Characterization of the MC Carbides and Mechanical Properties in a TiC Particles-Strengthened Cobalt-Based Alloy through HIP, Solid-Solution and Aging Treatments

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In previous studies, we mixed and added different amounts of TiC powders (0, 10, 15 and 20 mass%) to the cobalt-based alloy powders. The results showed that adding 15 mass% TiC powder to the cobalt-based alloy and sintering at 1280°C for 1 h was the optimal process. The aim of this paper is to continue exploring a series of HIPping processes and various heat treatments for T0 and T15 composite materials, and examining the effects on the microstructure and mechanical properties of TiC particles-strengthened cobalt-based alloy. The experimental results showed that the highest TRS value of 1566.7 MPa was obtained by the 15 mass% TiC additive powders, which was sintered at 1280°C for 1 h, followed by HIP plus solid-solution heat treatment. The experiment proved that the closed pores can be effectively eliminated (1.34% → 0.69%) by HIP treatment. In addition, the more uniform precipitation of MC carbides appeared in the grain-boundary and matrix after aging treatment. Moreover, the added amounts of TiC powder play an important role in improving the mechanical properties of cobalt-based alloy.

1. Introduction

Cobalt-based alloys with excellent high-temperature wear/corrosion resistance; which are important industrial material for gas turbine, machine tools and wear-resistance coatings.1) Their design is aimed primarily at improving elevated temperature strength by use of solid-solution and carbide-strengthening mechanisms.2,3) In the cobalt-based alloys, chromium improves oxidation and heat-corrosion resistance; producing strengthening by the formation of MC and M23C6 carbides. Molybdenum and tungsten are solid-solution strengtheners; producing strengthening by formation of inter-metallic compound of CO3M and MC carbides; and the formation of MC carbide. Carbon produces strengthening by the formation of MC, M2C3, M23C6 and possibly M6C carbides.4) Titanium carbide (TiC) is extremely hard carbide, which has special advantages in comparison with other carbides.5) There are many materials that can be used in the iron or cobalt matrix composites, but TiC is more favorable because of the advantages such as high hardness, good wet-ability and satisfactory resistance against thermal shocks.5,6) Metal matrix composites (MMCs) are known to be very hard and to exhibit exceptional wear resistance. In this respect, several investigators used TiC as reinforcing medium in ferrous metal in order to enhance these properties. Particularly, most of the work on composites is through powder metallurgy route.7-9)

In the Hot Isostatic Pressing (HIP) technology, high temperature and high gas pressure can be simultaneously applied to work-pieces resulting in fully isotropic material properties.10,11) It provides uniform density very close to theoretical density, elimination of porosity, improved fatigue, creep and tensile properties.10-13) In addition, precipitation strengthened cobalt-based alloys contain Cr, Mo and W elements, which trend to cause precipitation of carbides (such as M6C and M23C6) during appropriate heat treatments.1,4)

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3. Results and Discussion

3.1 Effects of HIP plus solid-solution and various heat treatments on the MC carbides

This study explored a series of HIPping processes, solid-solution and aging heat treatments for T0 and T15 specimens, and examined the effects on the microstructure and mechanical properties of TiC particles-strengthened cobalt-based alloy. In the research, the mean particle size of TiC powders was about 2–3 µm and density was 4.9 g cm\(^{-3}\). The mean particle size of cobalt-based alloy powder was 5–10 µm, and the chemical composition (mass%) is as follows: 29–33% Cr, 8–10% W, ≤3.0% Fe, 1.5–3.0% Ni, 1.4–1.7% C, 1–1.5% Si, ≤1.0% Mo, ≤0.5% Mn and the balance is Co.

Figure 1 compares the porosity and sintered density of the T0 and T15 specimens after sintering, HIP plus solid-solution and various heat treatments. As seen, the porosity of T0 specimen (sintered at 1280°C for 1 h) had a slight decreasing trend (1.2% → 0.86%) after HIP plus solid-solution treatments. However, there was almost no significant difference in porosity for T0 specimen after various aging treatments, as shown in Fig. 1(a). According to the experimental result, the sintered density of T0 specimen was maintained stably after sintering, HIP plus solid-solution and various aging treatments. It is reasonable to suggest that the relative density of T0 specimen has reached over 99% after optimal sintering process; thus, the elimination of closed pores does not show more a pronounced effect by the HIPping process. The minimum porosity (0.74%) and maximum sintered density (8.47 g cm\(^{-3}\)) appeared in HIP plus solid-solution and 12-h aging treatment.

Figure 1(b) shows the porosity and sintered density of T15 specimens after sintering, HIP plus solid-solution and various heat treatments. As seen, the porosity had a significantly decreasing trend (1.34% → 0.69%) after HIP plus solid-solution treatments. However, the sintered density was insignificantly changed after various aging treatments. The sintered density was slightly enhanced after HIP, solid-solution and aging treatments. There was a slight increase from 7.41 to 7.66 g cm\(^{-3}\) after HIP plus solid-solution treatments, and maintained at 7.59–7.67 g cm\(^{-3}\) after aging treatments. Due to the higher volume of TiC (15%) added to cobalt-based alloy, the external additive of TiC powder of T15 composite specimens was higher. Meanwhile, the liquid metal ratio was fixed during the 1280°C liquid phase sintering (LPS) process, which resulted in many residual gaps among the TiC powders of T15 sintered specimen, and were unable to be fully wetted. As a result, many internal pores appeared on the matrix. However, the specimen was compressed, which led to the need for the internal closed pores to be effectively eliminated after HIP treatment; therefore the sintered density could obviously be improved.

Figure 2 shows the OM observation of the T0 specimens by sintering, HIP plus solid-solution, and various aging treatments. As compared with the as-sintered specimen (Fig. 2(a)), it can be clearly observed that some of the grain boundary carbides (M\(_6\)C and M\(_{23}\)C\(_6\)) disappeared and the volume of carbides diminished after HIP plus solid-solution treatments (Fig. 2(b)). Increasing the soaking time of the aging treatment resulted in no continuous carbides precipitating on the grain boundary. Moreover, the carbide precipitations of matrix tended to increase as the aging time increased (6 h → 9 h → 12 h), as shown in Figs. 2(c), 2(d) and 2(e). It is reasonable to assume that with the effects of high temperature and high pressure by HIP plus solid-solution treatments, the carbides can be decomposed and
dissolved solute atoms, and then return to the matrix. In addition, the saturated solubility of the matrix’s solute atoms was higher under high temperature; thus, the matrix had supersaturated solute atoms and higher Gibbs free energy after the quenching process. When the study subjected the solution to the activation temperature, the carbide began to nucleate and grow as the aging time increased. As a result, the number and size of the carbides slightly increased, as shown in Figs. 2(d) and 2(e).

Figure 3 shows the OM observation of the T15 specimens by sintering, HIP plus solid-solution and various aging treatments. The carbide precipitations showed a slightly decreasing trend after HIP plus solid-solution treatments, as seen in Fig. 3(b). Moreover, carbide precipitations obviously increased in volume and grew along the distribution of TiC area as the aging times increased (6 h → 9 h → 12 h). The carbide began to grow while the smaller carbides also interconnected into large carbides, as shown in Figs. 3(c), 3(d) and 3(e). When the carbides of T15 sintered specimens underwent uniform dispersion (Fig. 3(a)), the carbide precipitations were more uniformly distributed after HIP and heat treatments. Judging from the microstructure, the T15 sintered specimens should be able to have better mechanical properties after HIP and various heat treatments.

Figure 4 shows the BEI observation of the T0 specimens by HIP plus solid-solution, and various aging treatments. It can be observed in Fig. 4(a) that many fine, small white M₆C carbides existed in the grain boundary. Because the external high pressure and high temperature of HIPing process may dissolve the carbon elements, and thus return to the matrix, the original plate M₆C carbide precipitations of sintered specimens transformed into small carbides after the HIP plus heat treatments. As the aging time increased, all of the small carbides gradually increased and grew into spherical shapes. Meanwhile, the M₆C carbides growth was found along the M₂₃C₆ surroundings, as shown in Figs. 4(b), 4(c) and 4(d). The literature shows that tungsten element is a solid-solution strengthener, by forming the inter-metallic compound of M₆C carbide. In addition, other literature also indicates that the W element is easily transformed to replace the Cr element; thus, the M₂₃C₆ transforms into M₆C carbide precipitations. As a result, it is reasonable to suggest that the matrix has greater W elements distribution than that appearing in the chromium-rich M₂₃C₆ carbide area. After prolonged aging treatment, more W elements were transferred...
to replace the Cr elements by diffusion into the $\text{M}_2\text{C}_6$ carbide, thereby becoming the $\text{M}_6\text{C}$ carbides, as shown in Fig. 4(d).

Figure 5 shows the BEI observation of the T15 specimens by HIP plus solid-solution, and various aging treatments. As seen, the small white $\text{M}_6\text{C}$ carbides precipitated onto the grain boundary and nucleation along the TiC area after HIP plus solid-solution treatments. Because the TiC distributed area of the sintered specimen had a higher volume of elements of W composition, they gradually precipitated the $\text{M}_6\text{C}$ carbides after high temperature of HIP and various heat treatments. In comparison with $\text{M}_2\text{C}_6$ carbides, TiC had better affinity for the W element. According to the literature, the $\text{M}_6\text{C}$ carbides begins to precipitate at the temperature of 1200°C.\(^{16}\) Under a solid-solution treated temperature of 1100°C in this study, the $\text{M}_6\text{C}$ carbides gave priority to precipitation around the TiC area. The mostly white $\text{M}_6\text{C}$ carbides were uniformly distributed in the TiC area after HIP plus solid-solution treatment, as shown in Fig. 5(a). Moreover, the carbide precipitations did not significantly change except for the slight increase after the aging treatment, as shown in Figs. 5(b), 5(c) and 5(d). Figure 6 shows the SEM observation and Mapping analysis of the T15 specimens by HIP plus solid-solution and 760°C 12-h aging treatments. It can be observed that the Co was evenly distributed in the matrix, and Cr was the main precipitated element of carbides, which distributed in the area of the matrix and grain boundary. Moreover, W elements were obviously distributed in the position around the TiC area.

### 3.2 Effects of HIP plus solid-solution and various heat treatments on the mechanical properties

Figure 7(a) shows the hardness test of T0 and T15 specimens by as-sintered HIP plus solid-solution, and various aging treatments. Obviously, adding 15 mass% of TiC powder to cobalt-based alloy can effectively increase the hardness after HIP and different heat treatments. In addition, the hardness of T0 specimens slightly decreased after HIP plus solid-solution treatments. The HIP temperature at 1250°C easily resulted in a large number of solute atoms dissolving and returning to the matrix.\(^{17,18}\) Therefore, the volume fraction of carbide decreased and led to a lower hardness. Although the $\text{M}_6\text{C}$ carbides began to precipitate under the extra high temperature of 1200°C, the matrix had many supersaturated solute atoms during the solid-solution treatment (1100°C 40 min). Therefore, $\text{M}_6\text{C}$ carbides gradually precipitated and grew after 760°C aging treatment. Increasing the soaking time of aging treatment enhanced the amount of carbide precipitations, thus resulting in a higher hardness. The highest hardness (HRA 74.7) of T0 specimens appeared after 12-h aging treatment. The result also agrees with the microstructure of Fig. 4. In addition, Fig. 7(a) displays the strengthening of TiC as the main factor in increasing the strength of cobalt-based composite materials, while TiC did not change the distribution pattern after heat treatment. In fact, the effect of hardness for cobalt-based composite materials depends on the amount of TiC powder added, thus, the hardness of T15 specimens was only slightly increased by different heat treatments. The highest hardness (HRA 79.5) of T15 specimens appeared after aging for 12 h.

Figure 7(b) shows the TRS test of T0 and T15 specimens by as-sintered HIP plus solid-solution, and various aging treatments. As seen, the carbides decomposition caused the solute atoms to be dissolved and to return to the matrix after HIP treatment. Therefore, the volume fraction of carbide decreased and resulted in lower TRS. Furthermore, the $\text{M}_6\text{C}$ carbides of the T0 specimen began to gradually precipitate after aging treatment at 760°C. As the aging time increased (12 h), the amount of carbide precipitations also increased, leading to higher TRS (1258.1 MPa). Moreover, as the T15
specimen had a great amount of TiC powder, the residual closed pores of sintered specimens were significantly removed by HIP treatment, whereby the TRS was slightly improved (1485.1 → 1566.7 MPa). However, M₆C carbides increased and grew as aging time increased, which was not helpful to the TRS of the T15 specimen.

Figures 8 and 9 show the fractographs observation of the T0 and T15 specimens by HIP plus solid-solution, and various aging treatments, respectively. Because the smaller carbide was decomposed, the larger carbides remained after HIP and solid-solution treatments (as seen in Figs. 2 and 3). The obvious destruction of large carbides formed the transgranular and large brittle fracture surface, as shown in Fig. 8(a). Additionally, the small carbide transgranular and dimple fracture surface were observed after the aging treatment, as shown in Figs. 8(b) and 8(c). With the increased aging time, this dimple fracture phenomenon became more evident, as shown in Fig. 8(d). TRS thus reached the largest value (1258.1 MPa) after a 12-h aging treatment. Figure 9 shows the fractographs observation of the T15 specimens by HIP and solid-solution, as well as various aging treatments. The fracture surface contained a cleavage shape of cobalt-based alloys, and some dimple structures, as shown in Fig. 9(a). In addition to some areas exhibiting a dimple fracture structure, most of the morphology showed brittle fractures of small carbides, which are detrimental to the TRS of the T15 specimen, as shown in Figs. 9(b), 9(c) and 9(d). Significantly, the solid-solution and aging treatments did not effectively change the distribution of TiC morphology; hence, the differences of mechanical properties were mainly generated by the distribution of carbide precipitations. In addition, the added amounts of TiC powder played an important role in improving the mechanical properties of cobalt-based alloys.

4. Conclusions

After the T0 specimen was vacuum sintered at 1280°C for 1 h, the fully dense material was yielded. As the carbide of the sintered specimens has a continuous network distribution, there was lower TRS (1069.1 MPa); therefore, it is necessary to impose the high temperature and pressure of HIP, solid-solution and aging heat treatment. The matrix’s carbides reprecipitated and strengthened the sintered materials. The T0 specimen reached the highest TRS (1258.1 MPa) and hardness (HRA 74.7) through the HIP, solid-solution and 12-h aging treatments.

The T15 composite specimen (15 mass% TiC) contained a lot of closed pores in the matrix after 1280°C sintering for 1 h. These closed pores resulted in relatively lower TRS (1485.1 MPa). However, the closed pores of sintered specimens could be effectively eliminated by HIP plus solid-
solution treatments, thus increasing the TRS to 1566.7 MPa. Moreover, the highest hardness (HRA 79.5) was obtained by HIP, solid-solution and 12-h aging treatments.

In this study, adding the TiC powders to cobalt-based alloy was provided effectively in the nucleation position of M6C carbides. In addition, W elements were easily integrated by diffusion into the chromium-rich M23C6 carbide and replaced the Cr, thereby becoming the M6C carbides. Most of the M6C carbide re-precipitated in TiC area after aging treatment, and transformed into the M23C6 carbides, which combined with the TiC to produce a continuous brittle structure. The cracks along these areas thus grew rapidly, thus resulting in the TRS decline.

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REFERENCES