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Effects of Heat Treatment on Mechanical and Tribological Properties of Cobalt-Base Tribaloy Alloys

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Cobalt-base Tribaloy alloys are important wear-resistant materials, especially for high-temperature applications, because of the outstanding properties of the strengthened cobalt solid solution and the hard Laves intermetallic phase that make up the alloys. The Laves intermetallic phase is so abundant (35-70 vol.%) in these alloys that its presence governs all of the material properties. Heat treatment may alter the volume fraction, the size/shape, and the distribution of the Laves phase in the microstructures as well as the phase and structure of the cobalt solid solution, thus influencing the mechanical and tribological properties of the alloys. In this work, the effects of heat treatment on two cobalt-based Tribaloy alloys, T-400 and T-200, were studied. The former is a well-known Tribaloy alloy, and the latter is a newly developed one. These two alloys were heat treated in different conditions. The phases and microstructures of the alloys before and after the heat treatments were analyzed using x-ray and scanning electron microscopy. The mechanical and tribological properties of the alloys were investigated using a nano-indentation technique and a pin-on-disc tribometer, respectively.

Keywords cobalt solid solution, elasticity, hardness, heat treatment, Laves phase, plasticity, Tribaloy alloy, wear

1. Introduction

Cobalt-base Tribaloy alloys are used as wear-resistant materials for industrial applications involving unlubricated systems or elevated temperatures. A substantial enhancement in mechanical properties of these alloys is attributed to the crystallographic nature of cobalt. Pure cobalt has a hexagonal-close-packed (hcp) structure at room temperature. At 417 °C, the hcp structure transfers to the higher temperature face-centered-cubic (fcc) form. The nature of the transformation has been classified as martensitic (Ref 1, 2). Additions of alloying elements change the temperature at which the martensitic transformation occurs and alter the range of thermodynamic stability of the fcc and hcp phases.

Cobalt-base Tribaloy alloys contain a large-volume fraction of a hard, intermetallic Laves phase in a much softer matrix. It is the presence of this large-volume fraction of Laves phase that enables the alloys to achieve their good wear resistance. The carbon content in Tribaloy alloys is kept low to prevent carbides forming in preference to the Laves phase (Ref 3-5). Tribaloy alloys are usually hypereutectic with 30~70 vol.% primary dendrites of the hard intermetallic phase in a eutectic matrix of smaller intermetallic particles embedded in a cobalt solid solution; there are also regions of cobalt solid solution that are free from the secondary Laves phase (Ref 6-12). The hard primary phase is a ternary Laves phase of the C-14 ($MgZn_2$) type having a melting point of about 1560 °C, and its compositions are approximately Co_3Mo_2Si or Co-Mo-Si. In addition to the crystallographic nature of cobalt, the outstanding mechanical and tribological properties of cobalt-based Tribaloy alloys also arise from the solid-solution-strengthening effects of alloying elements such as chromium, tungsten, and molybdenum, formation of the intermetallic Laves phase by silicon and molybdenum, and the corrosion resistance imparted by chromium (Ref 1, 2).

The effect of heat treatment on Tribaloy alloys is arguable. Previous research reported that the microstructures of Tribaloy 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 (Ref 8). The research by Schmidt and Ferriss (Ref 9) also reported that the structure of Tribaloy was stable from cryogenic temperatures to just below the eutectic temperature, where some grain and phase growth did occur; consequently, the alloys were essentially not heat treatable. However, Halstead and Rawlings (Ref 10) demonstrated that the cast alloys could be softened or hardened by heat treatment, which was mainly a result of precipitation within the cobalt solid solution but with some contribution from the fcc → hcp allotropic transformation. It was also found that by heat treatment in the range 600-1100 °C it was possible to obtain precipitation within the cobalt solid solution in either a spheroidal or a Widmanstätten form (Ref 11), and when T-400 and T-800 were heat treated in the range 600-900 °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 (Ref 12).

The present research aimed to investigate the effects of heat treatment on mechanical and tribological properties of two cobalt-based Tribaloy alloys, T-400 and T-200. The former is

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a well-known Tribaloy alloy, and the latter is a newly developed one. These alloys were heat treated in different conditions. The microstructures, mechanical properties of individual phases, and wear resistance of the alloys before and after the heat treatments were studied, and the experimental results were compared and discussed.

2. Experimental Details

2.1 Specimens and Heat Treatments

The tested T-400 and T-200 were cast alloys. Their chemical compositions are listed in Table 1. It can be seen that T-200 differs from conventional Tribaloy alloys in that it contains high contents of nickel and niobium, low content of silicon, and it does not contain molybdenum.

The heat treatments conducted on the two alloys were different, and they are described below, respectively:

- For T-400, the specimenas experienced a solution treatment, which meant heating the specimens to 1232, 1257, and 1280 °C, respectively, holding for 2 h, and then water quenching.
- For T-200, the heat treatment was conducted in two steps. The specimens were first homogenized at 1100 °C for 8 h followed by air cooling and then aged at 800 °C for 16 and 48 h, respectively, followed by air cooling.

2.2 Macrohardness and Wear Tests

The macrohardness of the specimens was tested through indentation on a Wilson Rockwell machine. The wear test was conducted on a pin-on-disc tribometer. A ball made of 94% tungsten carbide and 6% cobalt, with the hardness of HV 1534, was the counterface to the specimen surface, which was spinning with the rotational speed of 319 rpm under a compressive force of 10 N. As a result, there would be a wear track formed in the surface. The wear loss of T-400 was evaluated by calculating the volume of the wear track after the specimen surface was worn for 10^4 s and that of T-200 was worn for 2×10^3 s because this alloy is softer than T-400. The diameters of the ball and the wear track were 5 and 6 mm, respectively.

2.3 Microstructural Analyses

The microstructures of the specimens were analyzed on a Hitachi model S-570 (Hitachi, CA) scanning electron microscope (SEM) using backscatter electron imaging. The phases present in the alloys were examined with the x-ray technique, using Cu K_α radiation. The specimens were prepared by grinding with grit papers from No. 180 to 600 and then polishing with abrasive cloth plus 1 μm alumina powders. The etch solution was the mixture of 15 ml of HNO_3, 15 ml of acetic acid, 60 ml of HCl, and 15 ml of H_2O.

2.4 Nanoindentation Tests

The nanohardness and mechanical behavior of individual phases in the alloys were investigated using a load and displacement sensing indentation technique on a CSM nanohardness machine (CSM Instruments, Switzerland). The nanoindentation effective Young's modulus $E^* = E/(1 - \nu^2)$ and hardness H are calculated based on the loading/unloading curves, which are measured with a Berkovich indenter (CSM Instruments, Switzerland) using the Oliver-Pharr method (Ref 13), where E and ν are the Young's modulus and Poisson ratio of the tested material, respectively. The load ~ depth curves of loading and unloading are recorded automatically during the indentation. The area enclosed by the loading and unloading curves represents the dissipated energy caused by plastic deformation (Ref 14). The maximum load applied in each indentation for the present test was 50 mN.

Table 1 Chemical compositions of tested alloys

Alloy	Co	Cr	Mo	Si	Ni	Nb
T-400	Bal.	8.5	28.5	2.6		
T-200	Bal.	11		0.75	20	6.5

3. Results

3.1 Macrohardness and Wear Loss

Five tests of macrohardness 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 because of the wear. To calculate the volume, the cross-sectional area of each wear track must be evaluated first. In this study, the cross section of each wear track at three positions along the wear track was simulated using a surface profiler, and the average of the three cross-sectional areas was used to calculate the volume. The average hardness and wear loss of the tested specimens are presented in Table 2.

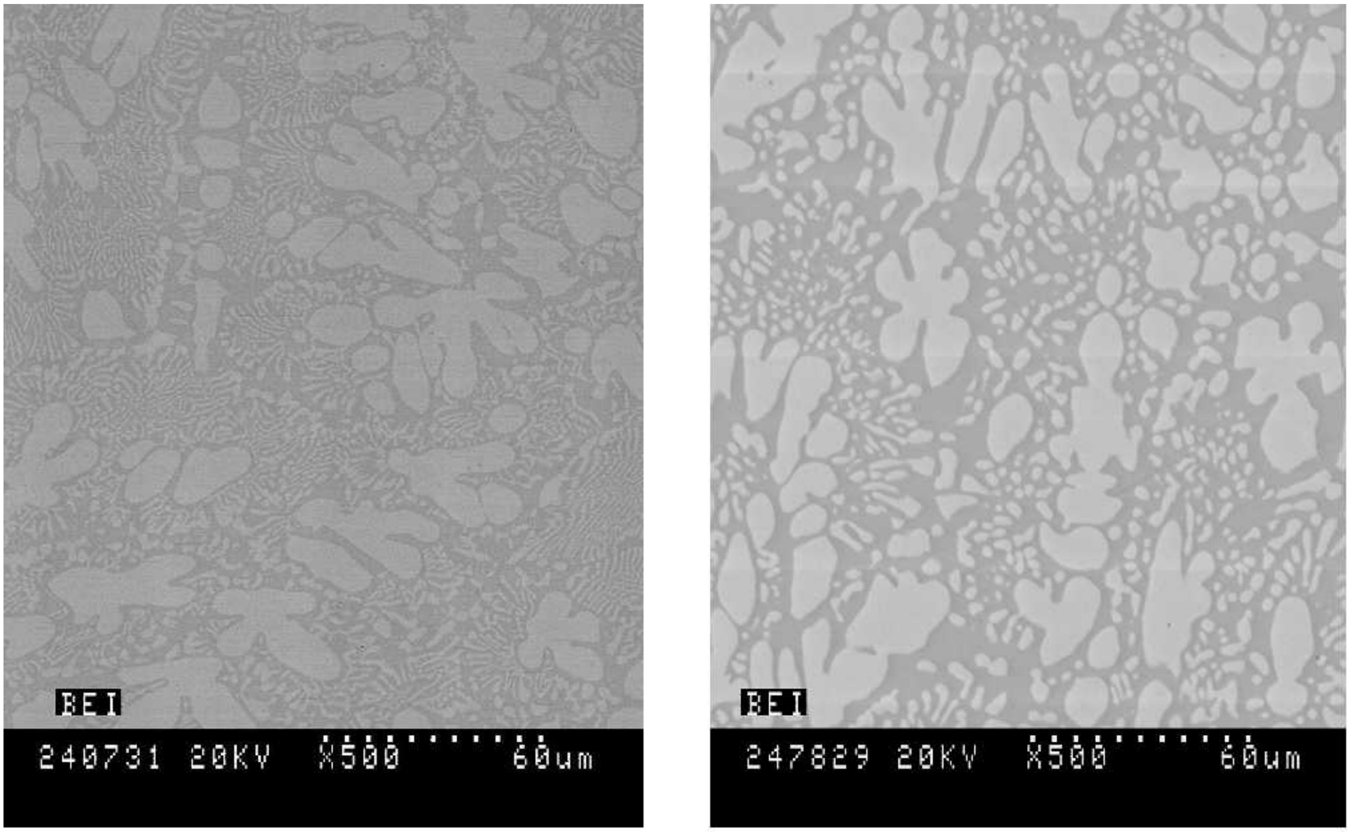
It is shown that the heat treatment had little effect on the hardness and wear resistance of T-400. As seen in Table 2, the hardness of T-400 decreased slightly with the heat treatment, and the alloy became softer with the increase in the heat treatment temperature up to 1282 °C, but the wear resistance of T-400 was unchanged by the heat treatment. Regarding T-200, it is evident from Table 2 that both the hardness and the wear resistance of the alloy were enhanced significantly by the heat treatment, and the aging time affected the hardness but not the wear resistance.

3.2 Microstructures and X-Ray Patterns

It was demonstrated from the macrohardness test that T-400 was softened slightly and T-200 hardened greatly by the heat treatments. These changes can be related to the microstructures

Table 2 Macrohardness and wear loss

	T-400 as-cast	T-400 1232, °C	T-400 1257, °C	T-400 1282, °C	T-200 as-cast	T-200 16, h	T-200 48, h
Hardness, HRC	55	53	50	50	17	30	37
Wear loss, mm^3	0.025	0.027	0.023	0.028	0.187	0.132	0.141



(a) (b)

Fig. 1 SEM microstructures of T-400: (a) as-cast and (b) heat-treated at 1282 °C

and the mechanical properties of individual phases in the alloys. It is found from the SEM microstructural analyses that the primary phase in the T-400 specimens is the dendritic Laves phase, which is distributed in the eutectic matrix consisting of the Laves phase and cobalt solid solution, as seen in Fig. 1. However, the difference in the eutectic structure between the as-cast and the heat-treated T-400 specimens can be observed: the eutectic matrix of the as-cast T-400 exhibits a laminar structure, and the fine/sharp Laves phase is layered with the cobalt solid solution, whereas in the heat-treated T-400, the shape of the Laves phase in the eutectic matrix is coarse and blunt. No significant difference in microstructure is observed between the specimens treated at different temperatures. The x-ray patterns of the as-cast and the heat-treated T-400 specimens are presented in Fig. 2. It is shown that the Laves phase in the alloys is the intermetallic compound of Co_3Mo_2Si with a C-14 hexagonal structure. In addition, the cobalt solid solution in the as-cast T-400 is a mixture of the fcc and hcp phases, whereas that in the heat-treated T-400 is mainly the fcc phase.

Unlike conventional Tribaloy alloys, which have a primary Laves phase, T-200 is a hypoeutectic alloy with the primary phase being the cobalt solid solution. This alloy is designed for good tensile strength and moderate ductility and good creep rupture resistance at high temperature. It is observed that the heat treatment increased the volume fraction of the eutectic phase, that is, the Laves phase, and also the higher the temperature of the heat treatment, the larger the volume fraction of the Laves phase. As seen in Fig. 3, the eutectic mixture of the Laves phase and cobalt solid solution is distributed uniformly in the cobalt solid solution matrix. It is apparent that the volume fraction of the Laves phase in the heat-treated specimen is larger than that in the as-cast one. It was been calculated using the SEM technique that the volume fractions of the Laves phase in the as-cast specimen and heat-treated specimens for 16 and 48 h are approximately 14, 21, and 26%, respectively. The x-ray patterns of the as-cast and the heat-treated T-200 specimens are presented in Fig. 4. It is shown that there is no difference in phase between the as-cast specimen and heat-treated specimens. The Laves phase in the alloys is the intermetallic compound Co_2Nb with a C-15 structure, and the cobalt solid solution is mainly the fcc phase.

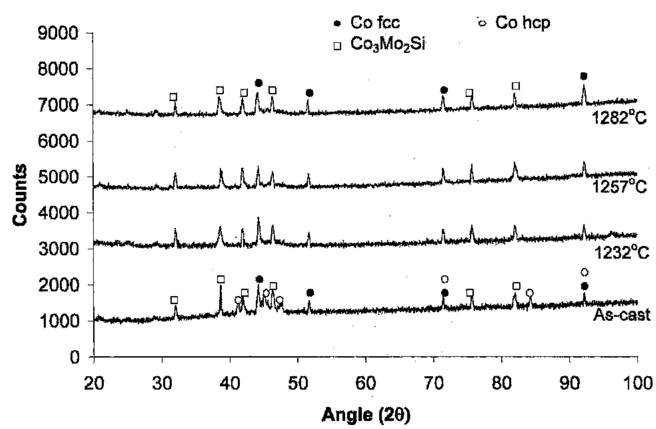


Fig. 2 X-ray patterns of the as-cast and the heat-treated T-400 specimens

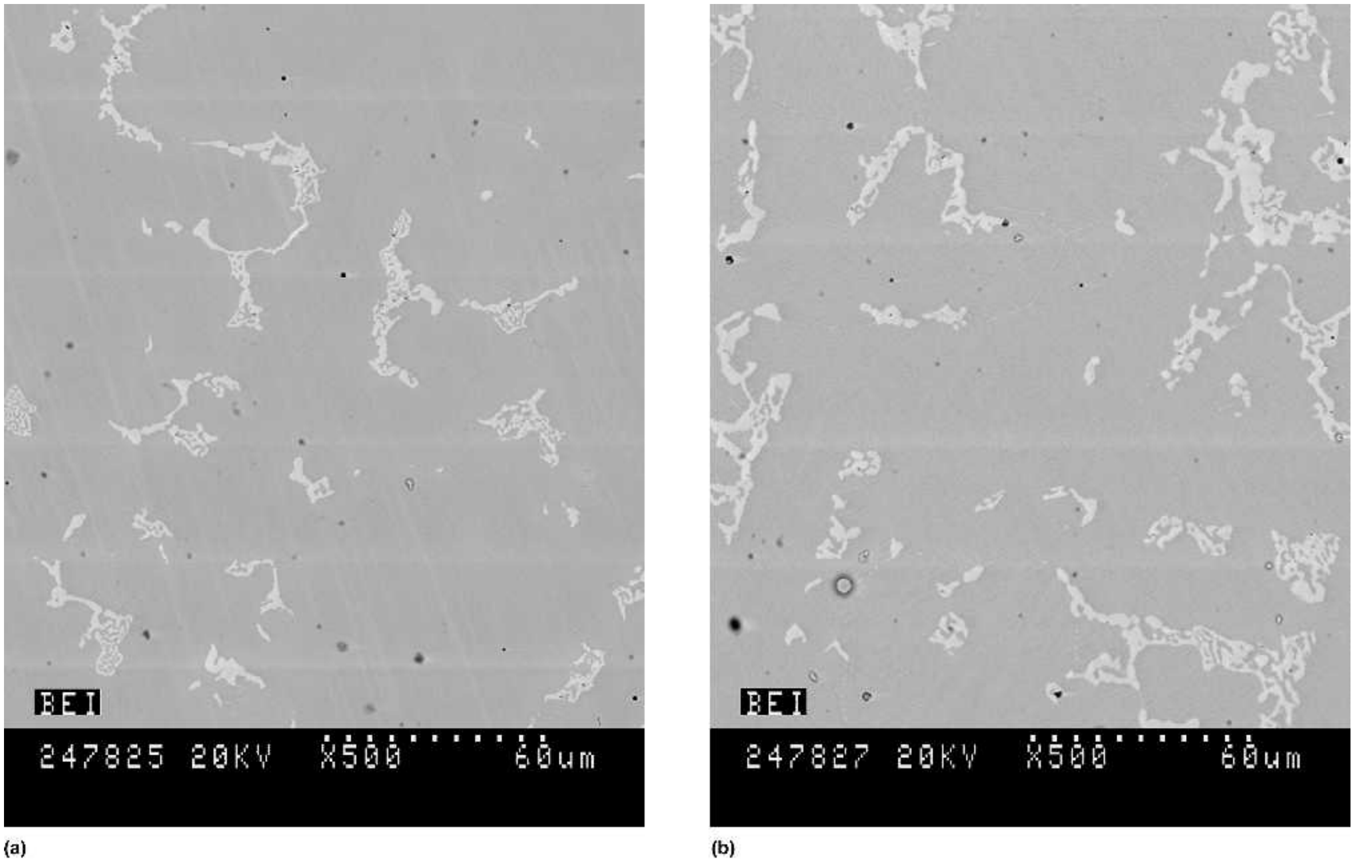


Fig. 3 SEM microstructures of T-200: (a) as-cast and (b) heat-treated for 48 h

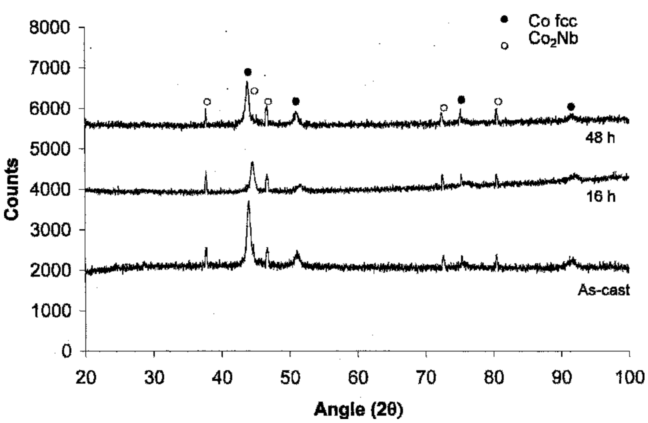


Fig. 4 X-ray patterns of the as-cast and the heat-treated T-200 specimens

3.3 Nanohardness and Mechanical Properties

The nanoindentation test was performed on the primary Laves phase and the eutectic mixture of the T-400 specimens, respectively, and the loading and unloading curves of the indentation are presented in Fig. 5 and 6. For T-200, the test was conducted on the primary cobalt solid solution and the eutectic mixture, respectively, and the loading and unloading curves of the indentation are presented in Fig. 7 and 8. In Fig. 5 to 8, the area enclosed by the loading curve represents the total deformation energy, and that enclosed by the unloading curve is the elastic deformation energy. Defining η_e as the ratio of the elastic deformation energy to the total deformation energy and η_p as the ratio of the plastic deformation energy to the total deformation energy, then $\eta_e + \eta_p = 1$. The nanohardness and mechanical properties such as Young's modulus, η_e and η_p values, which are calculated from the loading and unloading curves, are presented in Table 3.

First, 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 much. The hardness was increased only slightly. There was no obvious difference in the Young's modulus and the η_p value of both the Laves phase and the eutectic, but a slight decrease in the Young's modulus and a slight increase in the η_p value of the primary Laves phase were observed (Table 3). Second, 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 (Table 3).

4. Discussion

4.1 T-400

For T-400, the overall hardness was reduced slightly by the solution treatment, as seen in Table 2, the Laves phase was softened significantly and the eutectic mixture was hardened slightly, as seen in Table 3. Comparing the microstructures in Fig. 1, it is found that the high-temperature treatment increased

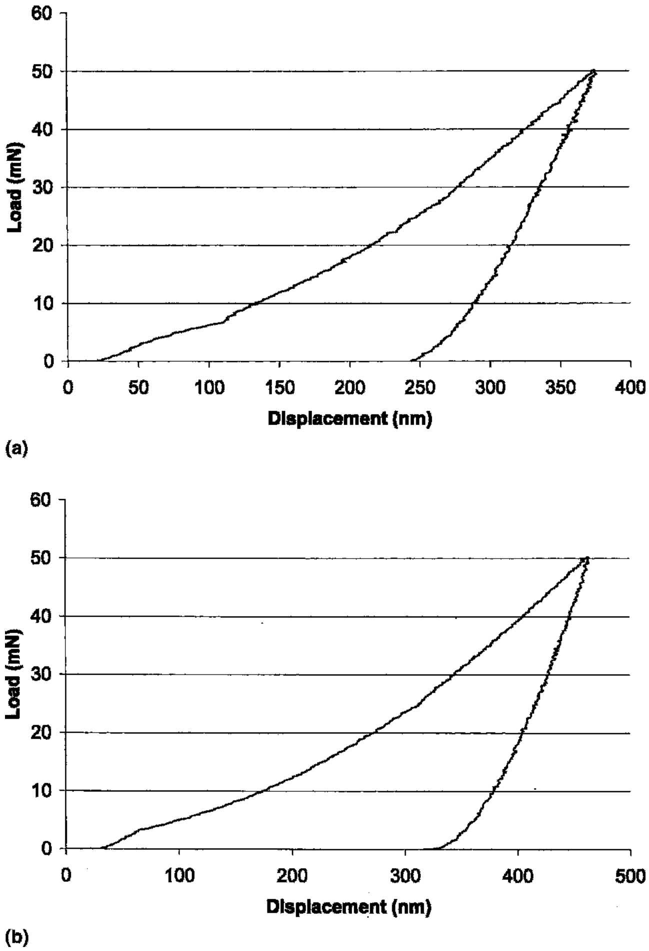


Fig. 5 Nanoindentation loading/unloading curves of as-cast T-400: (a) primary Laves phase and (b) eutectic mixture

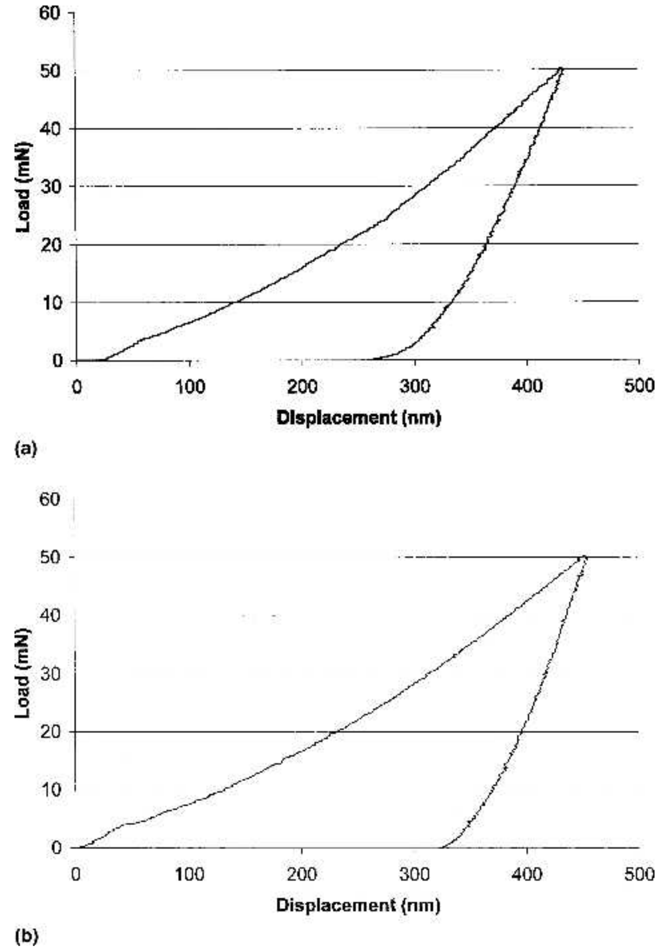


Fig. 6 Nanoindentation loading/unloading curves of heat-treated T-400 at 1280 °C: (a) primary Laves phase and (b) eutectic mixture

the proportion of the Laves-free solid solution regions and produced coarsening and spheroidization of the eutectic structure. This phenomenon was also observed by Halstead and Rawlings in an investigation of heat treatment effects on T-400 and T-800 (Ref 11). During the treatment at 1282 °C the structure of the Laves phase was homogenized, and strains and dislocations at the grain boundaries were removed, which caused softening of the Laves phase. The homogeneous Laves phase has higher ductility and thus provides the alloy with high rupture strength. The strengthening of the eutectic matrix resulted from the dissolution of the Laves phase into the cobalt solid solution, which contributed to the increase in the hardness of the eutectic matrix. Meanwhile, from the x-ray pattern in Fig. 2, the hcp cobalt solid solution in the eutectic disappeared after the heat treatment, which reduced the hardness. The co-contribution of the dissolution of the Laves phase and the hcp → 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 3), which was attributed to the hcp → fcc transformation. This result was also obtained by Halstead and Rawlings (Ref 11). The small particles of the dissolved Laves phase were dispersed uniformly in the cobalt solid solution, functioning as precipitates and strengthening the matrix without detriment to the ductility. The hardness decrease of the Laves phase and the increase of the eutectic matrix resulted in little reduction of the overall hardness and nearly unchanged wear resistance of the alloy.

4.2 T-200

Regarding T-200, there was an increase in the volume fraction of the Laves phase after the heat treatment. This might be attributed to the aging process, which caused secondary 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 (Table 2). The nanoindentation test demonstrated that both the primary cobalt solid solution and the eutectic mixture were hardened by the heat treatment. The hardening of the primary cobalt solid solution might result from dissolution of the Laves phase into the cobalt solid solution when the alloy was heated to 1100 °C. The x-ray pattern shows that there was no fcc → hcp transformation occurring during the air cooling. As concerns the eutectic mixture, the additional volume fraction of the Laves phase precipitated during the heat treating contributed greatly to the increase of the hardness, but severely deteriorated the ductility, as seen in Table 3.

5. Conclusions

T-400 alloy was subjected to a solution treatment, and T-200 was under a solution treatment first and then followed by an aging treatment. It was found that the heat treatments affected the mechanical and tribological properties of the alloys. For T-400, the solution treatment softened the primary phases,

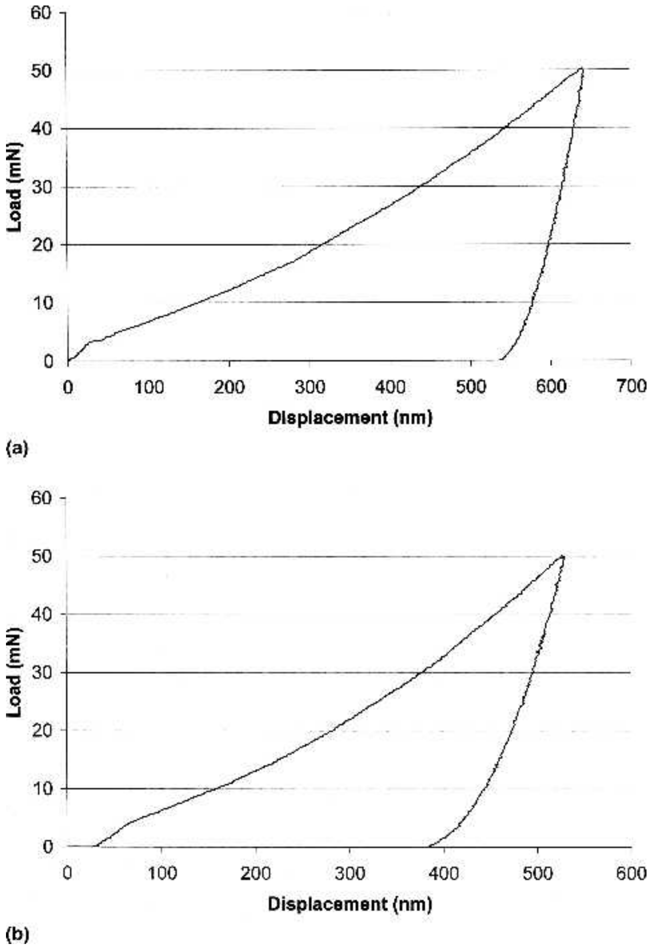


Fig. 7 Nanoindentation loading/unloading curves of as-cast T-200: (a) cobalt solid solution and (b) eutectic mixture

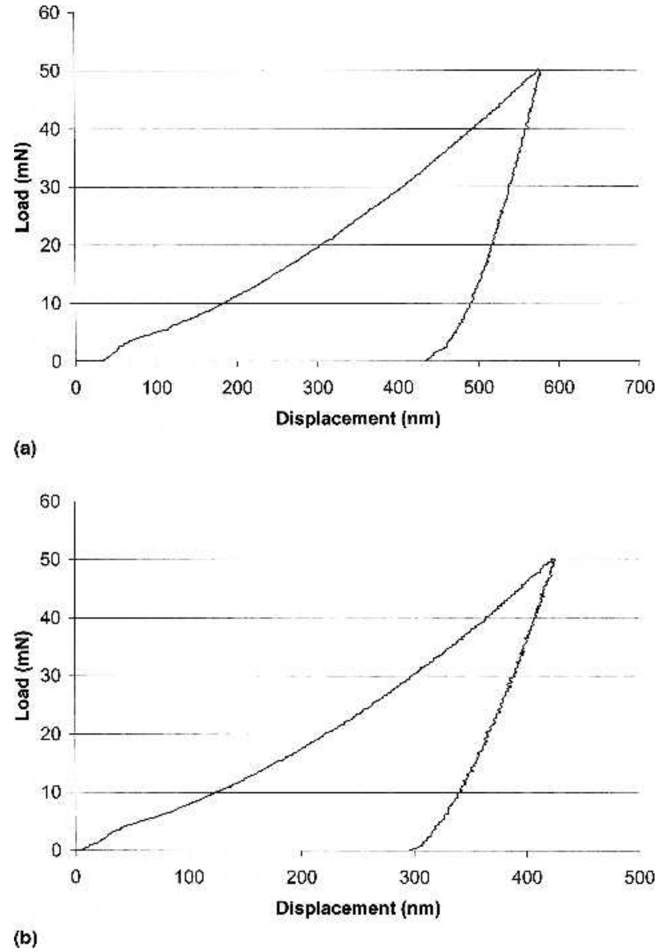


Fig. 8 Nanoindentation loading/unloading curves of heat-treated T-200 for 48 h: (a) cobalt solid solution and (b) eutectic mixture

Table 3 Nanohardness and mechanical properties of tested alloys

Property/phase	Hardness, GPa	Young's modulus, GPa	Maximum deformation, nm	Residual deformation, nm	η_e, %	η_p, %
As-cast T-400/primary Laves phase	21.81	397.5	376.45	243.46	35.3	64.7
As-cast T-400/eutectic mixture	13.78	310.52	460.48	316.64	31.2	68.8
Heat-treated T-400 at 1282 °C/primary Laves phase	16.79	342.0	424.98	294.87	30.6	69.4
Heat-treated T-400 at 1282 °C/eutectic mixture	14.26	330.44	454.36	321.42	29.3	70.7
As-cast T-200/cobalt solid solution matrix	6.63	273.70	640.80	537.76	16.1	83.9
As-cast T-200/eutectic mixture	10.25	279.03	529.94	381.35	28.0	72.0
Heat-treated T-200 for 48 h/cobalt solid solution matrix	8.76	224.37	578.50	433.20	25.1	74.9
Heat-treated T-200 for 48 h/eutectic mixture	16.56	288.47	430.12	260.33	39.5	60.5

increased the ductility, and hardened the eutectic. The overall hardness of the alloy was reduced slightly by the heat treatment, but the wear resistance was not changed.

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

Acknowledgments

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