Effects of MC Carbide Precipitates on the Microstructure and Mechanical Properties of Cobalt-Based Alloys Adding TiC Powder via Vacuum Sintering Process

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In this study, different amounts of fine TiC powders (0, 10, 15 and 20 mass%) were mixed and added to cobalt-based alloy powders. Then, the mixed composite materials (cobalt-based alloy and TiC powders) were vacuum sintered at 1260, 1270, 1280 and 1290°C for 1 h, respectively. The experimental results showed that the highest TRS value of 1485.1 MPa was obtained by the addition of 15 mass% TiC powder and sintering at 1280°C for 1 h; while the highest hardness value of HRA 80.4 was obtained by 20 mass% TiC powder sintered at 1290°C for 1 h. In addition, two types of carbide precipitates appeared in the microstructure. Without added TiC powder of the specimen, fine plate-like precipitates of M6C and M23C6 carbides were obvious on the grain boundary; but when TiC powder was added to the specimens, only M23C6 carbides were observed after sintering treatment. The result also showed that a suitable amount of TiC additive (15 mass%) effectively inhibits carbide precipitation and growth.

1. Introduction

Cobalt-based alloys have good hot-corrosion resistance, anti-oxidation, fatigue properties and high-temperature strength. They are widely used in manufacturing nozzle guide vanes and turbine blades and combustor lines in gas turbine engines. As compared with nickel-based alloys, cobalt alloys are generally not suit for very high temperature application since they often need to be necessary reinforced by carbides.\(^{1,2}\) Cobalt-based alloys are usually strengthened by carbides (such as \(\text{M}_6\text{C}\) and \(\text{M}_2\text{C}_6\)) and solid-solution atoms (such as W, Mo and Ta). Besides, Cr provides oxidation and corrosion resistance, as well as strength by the formation \(\text{M}_2\text{C}_6\) carbides.\(^{1,3-5}\)

Titanium carbide (TiC) has special advantages in comparison with other carbides. For example, the hardness of TiC is 33% higher than WC. Furthermore, it possesses lower density and higher thermal stability than WC.\(^{6,7}\) 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.\(^{8}\) Over the last decade, attempts to produce TiC particle reinforced composite materials have intensified. Basically, there are two ways to obtain a high volume fraction of TiC particles in an alloy: through melt solidification (M/S) processing or via powder metallurgy (P/M) processing techniques.\(^{9}\)

Metal matrix composites (MMC) are known to be very hard materials and to exhibit exceptional wear resistance. In this respect, several investigators used TiC as reinforcing medium in a ferrous metal matrix in order to enhance mechanical properties. Furthermore, wear resistance of MMC have been developed, which are produced by powder metallurgy.\(^{9,10}\) Mixing of the matrix powder and reinforcing particles must be through a milling procedure in order to achieve uniform dispersion of the reinforcing phase. The vacuum-sintering cycle and environment must be chosen to obtain components with near theoretical density.\(^{12}\) This study used different volume fractions of TiC powders added to cobalt-based powders to investigate the effect of various sintering temperatures on the composite material in order to produce a higher strength and hardness of materials, and to evaluate the effects of microstructures and mechanical properties on cobalt-based alloys with added TiC powders.

2. Experimental Procedure

In this research, different amounts of TiC powders (0, 10, 15 and 20 mass%) were mixed and added to cobalt-based alloy powders as composite materials. The cobalt powder was added to the various TiC specimens, which were designated as T0, T10, T15 and T20, respectively. The mixing process was finished by planetary ball milling and granulation in a laboratory. In the experiment, the weight ratio of TiC powder and the WC ball was 1 : 8; the rotation speed was kept at 300 rpm and the milling continued for 12 h. After being milled, the powders were passed through a 200-mesh screen, with PVA (polyvinyl alcohol) used as a binder. The green body (6 × 5.5 × 40 mm) of the composite specimen was produced by a single-axis hydraulic machine, using a forming pressure of 2 tons and a holding pressure time of 15 s. In addition, the vacuum was maintained at 1.33 × 10^-3–1.33 × 10^-9 MPa, and the vacuum sintering temperature was kept at 1260, 1270, 1280 and 1290°C for 1 h, respectively.

To evaluate the effects of MC carbide precipitations on the cobalt-based alloy adding TiC powder via vacuum sintering process, this study conducted apparent porosity, relative density, hardness, Transverse Rupture Strength (TRS) tests, Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) microstructure inspections. The Hung Ta universal material test machine (HT-9501A) with a maximum load of
25 tons was used for 3-point bending (TRS) tests (ASTM B528-05). $L$ was 30 mm, $b$ and $h$ were 5 mm in the equation $R_{e} = 3FLk/2bh^2$, respectively. The specimen dimensions of the 3-point bending test were $5 \times 5 \times 40$ mm. Porosity test was conducted in accordance to the ASTM C373-88 standard. Hardness tests were measured by HRA with a loading of 60 kg, which followed the ASTM B294 standard.

3. Results and Discussion

3.1 Effects of TiC powder and sintering temperature on the microstructure

TiC has been proven suitable in Co- or Fe-based alloys due to its high hardness values, low density and chemical stability with alloys. Therefore, several investigators have used TiC as a reinforcing medium in a metal matrix in order to enhance the properties.

The surface morphology of TiC powder is shown in Fig. 1(a). The mean particle size of the powders was about $2 \pm 1 \mu$m, the density was 4.9 g cm$^{-3}$, the shape was irregular and there were no smooth or undulating surfaces. Gas-atomized cobalt-based alloy powders were used as the substrate, and the mean particle size was $8 \pm 1\mu$m. The chemical composition (mass%) of the cobalt-based alloy powder was: 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 and a balance of Co. The morphology showed the round and equiaxed particles characteristic of gas-atomized powder, as shown in Fig. 1(b).

Figure 2 shows the porosity of the cobalt-based alloy after various TiC powders were added at different sintering temperatures. The porosity of the T0 specimen was higher and reached 22.52% after being sintered at 1260°C for 1 h. The liquid-phase sintering (LPS) involves the formation of a liquid phase to promote higher densification rates and lower the sintering temperatures. It was clearly shown that the specimen did not completely reach the LPS temperature. When the sintering temperature was raised to 1280°C, the porosity of the T0 specimen rapidly decreased to 1.20%, as the porosity decreased significantly as the sintering temperature increased. Similarly, the T10, T15 and T20 specimens sintered at 1260°C for 1 h also had a higher porosity of over 30%. Analysis of the above results found that the major factors were as follows: the shape of TiC was sheeted, which resulted in a loosely arranged green body after the forming process.

When more TiC powder was added, the binder was quickly exhausted and pores remained in the sample after sintering. Adding more TiC powder required a higher temperature to approach LPS and provide sufficient sintering energy.

In this study, due to the melting point of TiC is 3160°C, adding more TiC powders require a high temperature to approach LPS. The literatures also pointed out that increased the amount of TiC powders must to enhance the sintering temperature of composite materials. Therefore, it can reach the optimal microstructure and mechanical properties. Thus, the porosity of the T10 and T15 specimens decreased to 0.94 and 1.34% after being sintered at 1280°C for 1 h, respectively. The T20 specimen was sintered at 1290°C for 1 h to achieve the densification mechanism; the apparent porosity was 0.40%. The formation temperature of liquid phase in T10 and T20 does not seem to be widely different and seems to depend on their phase relations. According to the experimental results, the sintered density of T0 specimen was maintained at 8.39 g cm$^{-3}$. In addition to the higher volume of TiC added to cobalt-based alloy, it results in many residual gaps among the TiC powders of sintered specimen, which cannot be fully wetted, causing the lower sintered density. The sintered density of T10, T15 and T20 specimen was 7.76, 7.41 and 7.39 g cm$^{-3}$, respectively.

The etching solution utilized hydrochloric acid and hydrogen peroxide (ratio of 10:1), and the etching time was about 30 min. Figure 3 shows the OM observation of the T0 specimens at different sintering temperatures. Since the sintering temperature was lower, the particle boundaries appearing in the T0 specimen could be easily observed after sintering at 1260°C for 1 h, as shown in Fig. 3(a). Some particle boundaries combined the connected pores and caused open porosities of up to 22%, while the carbide precipitation was lower. As the pores became round in shape, the particle...
boundaries gradually disappeared and carbides uniformly grew up after sintering at 1270°C for 1 h, as shown in Fig. 3(b). Even through it seems to be an uneven condition. However, almost no pores were observed after sintering at 1280 and 1290°C for 1 h. Clearly, the grain coarsening phenomenon and the rapid growth of carbides into a continuous network microstructure were obvious, as shown in Figs. 3(c) and 3(d). According to the literature, it indicated that the microstructure appearing in the sample would result in inside cracks in the materials, thus, reducing the mechanical properties.

Figure 4 shows OM observations of the T10 specimens at different sintering temperatures. As Fig. 4(a) shows, the sintering temperature did not reach the LPS. It was clearly observed that numerous TiC powders were coated on the surface of the composite powder, and that a number of powder particles on the grain boundary had not yet disappeared. The carbide precipitation of the matrix was also lower. When the sintering temperature was raised to 1270°C, the LPS phenomenon was still not obvious, but the pores gradually became round, as shown in Fig. 4(b). Conversely, few pores appeared after sintering at 1280 and 1290°C for 1 h, as shown in Figs. 4(c) and 4(d). Meanwhile, the carbide precipitates showed rapid growth, but the microstructure was not similar to that of the continuous network structure which formed in the T0 specimens (Fig. 3). This seemed to suggest that adding TiC powder hindered the growth of MC carbides into a continuous network structure, and helped to avoid the rapid growth of cracks. Besides, as Fig. 4(d) shows, various plate-like carbide precipitates appeared after sintering at 1290°C for 1 h. The distribution of TiC no longer coated the surface of the composite powder; conversely, the flow direction of LPS seemed to generate a dense structure.

Figure 5 shows the OM observation of the T15 specimens at different sintering temperatures. It was observed that the distribution of TiC obviously increased, as compared with the T0 and T10 samples. A comparison with the microstructure of the T15 specimens under various sintering temperatures showed that the optimal sintering temperature was at 1280°C for 1 h. As shown in Figs. 3(c) and 4(c), the distribution of carbide precipitates was more scattered and the particles were smaller in the T15 specimens. The results also showed that a suitable amount of TiC additive (15 mass%) effectively inhibited carbide precipitation and growth, and so increased the strength of the composite materials. According to the above discussion and results, it was supposed that the T15 specimens sintered at 1280°C for 1 h would have better mechanical properties.

Figure 6 shows OM observations of the T20 specimens at different sintering temperatures. The distribution of TiC had an increasing trend as compared with the T0, T10 and T15 samples. A comparison with the microstructure of the T15 specimens under various sintering temperatures showed that the optimal sintering temperature was at 1280°C for 1 h. As shown in Figs. 3(c) and 4(c), the distribution of carbide precipitates was more scattered and the particles were smaller in the T15 specimens. The results also showed that a suitable amount of TiC additive (15 mass%) effectively inhibited carbide precipitation and growth, and so increased the strength of the composite materials. According to the above discussion and results, it was supposed that the T15 specimens sintered at 1280°C for 1 h would have better mechanical properties.
Figure 6(d) shows that TiC and the carbide precipitates were closely linked and represented the network microstructure. At the same time, the matrix structure was obviously extended. The literature also indicates that the phenomenon (Fig. 6(d)) will cause greater hardness and brittle properties, which results in lower strength of the material. It was suitable to suggest that the T0, T10 and T15 specimens sintered at 1280°C for 1 h and the T20 specimen sintered at 1290°C for 1 h would have better mechanical properties.

Figure 7 shows the BEI observations of various composite specimens by optimal vacuum sintering process: (a) T0 1280°C/1 h, (b) T10 1280°C/1 h, (c) T15 1280°C/1 h, and (d) T20 1290°C/1 h.

Figure 6(d) shows that TiC and the carbide precipitates were closely linked and represented the network microstructure. At the same time, the matrix structure was obviously extended. The literature also indicates that the phenomenon (Fig. 6(d)) will cause greater hardness and brittle properties, which results in lower strength of the material. Accordingly, it was suggested that the T0, T10 and T15 specimens sintered at 1280°C for 1 h and the T20 specimen sintered at 1290°C for 1 h would have better mechanical properties.

Figure 7 shows the BEI observations of various composite specimens using an optimal vacuum sintering process. Two types of carbides in the T0 specimen could be observed: white M₆C and gray M₂₃C₆ carbides. The carbides precipitated on the grain boundary and exhibited fine plate-like precipitates, as shown in Fig. 7(a). These plate-like carbide precipitates easily led to an intergranular fracture of the materials. However, there were no white M₆C carbide precipitates in the other composite specimens; only the gray M₂₃C₆ carbides randomly dispersed in the matrix, as shown in Figs. 7(b), 7(c) and 7(d). It was concluded that TiC powders inhibited M₆C carbides from being produced during the sintering process. In addition, TiC additive and carbide still displayed the cluster distribution and a uniform distribution in all matrices, respectively. Moreover, the TiC particles and M₂₃C₆ carbide precipitates of the T15 specimens had a more uniform distribution, as shown in Fig. 7(c).

Figure 8 shows SEM observations of the T0 and T15 specimens sintered at 1280°C for 1 h, respectively. The elemental composition of each area is listed in Table 1. Point A represents the matrix structure, with chromium as the main element; and point B shows the chromium-base M₂₃C₆ carbide, with the white area of C containing a lot of W elements (12.88%) of M₆C carbides, as shown in Fig. 8(a). The literature indicates that the W element can easily replace Cr; thus, M₂₃C₆ transferred to M₆C carbide precipitates, which was in agreement with the above discussion and results. As shown in Fig. 8(b), no white M₆C carbides appeared in the microstructure of the T15 specimen. Point D shows the matrix structure of a cobalt-based alloy; point E marks the chromium-base M₂₃C₆ carbide; while point F is TiC clusters. It was found that the W element contents (2.65%) of point F were higher than that of the matrix (1.17%). In addition, due to the effect of liquid phase sintering, the liquid phase of the alloy wetted the composite powders, resulting in saturated W element production after solidification, as shown in Fig. 8(b).

### 3.2 Effects of TiC powder and sintering temperature on the mechanical properties

A comparison of the porosity and hardness test results for various specimens after different sintering temperature treatments are shown in Figs. 2 and 9(a). It was readily apparent that the porosity of the specimens significantly decreased as the sintering temperature increased, thus enhancing their
hardness. Sintering the T15 sample at 1280°C for 1 h removed most of the porosities, while the hardness only slightly increased after sintering at 1290°C for 1 h. However, the T20 specimen sintered at 1290°C for 1 h achieved densification and the highest hardness that could be reached at HRA 80.4. As compared with the hardness of the T0, T10, T15 and T20 specimens under optimal sintering parameters, it was clear that the hardness significantly increased as the TiC additive increased.

Figure 9(b) shows the TRS test results for a cobalt-based alloy after the adding of various TiC powders using different sintering temperatures. T0 specimens sintered at 1270°C for 1 h had the maximum value (1128.8 MPa) after the TRS tests, and sintering at 1280°C for 1 h gave a lower value (1069.1 MPa). The result, when further compared with Fig. 3(b), showed that the carbide precipitates were smaller and distributed in a random manner in the matrix after sintering at 1270°C. This could be a factor in improving the TRS value. According to Orowan’s mechanism theory, because of the precipitate volume fraction under certain conditions, there will be smaller precipitate particles and these will be more uniformly dispersed, thus creating the higher strength. Furthermore, if the sintering density is poor, the TRS improvement is limited. On the other hand, a continuous network of carbide precipitates was distributed on the grain boundaries after sintering at 1280°C for 1 h, which caused cracks to rapidly spread and extend along the grain boundary extension. This could be another factor affecting the TRS value. As a result, the TRS of the T0 sample decreased to 1069.1 MPa after sintering at 1280°C for 1 h. In this study, the densification of T10 and T15 specimens dramatically improved after sintering at 1280°C for 1 h, which led to a higher TRS. In addition, the higher sintering temperature easily caused a coarsening phenomenon of the carbides, which resulted in a lower TRS for the T10 and T15 specimens after sintering at 1290°C for 1 h. Conversely, the highest amount of TiC powder in the T20 specimens required sintering at 1290°C for 1 h to reach full densification and gain its optimal TRS value.

Comparing the optimal sintering temperature for all composite specimens, it was clear that T15 had the highest value of TRS (1485.1 MPa). It was reasonable to suggest that due to the distribution of carbide precipitates on the matrix being more uniformly dispersed, TiC effectively inhibited rapid carbide growth during the sintering process. However, the TRS showed no obvious improvement by the addition of 20 mass% TiC powder. Meanwhile, the higher sintering temperature easily led to the rapid growth of carbides, which caused the coarsening phenomenon detrimental to mechanical properties.

Figure 10 shows the fractographs observation of the optimal T0 and T15 specimens after 1280°C sintered for 1 h, respectively. The small carbide transgranular fracture surface of T0 specimen could be observed after 1280°C sintered for 1 h, as shown in Fig. 10(a). As mentioned previously, the T0 specimens had a continuous and network distribution of carbide precipitates after sintering at 1280°C for 1 h, which resulted in a lower TRS (1069.1 MPa). Figure 10(b) shows the fractographs observation of the T15 specimens by 1280°C sintered for 1 h; significantly, the fracture surface is almost the close pores. In addition to some areas exhibiting a dimple fracture structure, most of the morphology showed brittle fractures of small carbides. Therefore, TRS can reach the higher value (1485.1 MPa).

4. Conclusions

T0 specimens sintered at 1270°C for 1 h had the maximum TRS value (1128.8 MPa). However, the T0 specimens had a continuous and network distribution of carbide precipitates after sintering at 1280°C for 1 h, which resulted in a lower TRS (1069.1 MPa). Both the hardness and TRS of the composite materials were increased by adding the optimal volume of TiC powder to a cobalt-based alloy. The highest hardness value, HRA 80.4 was obtained by adding 20 mass% TiC powder; the TRS was not significantly enhanced due to the micro-cracks of nucleation. In addition, adding 15 mass% TiC of composite material created the highest TRS value (1485.1 MPa), and the hardness reached HRA 79.1. Therefore, adding 15 mass% TiC powder to a cobalt-based alloy and sintering at 1280°C for 1 h was the optimal process.
Two types of carbide precipitates were observed in the T0 specimen after vacuum sintering: M₆C and M₂₃C₆ carbides, both of which showed fine plate-like precipitates on the grain boundary. These precipitates along the grain easily led to the brittle fracture of the materials. Conversely, there were no M₆C carbide precipitates for the cobalt-based alloy when TiC powder (T10, T15 and T20) was added after the sintering process; only M₂₃C₆ carbides were randomly dispersed in the matrix. This study showed that a suitable amount of TiC powder (15 mass%) effectively inhibited the rapid growth of carbide precipitates, thereby increasing both the strength and hardness of the cobalt-based composite materials.

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