidus	Solidifying range
T-400	1302	1367	65	1384	1198	186
T-401	1215	1330	115	1286	1212	74
T-400C	1296	1367	71	1355	1175	180
T-800	1300	1380	80	1406	1239	167
T-200	1212	1441	229	1386	1188	198

Table 4.2 Nano mechanical properties of individual phases in the tested alloys

Property Phase	Young's modulus (GPa)	Hardness (GPa)	Maximum deformation (nm)	Residual deformation (nm)	η_e (%)	η_p (%)
T-400 Primary Laves phase	397.51	21.21	376.45	243.46	35.3	64.7
T-400 Eutectic (Laves phase + Co solid solution)	310.52	13.78	460.48	316.64	31.2	68.8
T-401 Primary Co solid solution	274.03	7.48	605.38	500.91	17.3	82.7
T-401 Eutectic (Co solid solution + Laves phase)	270.98	11.38	505.94	373.15	26.2	73.8
T-400C Primary Laves phase	390.07	20.78	386.42	251.86	34.8	65.2
T-400C Eutectic (Laves phase + Co solid solution)	306.04	10.62	511.05	366.83	28.2	71.8
T-800 Primary Laves phase	310.88	18.33	414.62	266.59	35.7	64.3
T-800 Eutectic (Laves phase + Co solid solution)	292.73	11.52	521.30	365.76	29.8	70.2
T-200 Primary Co solid solution	273.70	6.63	640.80	537.76	16.1	83.9
T-200 Eutectic (Co solid solution + Laves phase)	279.03	10.25	529.94	381.35	28.0	72.0

Table 4.3 Nano mechanical properties of individual phases in the as-cast and heat-treated alloys

Property Phase	Young's modulus (GPa)	Hardness (GPa)	Maximum deformation (nm)	Residual deformation (nm)	η_e (%)	η_p (%)
T-400 Primary Laves phase	397.52	21.21	376.45	243.46	35.3	64.7
T-400 Eutectic (Laves phase + Co solid solution)	310.52	13.78	460.48	316.64	31.2	68.8
Heat treated T-400 at 1282°C Primary Laves phase	342.03	16.79	424.98	294.87	30.6	69.4
Heat treated T-400 at 1282°C Eutectic mixture	330.44	14.26	454.36	321.42	29.3	70.7
T-200 Primary Co solid solution	273.70	6.63	640.80	537.76	16.1	83.9
T-200 Eutectic (Co solid solution+ Laves phase)	279.03	10.25	529.94	381.35	28.0	72.0
Heat treated T-200 for 48 hrs Primary Co solid solution	224.37	8.76	578.50	433.20	25.1	74.9
Heat treated T-200 for 48 hrs Eutectic mixture	288.47	16.56	430.12	260.33	39.5	60.5

(a)

(b)

(c)

Figure 2.1 SEM backscatter images of microstructures:
 (a) Stellite HS4 HIP'ed at $1200^{\circ}C$, (b) Stellite HS6 HIP'ed at $1200^{\circ}C$
 and (c) Stellite HS7 HIP'ed at $1200^{\circ}C$
 (HIP- hot isostatic pressing)

Figure 2.2 Macro hardness of various Stellite alloys

(a)

(b)

Figure 2.3 SEM microstructure of PTA T-400:
(a) 500X and (b) 1500X
(PTA- plasma transferred arc)

Figure 2.4 Macro hardness of various Triballoy alloys

(c)

Figure 3.1 Centrifugal casting technique:

(a) operating model, (b) front side view and (c) back side view

Figure 3.2 Differential scanning calorimetry (DSC) device

Figure 3.3 DSC heating/cooling cycle

Figure 3.4 Nano mechanical testing machine

Figure 3.5 Typical loading/unloading curve under indentation

Figure 3.6 Tensile testing machine

Figure 3.7 Rotating-bending fatigue machine

Figure 3.8 Wilson Rockwell hardness tester

Figure 3.9 Pin-on-disc tribometer

Figure 3.10 Schematic drawing of the wear track and the pin

Figure 3.11 Profiler used to simulate the wear tracks

Eutectic (Laves phase
+ Co solid solution)
Figure 4.1 (d)

Primary Laves phase
Figure 4.1 (c)

(a)

(b)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	7.53	16.99	0.242	0.7227
Cr	9.81	11.96	0.713	0.4848
Fe	0.07	0.07	0.681	0.0352
Co	39.62	42.60	0.683	0.9523
Mo	42.96	28.37	0.390	1.7296
Total	100.00			

(c)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	1.37	2.88	0.178	0.1962
Cr	17.34	19.71	0.849	0.3219
Fe	0.38	0.40	0.706	0.0455
Co	70.26	70.46	0.700	0.6831
Mo	10.64	6.55	0.341	0.5024
Total	99.99			

(d)

Figure 4.1 SEM microstructure of T-400:

(a) 500X, (b) 1500X, (c) EDX spectrum of primary Laves phase,
and (d) EDX spectrum of eutectic mixture

Eutectic
Co solid solution +
Laves phase)
Figure 4.2 (d)

Primary
Co solid solution
Figure 4.2 (c)

(a)

(b)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	1.83	3.87	0.190	0.2151
Cr	24.24	27.68	0.819	0.3799
Fe	0.41	0.44	0.673	0.0477
Co	57.93	58.36	0.673	0.6199
Mo	15.59	9.65	0.357	0.5824
Total	100.00			

(c)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	3.55	8.09	0.231	0.2590
Cr	20.35	25.06	0.734	0.3505
Fe	0.33	0.38	0.657	0.0412
Co	37.94	41.22	0.663	0.4821
Mo	37.83	25.25	0.402	0.8153
Total	99.99			

(d)

Figure 4.2 SEM microstructure of T-401:
 (a) 500X, (b) 1500X, (c) EDX spectrum of primary Co solid solution,
 and (d) EDX spectrum of eutectic mixture

Eutectic (Laves phase
+ Co solid solution)
Figure 4.3 (d)

Primary
Laves phase
Figure 4.3 (c)

(a)

(b)

Element	wt. %	atom %	ZAF factor	3 sigma
Si	7.90	17.73	0.249	0.7420
Cr	13.10	15.89	0.707	0.5719
Fe	0.62	0.70	0.668	0.1118
Co	34.34	36.74	0.672	0.9091
Mo	44.03	28.94	0.396	1.7682
Total	100.00			

(c)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	3.65	7.66	0.198	0.5831
Cr	22.75	25.80	0.802	0.7284
Fe	1.28	1.35	0.672	0.1644
Co	53.70	53.74	0.672	1.1701
Mo	18.62	11.44	0.358	1.2449
Total	99.99			

(d)

Figure 4.3 SEM microstructure of T-400C:

(a) 500X, (b) 1500X, (c) EDX spectrum of primary Laves phase,
and (d) EDX spectrum of eutectic mixture

Eutectic (Laves phase
+ Co solid solution)
Figure 4.4 (d)

Primary
Laves phase
Figure 4.4 (c)

(a)

(b)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	7.33	16.45	0.248	0.7011
Cr	15.68	19.01	0.710	0.6112
Fe	0.23	0.26	0.661	0.0672
Co	33.54	35.88	0.666	0.8832
Mo	43.22	28.40	0.399	1.7091
Total	100.00			

(c)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	4.13	8.62	0.204	0.5958
Cr	26.81	30.27	0.792	0.7759
Fe	0.14	0.14	0.655	0.0533
Co	48.87	48.69	0.658	1.0997
Mo	20.05	12.27	0.364	1.2497
Total	99.99			

(d)

Figure 4.4 SEM microstructure of T-800:
 (a) 500X, (b) 1500X, (c) EDX spectrum of primary Laves phase,
 and (d) EDX spectrum of eutectic mixture

Primary
Co solid solution
Figure 4.5 (c)

Eutectic
(Co solid solution +
Laves phase)
Figure 4.5 (d)

(a)

(b)

Element	wt. %	atom %	ZAF factor	3 sigma
Si	1.56	3.23	0.168	0.4091
Cr	18.35	20.43	0.854	0.6263
Fe	0.85	0.88	0.722	0.1277
Co	52.01	51.10	0.695	1.1186
Ni	20.40	20.11	0.676	0.7315
Nb	6.82	4.25	0.282	0.8543
Total	99.99			

(c)

Element	wt.%	atom%	ZAF factor	3 sigma
Si	4.07	9.36	0.217	0.5696
Cr	4.96	6.15	0.741	0.3425
Fe	0.31	0.36	0.726	0.0755
Co	37.53	41.10	0.706	0.9235
Ni	15.09	16.59	0.691	0.6099
Nb	38.04	26.43	0.329	1.8338
Total	99.99			

(d)

Figure 4.5 SEM microstructure of T-200:
 (a) 500X, (b) 1500X, (c) EDX spectrum of primary Co solid solution,
 and (d) EDX spectrum of eutectic mixture

Figure 4.6 X-ray diffraction pattern of T-400

Figure 4.7 X-ray diffraction pattern of T-401

Figure 4.8 X-ray diffraction pattern of T-400C

Figure 4.9 X-ray diffraction pattern of T-800

Figure 4.10 X-ray diffraction pattern of T-200

(a)

(b)

(c)

(d)

Figure 4.11 DSC heating and cooling curves:
 (a) T-400, (b) T-401, (c) T-400C, (d) T-800, and (e) T-200

(a)

(b)

Figure 4.12 Loading/unloading curves of T-400 under indentation:
(a) primary Laves phase and (b) eutectic mixture

(a)

(b)

Figure 4.13 Loading/unloading curves of T-401 under indentation:
(a) primary Co solid solution and (b) eutectic mixture

(a)

(b)

Figure 4.14 Loading/unloading curves of T-400C under indentation:
(a) primary Laves phase and (b) eutectic mixture

(a)

(b)

Figure 4.15 Loading/unloading curves of T-800 under indentation:
(a) primary Laves phase and (b) eutectic mixture

(a)

(b)

Figure 4.16 Loading/unloading curves of T-200 under indentation:
(a) primary Co solid solution and (b) eutectic mixture

Figure 4.17 Macro hardness of the tested alloys

Figure 4.18 Wear loss of the tested alloys

Figure 4.19 Stress - Strain curve of T-401 under tension

Figure 4.20 Stress ~ life (S ~ N) curve of T-401 under rotating-bending

(a)

(b)

(c)

Figure 4.21 Fractured surfaces of T-401 under rotating-bending:

- (a) an enlarged view of the fracture surface,
letter A indicates the fatigue region; B indicates the overload (tensile mode) region,
- (b) the detailed feature of fatigue fracture,
- and (c) the alveolate structure of the tensile fracture mode

10% H₂SO₄ 102°C

(a)

65% HNO₃ 66°C

(b)

Figure 4.22 Corrosion resistances of T-400, T-401 and T-400C:
(a) in H_2SO_4 , (b) in HNO_3 and (c) in HCl

(a)

(b)

(c)

(d)

Figure 4.23 SEM microstructures of the as-cast and the heat-treated T-400 specimens:
(a) as-cast, (b) heat-treated at 1232°C,
(c) heat-treated at 1257°C, and (d) heat-treated at 1282°C

Figure 4.24 X-ray patterns of the as-cast and the heat-treated T-400 specimens

(a)

(b)

(c)

Figure 4.25 SEM microstructures of the as-cast and the heat-treated T-200 specimens:

(a) as-cast, (b) heat-treated for 16 h, and (c) heat-treated for 48 h

Figure 4.26 X-ray patterns of the as-cast and the heat-treated T-200 specimens

(a)

(b)

Figure 4.27 Loading/unloading curves of the heat-treated T-400 at 1282°C under indentation:

(a) primary Laves phase and (b) eutectic mixture

(a)

(b)

Figure 4.28 Loading/unloading curves of the heat-treated T-200 for 48 h under indentation:

(a) Co solid solution and (b) eutectic matrix

(a)

(b)

Figure 4.29 Macro hardness of the as-cast and heat-treated alloys:

(a) T-400 and (b) T-200

(a)

(b)

Figure 4.30 Wear loss of the as-cast and heat-treated alloys:
(a) T-400 and (b) T-200

Figure 4.31 Relationships between Laves phase volume fraction, hardness and wear loss

Figure 4.32 Relationships between Cr content and corrosion resistance

* Corrosion rate of T-800 was obtained by R. D. Schmidt, and D. P. Ferriss [10].

(a)

(b)

Figure 4.33 SEM images of indentation surface of T-400:
(a) 100X and (b) 500X

(a)

(b)

Figure 4.34 SEM images of indentation surface of T-401:
(a) 100X and (b) 500X

(a)

(b)

Figure 4.35 SEM images of indentation surface of T-400C:
(a) 100X and (b) 500X