The Effects of HIP, Solution Heat Treatment and Aging Treatments on the Microstructure and Mechanical Properties of Sintering Cobalt-Based Alloys Strengthened with Tantalum Carbide Additives

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This study explored a series of HIP processes, solution heat treatments and aging treatments, in which various amounts of tantalum carbide (TaC) powder are added for sintering cobalt-based composite materials. Experimental results showed that the highest transverse rupture strength (TRS) of 1812.4 MPa was obtained by the 10 mass% TaC added to cobalt-based alloys, which was sintered at 1270°C, and followed by HIP processes, solution heat treatments, and aging treatments for 12 h. The hardness increased to 80.1 HRA. In addition, the added amounts of TaC powder and aging times played important roles in improving the mechanical properties of the cobalt-based alloys. By microstructural observations, it was found that both M_6C and $M_{23}C_6$ carbides precipitated in the matrix of the 0% TaC specimens after various aging treatments. However, the more refined and uniform precipitations of M_6C , $M_{23}C_6$ and MC carbides were precipitated in the matrix of the TaC powders added to cobalt-based alloys after 12 h of aging treatment at 850°C. This result was effective in improving the mechanical properties of the cobalt-based alloys. Conversely, 15 h of aging treatment at 850°C generated an over-aging phenomenon, which resulted in a decrease in TRS value. [doi:10.2320/matertrans.M2014066]

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1. Introduction

Generally, superalloys are widely used under different application conditions. For example, cobalt-based alloys have good wear resistance, corrosion resistance at high temperature and excellent heat fatigue resistance. Those are exactly consistent with the requirements of critical or supercritical high temperature steam valves that demand higher wear resistance and corrosion resistance. Many of the properties of these alloys arise from the crystallographic nature of cobalt, the solid-solution strengthening effects of chromium, tungsten, and molybdenum of the metal carbides.^{1–3)} Tantalum carbide (TaC) is a very important and promising material due to its unique combination of properties,⁴⁾ such as a melting point in excess of 3800°C. Unique combination of good chemical stability, good corrosion resistance, high hardness and other good mechanical properties make it potential for rocket nozzles and scramjet component applications.^{5,6)}

Metal matrix composites (MMC) are known to be very hard materials and to exhibit exceptional wear resistance. In this respect, several investigators used TaC as reinforcing medium in a cobalt-based alloy in order to enhance mechanical properties. Furthermore, wear resistance of MMC have been developed, which are produced by powder metallurgy (P/M).^{7,8)} Conventionally sintered P/M parts usually have over 5% porosity. Enhanced sintering techniques can be applied to obtain higher density and reduced porosity in sintered parts.^{7–9)} Powder metallurgy, such as hot isostatic pressing (HIP) can be used for upgrading casting, packing pre-sintered components and consolidating powders; it involves the simultaneous application of high pressure and elevated temperature in a specially constructed vessel. Besides, HIP is largely concerned with the removal of pores.^{10–13)}

Furthermore, the precipitation strengthened cobalt-based alloys contain Cr, Mo and W elements, which trend to cause precipitation of carbides (such as MC, M_6C and $M_{23}C_6$) during appropriate heat treatment.^{9,14)} Our previous studies added different amounts of TaC powders (0, 10, 15 and 20 mass%) to the cobalt-based alloy powders. The experimental results showed that adding 10 mass% TaC powder to cobalt-based alloys and sintering at 1270°C for 1 h was the optimal process. The aim of this work was to explore a series of HIP processes, solution heat treatments, and aging treatments for cobalt-based composite materials, and examine the effects on the microstructure and mechanical properties of TaC strengthened cobalt-based alloys.

2. Experimental Procedures

In our previous work, different amounts of TaC powders (0, 10, 15 and 20 mass%) were added to cobalt-based alloy powders. The cobalt-based powder samples, with various TaC specimens added, were denoted by 0% TaC, 10% TaC, 15% TaC and 20% TaC. The vacuum sintering temperature was maintained at 1260, 1270, 1280 and 1290°C for 1 h. The HIP equipment used in this experiment was from Flow Autoclave Pressure Systems, Inc. The equipment used for the solution heat treatment was a commercial Germanic Schmetz vacuum heat treatment furnace. The aging treatments were performed using a vacuum tube furnace. The parameters of the HIP process were 1250°C, 125 MPa and 100 min. After the HIP process, the samples were heated to 1100°C for solution heat treatment and maintained for 40 min; then they were quenched and aged at 850°C for soaking times of 9, 12 and 15 h, respectively.

To evaluate the influences of HIP and various heat treatments on microstructure and mechanical properties of TaC strengthened cobalt-based alloys, this study conducted apparent porosity, hardness, transverse rupture strength

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(TRS) tests, optical microscope (OM, Nikon Eclipse Lv150) and scanning electron microscopy (SEM, Hitachi-S4700) microstructure inspections. The Hung Ta universal material test machine (HT-9501A) with a maximum load of 245 kN was used for 3-point bending (TRS) tests (ASTM B528-05). R_{bm} was the transverse rupture strength, which determined as the fracture stress in the surface zone. F was maximum fracture load, L was 30 mm, k was chamfer correction factor (normally 1.00–1.02), b and h were 5 mm in the equation $R_{bm} = 3FLk/2bh^2$, respectively. The specimen dimensions of the 3-point bending test were 5 mm × 5 mm × 40 mm. Porosity test was conducted in accordance to the ASTM C373-88 standard. Hardness tests were measured by Rockwell A hardness (HRA, Indentec 8150LK) with a loading of 588 N, which followed the ASTM B294 standard.

3. Results and Discussion

In this experiment, the mean particle size of TaC powders was $1.45 \pm 0.5 \mu\text{m}$, and the density was 13.9 g cm^{-3} . The mean particle size of cobalt-based powder was $8 \pm 1 \mu\text{m}$, and the chemical composition (mass%) is as follows: 29–33% Cr, 8–10% W, $\leq 3.0\%$ Fe, 1.5–3.0% Ni, 1.4–1.7% C, 1–1.5% Si, $\leq 1.0\%$ Mo, $\leq 0.5\%$ Mn. The balance was Co.

All cobalt-based composite specimens were sintered at 1270°C for 1 h. Figure 1 shows the porosity of the different composite specimens after as-sintered, HIPed, HIP plus and different aging treatments. Our previous study⁸⁾ found that the liquid-phase sintering (LPS) effect was observed in decreasing porosity. Figure 1 shows that the porosity of the 0% TaC specimens decreased to 2.2%, and the 10, 15 and 20% TaC specimens decreased to less than 2% after the optimal sintering temperature (1270°C). Furthermore, the porosity of 0% TaC sintered specimens had a slight decrease ($2.2\% \rightarrow 1.8\%$) after HIP process. According to the literature,¹⁵⁾ the closed pores can be effectively eliminated by the HIP process. When the specimen was under a uniform pressure, there was a reduction in internal closed pores, and the microstructure and mechanical properties showed a very substantial improvement. However, the sintered specimen itself provided good densification after 1270°C sintering. Thus, a small improvement in the porosity level was displayed.

In addition, the porosities of 10, 15 and 20% TaC specimens only experienced a slight decrease after the HIP process. When the sintered specimen was compressed, the internal closed pores were effectively eliminated after the HIP process; therefore, the sintered density was improved. When the sintered density was low, the improvement efficiency of the HIP treatment was limited. Compared with 0% TaC specimens, the 10 mass% TaC powder added to the cobalt-based alloys obviously affected the diffusion of particles, which resulted in a slight decrease in the porosity level after the HIP process. However, for the 15% TaC specimens, the porosity was not clearly improved after the HIP process; this is because the LPS effect decreased the porosity after the optimal sintering process. Moreover, adding a higher content (15 mass%) of the TaC powder resulted in an increased concentration of micro pores after the sintering process. There were still many gaps between the TaC and

Fig. 1 Comparison of the porosity of different composite specimens by as-sintered, HIPed (1250°C , 125 MPa and 100 min) and different solution heat treatment and aging treatments (9, 12 and 15 h).

cobalt-based powders that could not be wetted, which caused several internal pores to remain in the specimen. Consequently, these closed pores were not completely and effectively eliminated by the HIP process.

On the other hand, the solution heat treatment and aging treatment contributed to a better strengthening phase of the carbide precipitations for cobalt-based composite materials, as well as the re-distribution of carbide precipitations. Therefore, the porosity level was affected. Figure 1 shows that the porosity of the 0% TaC specimens was obviously reduced to below 1.1% after the solution heat treatment and aging treatment (9, 12 and 15 h). The results suggested that the porosity decreased through slow diffusion of the particles after a long-time and high-temperature aging treatment (850°C - 9, 12 and 15 h). Moreover, 10, 15 and 20% TaC specimens only showed a slight evolution in porosity after the aging treatment. For example, the porosity of the 20% TaC specimens decreased to 1.0% after 9 h of aging treatment, but a slight increase of 0.7% was observed after a longer aging treatment (15 h). The aging treatments contributed to a redistribution of carbide precipitates, which resulted in a decrease in the porosity level.

Figure 2 shows the hardness and TRS tests of different composite specimens by as-sintered, HIP processes, and heat treatments. The hardness obviously increased as the TaC added to cobalt-based powders increased after optimal sintering treatment. In addition, the hardness of 0% TaC specimens rapidly increased ($70.2 \rightarrow 75.7$ HRA) after the HIP process, as shown in Fig. 2(a). Since HIP can effectively eliminate internal micro pores, when the specimens were subjected to the high compressive stress, the densification of the specimens was significantly improved and the treatment enhanced the hardness. A large number of solute atoms dissolved, and re-dissolved back into the matrix after the solution heat treatment. Meanwhile, the re-dissolved atoms began to generate carbide precipitations through the long aging process. Normally, suitable and longer aging treatment will result in more carbide precipitations which affect the hardness of the material. As a result, the hardness of 0% TaC specimens was increased as the aging time increased. The highest hardness of 0% TaC specimens was 77.3 HRA, which appeared after 15 h of aging treatment.

Fig. 2 Comparison of the hardness and TRS tests of different composite specimens by as-sintered, HIPed (1250°C, 125 MPa and 100 min) and solution heat treatment and aging treatments (9, 12 and 15 h).

In addition, all the hardness of 10% TaC, 15% TaC and 20% TaC specimens effectively increased after the HIP process, as shown in Fig. 2(a). Compared with the only sintered specimens, the hardness was enhanced about 5% in 20% TaC specimens. In particular, the hardness of 20% TaC specimens reached 82.3 HRA after the HIP process. However, the hardness of 10% TaC, 15% TaC and 20% TaC specimens showed a downward trend after 9 h of aging treatment. This was mainly due to the carbide distributions, which were not stable and uniform, and resulted in poor hardness after a shorter aging treatment (9 h). By increasing the aging duration, all the hardness of the 10% TaC, 15% TaC and 20% TaC specimens showed an upward trend because the high temperature environment (850°C) of the aging treatments was conducive in the strengthening phases to precipitate various carbides. Meanwhile, the carbide precipitations increases and the hardness enhanced under a longer aging time. The results suggested that the HIP process, along with a suitable aging treatment, is advantageous to the hardness of cobalt-based composite specimens.

Figure 2(b) shows that all the TRS values of the 0% TaC, 10% TaC, 15% TaC and 20% TaC specimens significantly increased after the HIP process. The TRS of 0% TaC specimens increased from 1120.5 MPa (sintered) to 1620.8 MPa (HIPed), 10% TaC increased from 1160.6 MPa to 1724.5 MPa, 15% TaC increased from 1063.3 MPa to 1682.7 MPa and 20% TaC increased from 964.6 MPa to 1664.2 MPa, respectively. The maximum increase per sample was 72.5%

after the HIP process. The HIP process effectively and significantly strengthened cobalt-based composite materials. Moreover, all the TRS values of 0%, 10% TaC, 15% TaC and 20% TaC specimens showed a downward trend after 9 h of aging treatment. By increasing the aging time to 12 h, the TRS value was obviously increased. It is reasonable to suggest that the distribution of carbide precipitations in the cobalt-based composite specimens was more uniform after 12 h of aging treatment, which is advantageous to the TRS value. The optimal TRS value (1812.4 MPa) appeared in 10% TaC specimens after 1270°C of sintering, HIP process, solution heat treatment, and 12 h of aging treatment. However, the over-aging effects obviously appeared after 15 h of aging treatment. Because the excessive precipitations of carbides resulted in continuous accumulation, the strength showed a decreasing trend, as seen in Fig. 2(b). According to the above results and discussion, the optimal process and relatively better mechanical properties were obtained through 10% TaC specimens sintered at 1270°C, followed by the HIP process (1250°C 125 MPa 100 min) and 12 h of aging treatments at 850°C.

Figure 3 shows the SEM observation and EDS analysis of 0% TaC sintered specimens after the HIP process. The main elements of the grain boundary (Point A) were Co, Cr and W, which belong to the W-rich of M_6C carbide distributions.¹⁴⁾ This result indicates that the HIP process did not change the carbide precipitation types of original cobalt-based alloys (0% TaC). The strengthened mechanisms of 0% TaC specimens, which belong to the M_6C carbide precipitation types, did not differ after the HIP process. Figure 4 shows the SEM and EDS analysis of 0% TaC sintered specimens after the HIP process, the solution heat treatment, and 12 h of aging treatment at 850°C. A gray area (Point A) of W-rich M_6C and a black area (Point B) of Cr-rich $M_{23}C_6$ carbide precipitations existed in the matrix and grain boundaries.¹⁴⁾ A comparison of Fig. 4 with Fig. 3 shows that the carbide precipitation types of 0% TaC specimens transformed M_6C into M_6C and $M_{23}C_6$ after the solution heat treatment and aging treatment because the M_6C carbides re-dissolved back into the matrix after a solution heat treatment, while the aging heat treatment attributed to the growth of $M_{23}C_6$ carbides. According to the literature,¹⁶⁾ the $M_{23}C_6$ precipitation began from the grain boundary, which has better effect to obstruct the dislocation slip. If the aging time were too long, the cobalt-based alloy was likely to cause coarsening precipitation and become the network structure, which leads to a lower fracture toughness.

In the research, the carbide precipitation types from 10%, 15% and 20% TaC added to cobalt-based alloys were almost all the same. Therefore, this study selected the 10% TaC specimens as the representative for further analysis. Figure 5 shows the SEM observation and EDS analysis of the 10% TaC sintered specimens after the HIP process. There were three types of carbide distribution (as shown in points A, B and C) for the 10% TaC specimens after the HIP process. The gray area of Point A was W-rich M_6C , the black area of Point B was Cr-rich $M_{23}C_6$ and a light gray area in Point C was MC (M = Ta) carbides, respectively. Furthermore, Fig. 6 shows that the 10% TaC specimens also possessed three types of carbide distribution after the HIP process, the

Fig. 3 SEM observation and EDS analysis of the 0% TaC specimens by sintering at 1250°C, 125 MPa and 100 min HIP treatment.

Fig. 4 SEM observation and EDS analysis of the 0% TaC specimens by sintering at 1250°C, 125 MPa and 100 min HIP plus solution heat treatment and 850°C 12 h aging treatments.

Fig. 5 SEM observation and EDS analysis of the 10% TaC specimens by sintering at 1250°C, 125 MPa and 100 min HIP treatment.

solution heat treatment, and 12 h of aging treatments at 850°C. They were the W-rich M_6C of Point A, Cr-rich $M_{23}C_6$ of Point B and MC carbide of Point C, respectively. All carbides precipitated slowly and grew as the aging time increased. A comparison of results with Fig. 5 shows that the re-precipitated carbides were more refined and had uniform distribution after 12 h of aging treatment (Fig. 6); thus, the TRS value revealed a significant increase (Fig. 2(b)).

Figure 7 shows the BEI observation of the 0% TaC specimens after sintering, the HIP process, and different heat treatments. Some carbide precipitations (M_6C) distributed in

the matrix and grain boundaries after sintering and the HIP process, as shown in Figs. 7(a) and 7(b). Moreover, the carbide precipitation types (M_6C) obviously transformed into the M_6C and $M_{23}C_6$ after 9 h of aging treatment, as shown in Fig. 7(c). As the aging time increased to 12 h, these carbide precipitations produced more and uniform distribution, and many $M_{23}C_6$ carbides existed in the grain boundary, as shown in Fig. 7(d). The carbides coarsening phenomenon clearly appeared in the microstructure after 15 h of aging treatment at 850°C; meanwhile, the amounts of $M_{23}C_6$ decreased, and M_6C increased relatively, as shown in Fig. 7(e), resulting in

Fig. 6 SEM observation and EDS analysis of the 10% TaC specimens by sintering at 1250°C, 125 MPa and 100 min HIP plus solution heat treatment and 850°C 12 h aging treatments.

Fig. 7 BEI observation of the 0% TaC specimens by sintering, HIP and different heat treatments: (a) as-sintered, (b) HIPed, (c) 850°C 9 h aging, (d) 850°C 12 h aging, (e) 850°C 15 h aging.

Fig. 8 BEI observation of the 10% TaC specimens by sintering, HIP and different heat treatments: (a) as-sintered, (b) HIPed, (c) 850°C 9 h aging, (d) 850°C 12 h aging, (e) 850°C 15 h aging.

a lower strength (1412.5 MPa) of cobalt-based composite materials.

Figure 8 shows the BEI observation of 10% TaC specimens after sintering, the HIP process, and different heat treatments. There were three types of carbide distribution (MC, M_6C and $M_{23}C_6$) for 10% TaC specimens after sintering and the HIP process, as shown in Figs. 8(a) and 8(b). In addition, the initial precipitations of carbides were relatively small and few after 9 h of aging treatment. There were mainly M_6C carbides, as shown in Fig. 8(c). As the aging time increased to 12 h, carbide precipitations grew into more refined and uniform distribution, as shown in Fig. 8(d). Meanwhile, there were three kinds of carbide precipitations that clearly appeared. Consequently, the TRS test of 10% TaC specimens possessed the highest value (1812.4 MPa)

after 12 h of aging treatment. However, an excessive and continuous network of carbide precipitation appeared in the matrix, which resulted in lower strength (1628.1 MPa) after 15 h of aging treatment, as shown in Fig. 8(e).

The results were further compared in Fig. 2(b). The TRS tended to decrease as the added amount of TaC increased from 10 to 20 mass% after various aging treatments. It is predicted that after adding more TaC powders, more MC carbides ($M = Ta$) will be precipitated. A large amount of MC carbide accumulation and continuous precipitating in the grain boundaries affected and decreased the cobalt-based alloys strength during TRS tests. Moreover, adding TaC powder to the cobalt-based alloys was helpful in forming the $M_{23}C_6$ carbide precipitations, which are more effective in

Fig. 9 Fractographs observation of the 0% TaC specimens by different process: (a) 1250°C, 125 MPa and 100 min HIPed, (b) 850°C 9 h aging, (c) 850°C 12 h aging, (d) 850°C 15 h aging.

Fig. 10 Fractographs observation of the 10% TaC specimens by different process: (a) 1250°C, 125 MPa and 100 min HIPed, (b) 850°C 9 h aging, (c) 850°C 12 h aging, (d) 850°C 15 h aging.

improving the mechanical properties of cobalt-based alloys. As a result, suitable amounts of TaC powder play an important role in improving the mechanical properties of a cobalt-based composite material.

Figures 9 and 10 show the fractographs of 0% TaC and 10% TaC specimens by the HIP process and various heat treatments. The HIP process effectively decreased the internal pores of 0% TaC specimens. Figure 9(a) shows the main fracture morphology is intergranular fracture. As the aging time increased (9 h $\rightarrow$ 12 h), the reticular carbides accelerated

to rupture, as shown in Figs. 9(b) and 9(c). Moreover, there was an obvious brittle rupture and transgranular fracture after 15 h of aging treatment, as shown in Fig. 9(d). This result confirmed that the strength of 0% TaC specimens decreased as aging time increased. In addition, TaC powders added to the cobalt-based alloys effectively prevented the growth of micro-cracks after the HIP process, as shown in Fig. 10(a). The aging time was not long enough to cause a sufficient amount of carbide precipitation; the strength of the specimens did not effectively increase after 9 h of aging treatment.

Some brittle rupture appeared in Fig. 10(b). Furthermore, Fig. 10(c) shows that the relatively fine and small carbide precipitations led to a dimple rupture after the HIP process and 12 h of aging treatment, which is advantageous to the TRS value (1812.4 MPa). Figure 10(d) shows that both the continuous network of carbide precipitations and the over aging phenomenon caused some of the block ruptures, which are detrimental to the TRS value.

4. Conclusions

The internal pores and micro-cracks of the cobalt-based composite material were effectively reduced after the HIP process. In this study, the porosity level of 10% TaC specimens decreased after the HIP process (1.8% → 1.3%). Meanwhile, the TRS value of 10% TaC sintered specimens (1120.6 MPa) increased to 1724.5 MPa after the HIP process. In addition, the various carbide precipitations re-dissolved back to the matrix and re-precipitate after the solution heat treatment and aging treatment. The 0% TaC specimens possessed two different types of carbides after the solution heat treatment and the aging treatment at 850°C. They were M_6C and $M_{23}C_6$ carbides. However, 10% TaC specimens contained three type of carbides (MC , M_6C and $M_{23}C_6$) after the solution heat treatment and aging treatment.

The hardness and TRS value of 10% TaC specimens can increase to 80.1 HRA and 1812.4 MPa after HIP, solution heat treatment and 12 h of aging treatments. Compared with the 0% TaC sintered specimen, the hardness enhances 14.1% (70.2 → 80.1 HRA) and TRS increases 61.7% (1120.5 → 1812.4 MPa). Significantly, HIP plus solution heat treatment and aging treatment can be effective in improving and enhancing the mechanical properties of cobalt-based alloys with tantalum carbide additives.

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