Effect of ball-milling process in combination with the addition of carbide microparticles on the microstructure and wear resistance of a Co–Cr–W alloy prepared by powder metallurgy method

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Abstract

Co–Cr–W alloys were widely used in the inlet exhaust valve of aeroengine. However, the traditional manufacturing process of Co–Cr–W alloys cannot meet the demand for higher comprehensive performance, and an optimum method needs to be developed. Herein, a Co–Cr–W alloy reinforced by exogenous carbides was prepared by the powder metallurgy method. Effect of ball-milling time on the microstructure and wear resistance of the alloy was investigated, and the formation mechanisms of the reinforcing phases were discussed. Results showed that with prolonging the ball-milling time, the uniformity of the reinforcing phases was improved, grain refinement was achieved, the hardness increased, a suitable bonding interface was formed between the matrix and reinforcing phases, and better wear resistance was thus achieved. However, when the ball-milling time increased from 60 h to 70 h, local segregation of the reinforcing phases occurred, the hardness decreased from 64 HRC to 60 HRC, and the friction coefficient increased from 0.53 to 0.58. Based on our experimental results, we proposed two formation mechanisms of the reinforcing phases (carbides): In-situ precipitation from the matrix and in situ autogenic reaction between the elements of the matrix and the added carbides (WC and Cr3C2 particles). Both mechanisms contributed to the formation of M23C6 and MC carbides. Our results underscore the importance of added reinforcing phases and help to optimize the ball-milling process in preparing the Co–Cr–W alloys.

1. Introduction

Co–Cr–W alloy is a kind of Co-based alloy, and Cr, W, Mo, Ni, Fe, and other elements are added as the strengthening elements. Due to its high hardness, wear resistance, corrosion resistance, and high-temperature oxidation resistance, Co–Cr–W alloy is widely used as surfacing welding, thermal spraying, powder metallurgy, casting, and forging materials. It is widely used in aerospace, medical, automotive processing, and manufacturing industries [1–5].

In the late 1920s, the Co–Cr–W alloy, which represents the Stellite series alloys, was used in the inlet exhaust valve of aeroengine. Since the start of application, considerable attention has been paid to the alloy, and a series of Co–Cr–W alloys were developed and widely used in many fields. The main reinforcing phases (carbides) of the Co-Cr-W alloy are MC, M6C, and M23C6 [6–12]. In general, the content of W in the alloy is lower than 20 wt% (as is provided in table 1), and the hardness is less than 60 HRC. When the W content is greater than 20 wt%, the brittleness is increased, the crack propensity is enhanced, and the machinability is significantly reduced [13–17].

With the increase of the thrust-to-weight ratio of aeroengine, demands for key materials are becoming increasingly stringent. The hardness and wear resistance of traditional Co-Cr-W alloy has been unable to meet the application requirements. Therefore, it is necessary to prepare the Co-Cr-W alloy with higher hardness and wear resistance. Sciullia et al. [18] studied the wear mechanism of Co-Cr-W alloy and stainless steel under high contact pressure. They found that there was an exponential relationship between the wear rate of Co-Cr-W alloy
and the pressure applied to the alloy. They also found the index relationship was affected by the friction pair materials and the sliding rate. Ma et al.\cite{19} prepared the Co-Cr-W alloy by casting. They found (i) increasing the superheat degree during casting can increase the size of the carbides and lower the tensile properties of the alloy; (ii) high-temperature solution treatment can dissolve the massive eutectics, decrease the size of the carbides and make them scattered in the matrix, which can improve the strength and plastic of the alloy. It has been reported that increasing the content of W in the Co-Cr-W alloy, whether prepared by casting or by powder metallurgy method, can increase the number and size of the uniformly dispersed carbides and increase the hardness of the alloy. Thus the friction and wear properties are significantly improved\cite{20–23}.

Based on the contradiction that high W content in the matrix can increase the wear properties but lower the toughness, a Co-Cr-W alloy was prepared to solve this problem, namely, the heterogeneous mixture of granular carbides (high in W) was added to Co-Cr-W alloy, with continuous metal substrates and the reinforcing phases. The added carbides were assumed to react with the matrix and consume the solution-strengthening elements in the matrix, which can improve the strength and plastic of the alloy. It has been reported that increasing the content of W in the Co-Cr-W alloy, whether prepared by casting or by powder metallurgy method, can increase the number and size of the uniformly dispersed carbides and increase the hardness of the alloy. Thus the friction and wear properties are significantly improved\cite{20–23}.

Table 1. Chemical compositions (wt%) and hardnesses of Stellite alloy.

| Alloy   | Cr  | C   | W   | Mo | Ni | Si | Fe | Mn | Co | Hardness(HRC) |
|---------|-----|-----|-----|----|----|----|----|----|----|---------------|
| Stellite 1 | 33  | 2.45 | 13  | —  | 2.5 | 1  | 2.5 | 1  | Bal | 51–58         |
| Stellite 3 | 31  | 2.5  | 13  | —  | 2.5 | 1  | 2.5 | 1  | Bal | 51–58         |
| Stellite 4 | 31.5| 1    | 14  | —  | 2.0 | 1  | 2.0 | 1  | Bal | 45–49         |
| Stellite 6 | 28  | 1.2  | 5   | —  | 3.0 | 1  | 2.5 | 1  | Bal | 39–43         |
| Stellite 12 | 29  | 1.85 | 9   | —  | 2.5 | 1  | 2.5 | 1  | Bal | 47–51         |
| Stellite 20 | 33  | 2.45 | 17.5| —  | 2.5 | 1  | 2.5 | 1  | Bal | 55–59         |
| Stellite 31 | 26  | 0.5  | 7.5 | —  | 10.5| 1  | 2.0 | 1  | Bal | 30–35         |
| Stellite 8 | 27  | 0.6  | —   | 6  | 2   | —  | —   | —  | Bal | 30–35         |
| Stellite 306 | 25  | 0.4  | 2   | —  | 6.0 | 1  | 4.0 | 1  | Bal | 19–31         |

and the pressure applied to the alloy. They also found the index relationship was affected by the friction pair materials and the sliding rate. Ma et al.\cite{19} prepared the Co-Cr-W alloy by casting. They found (i) increasing the superheat degree during casting can increase the size of the carbides and lower the tensile properties of the alloy; (ii) high-temperature solution treatment can dissolve the massive eutectics, decrease the size of the carbides and make them scattered in the matrix, which can improve the strength and plastic of the alloy. It has been reported that increasing the content of W in the Co-Cr-W alloy, whether prepared by casting or by powder metallurgy method, can increase the number and size of the uniformly dispersed carbides and increase the hardness of the alloy. Thus the friction and wear properties are significantly improved\cite{20–23}.

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2. Experimental

Two methods were adopted to prepare the Co-Cr-W alloy (the Co-Cr-W alloy with high W content as the matrix, M₆C and M₂₃C₆ carbides as the reinforcing particles), namely: (1) the WC, Cr₃C₂ particles were mixed with Co-Cr-W alloy powder, the carbide particles reacted with matrix in the process of ball milling and sintering, new carbide reinforcing phases with excellent bonding interface with the matrix were formed (as shown in figure 1). The following will be referred to as the exogenous particles method (EXPM); (2) only pure Co-Cr-W alloy powder was processed by high-energy ball milling and high-temperature sintering. During this process, the carbide reinforcing phases were in situ generated, which was used to compare the microstructure and mechanical properties with that of the alloy prepared by EXPM. The following will be referred as the endogenous particle method (ENPM).
Co-Cr-W alloy powder was prepared by gas atomization. The preparation process was as follows: the pre-alloyed ingot with uniform composition was smelted by vacuum induction smelting equipment. Then the pre-alloyed ingot was prepared into spherical pre-alloyed powder by vacuum gas atomization method, the compositions of the alloy powder are listed in table 2. Finally, the alloy powder with a size of less than 50 μm was screened out. The WC and Cr3C2 particles are commercial products with a size of less than 5 μm. To obtain the alloy, 3% WC and 2% Cr3C2 particles were mixed with 95% Co-Cr-W alloy powder (mixing mass fraction) to prepare the mixed powder.

The Co-Cr-W alloy powder and the mixture of Co-Cr-W + 3% WC + 2% Cr3C2 (mass fraction) were mixed with the paraffin molding agent in a certain proportion and milled mechanically for 24–72 h in the QM-3SP2 planetary high-energy ball milling equipment to improve the surface activity of the powder. WC/Co carbide tank and cylindrical balls were used for the high-energy ball milling, and the ratio of ball to material was 6:1. The speed of ball milling was 240–360 r min−1. The powder after ball milling was pressed into 21 mm × 6.5 mm × 5.5 mm samples by the compression molding method. The samples were put into a vacuum sintering furnace, which was heated to 200 °C at the rate of 20 °C min−1 and kept for 30 min. Then it was continued to rise to 400 °C at a rate of 20 °C min−1 and kept for 60 min to make the molding agent fully volatile. Finally, raise the temperature to 1270 °C at a rate of 5 °C min−1 and kept for 240 min, then furnace cooling.

The microstructures of the Co-Cr-W powder, carbide particles, and sintered samples were obtained by an S-3400 scanning electron microscope (SEM). The average size and volume fraction of carbides in the matrix were analyzed by Image-Pro-Plus 6.0 software, and each value was measured three times on different samples. Tecnai-T20 transmission electron microscopy (TEM) and x-ray diffraction (XRD) were utilized to analyze the phases in the alloy. The SHIMADZU-1610 Electron Probing Microanalysis (EPMA) was used to analyze the composition of microregions. Nordysnano electron backscatter diffractometer (EBSD) was used to analyze the grains’ orientation in the alloys. FCR-500 hardness tester was utilized to test the hardness of the Co-Cr-W alloys prepared by EXPM. Six random positions were selected for hardness testing to get the average values. UMT-3 friction and wear testing machine was used to test the friction coefficient, and Instron-5569 universal testing machine was used to test the absorbed energy (toughness). The hardness, friction coefficient, and the absorbed energy of the samples were measured on three different samples to get the average value. TEM samples were thinned by double spray electrolysis. The electrolyte composition was 7% HClO4 + 93% C2H5OH (volume fraction), the coolant was dry ice, the voltage was 50V, the current was 30mA, and the temperature was below −20 °C. The sample observed by EBSD was electrolytic polished. The electrolytic etching solution was prepared with 42% H3PO4 + 34% H2SO4 + 24% H2O (volume fraction).

| Elements | Cr | W | Ni | V | Fe | C | Co |
|----------|----|---|----|---|----|---|----|
| Co-Cr-W  | 30 ~32 | 18 ~20 | 3 ~4 | 3 ~5 | 3 ~4 | 0.2 ~0.8 | Bal. |

Figure 2. SEM images of Co-Cr-W alloy and carbide powders. (a), (b) Co-Cr-W alloy powder prepared by atomization pulverization; (c) WC powder; (d) Cr3C2 powder; (e), (f) Co-Cr-W alloy powder prepared by ball milling.
3. Results and discussion

3.1. Microstructure of the raw materials

Figure 2 shows the morphology of the Co-Cr-W alloy and carbide powders. It can be seen the Co-Cr-W alloy powder particles have spherical morphology, and the average particle size is ~50 μm (figures 1(a) and (b)). The size of WC particles is less than 10 μm, as is shown in figure 1(c); the size of Cr3C2 particles is less than 5 μm, as is shown in figure 1(d). Figures 1(e) and (f) show the morphology of Co-Cr-W alloy powder after ball milling for 60 h.

Figure 3. Low (a), (c) and high (b), (d) magnified SEM images of Co-Cr-W alloy with 60 h ball-milling time and 1270 °C/240 min solid phase prepared by ENPM (a), (b) and EXPM (c), (d).

Figure 4. X-ray diffraction (XRD) analysis of phases in the EXPM prepared Co-Cr-W alloy.
Figure 5. The element distribution maps of a micro-area of the EXPM prepared Co-Cr-W alloy.

Figure 6. TEM image (a) and SAED patterns (b–e) of the Co-Cr-W alloy.

Table 3. The EPMA result of phases in Co-Cr-W alloy (at %).

| Position in figure 3 | C   | Co  | Cr  | Ni  | Fe  | V   | W   | O   | Phase     |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----------|
| 1                    | 4.5 | 37.6| 37.1| 3.5 | 4.7 | 5.8 | 6.8 | —   | γ-Co      |
| 2                    | 6.4 | 47.3| 26.0| 8.0 | 6.2 | 4.0 | 2.1 | —   | ε-Co      |
| 3                    | 16.5| 23.8| 22.4| 2.7 | 2.3 | 12.0| 20.3| —   | M_6C      |
| 4                    | 21.4| 7.3 | 54.9| 1.0 | 1.6 | 8.5 | 5.3 | —   | M_{23}C_6 |
| 5                    | 5.3 | 2.5 | 11.4| 2.0 | 1.7 | 32.0| 1.0 | 44.1| V_{2}O_{3}|

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3.2. Microstructure of the Co-Cr-W alloys

Figure 3 shows the SEM images of the microstructure of Co-Cr-W alloys obtained by EXPM and ENPM. Based on the contrast of the SEM images, it can be seen that the phase components of the two alloys are similar, and there are mainly five phases in the two alloys. The matrices are composed of dark gray and light gray phases (see phases 1 and 2 in figure 3(d)). There are two kinds of blocky phases. One is white, the other is gray (see phases 3 and 4 in figure 3(d)). Besides, there are a small amount of black granular phases, which are uniformly distributed in the matrices (see phase 5 in figure 3(d)).

Figure 4 shows the XRD patterns of the two alloys. The results indicate the presence of two cobalt solid solutions ($\gamma$-Co and $\varepsilon$-Co) and two carbides (M$_{23}$C$_6$ and M$_6$C). In order to identify the phases in the alloys (the five phases in figure 3(d)), EPMA and TEM were used. As the phase components of the two alloys are similar, only the EXPM prepared alloy was analyzed. Table 3 lists the EPMA result of the five phases in figure 3(d), and figure 5 shows the distribution of elements of a micro area containing the phases mentioned above (represented by 1, 2, 3, 4, and 5). It can be seen that Phase 1 is a Co rich phase, which contains a higher content of Cr, Ni, and a
small amount of V. Combined with the analysis of the selected area electron diffraction (SAED) pattern (shown in figure 6(c)), it can be confirmed the phase is γ-Co with FCC structure, namely a kind of Co-based solid solution. The solution elements are Cr, W, Ni, Fe, V, and a small amount of C. Phase 2 is also a Co rich phase, which contains Cr, W, Ni, Fe, V, and other elements. By analyzing the SAED pattern (shown in figure 6(b)), it can be confirmed phase 2 is ε-Co with HCP structure. The content of W in phase 3 is high and contains a small amount of Ni, Co, and Cr. The SAED pattern indicates the crystal structure of the phase is FCC. According to [12], M₆C type carbide is rich in W with FCC structure. Therefore, phase 3 can be identified as M₆C type carbide, namely (W, Co, Cr, Fe)₆C with FCC structure. Phase 4 is a Cr rich phase, and the SAED pattern indicates the crystal structure of the phase is also FCC. According to [13–16], M₂₃C₆ type carbides are usually rich in Cr and poor in W. Therefore, phase 4 can be identified as M₂₃C₆ type carbide, namely (Cr, W, V, Fe)₂₃C₆ with FCC structure. The EPMA result shows that the main component of phase 5 is V, Cr, and O. According to the Materials Project database, fourteen kinds of stable phases for the V–Cr–O system can be found. The ternary phase diagram for formation energy was obtained as shown in figure 7. It can be seen the formation energy of V₂O₃ is the lowest, which was more likely to form during the ball-milling process. Besides, the atomic ratio of O and V is 1.38, which is closer to V₂O₃. Therefore, phase 5 can be inferred to be V₂O₃.

Figures 8 and 9 shows the EBSD results of the Co–Cr–W alloy. It can be seen from the polar figures and orientation distribution function (ODF) that the matrix phase (γ-Co) has two kinds of textures, namely the \(<100>\) ∥Z0 and \(\{001\}<110>\) (see figures 9(a) and (c)), which might be produced in the process of compression. The polar density distribution is relatively uniform across the polar figure (figure 9(b)), which indicates the M₂₃C₆ has no obvious preferred orientation. One reason for this may be that the M₂₃C₆ phases were formed in cooling process of the sintering, which had little effect on the formation of texture. Another reason for this may attribute to the measuring errors as the the content of M₂₃C₆ phases is relatively low, which may lead to the measuring errors. According to the IPF figure (figure 8), it can be seen the grain is non-spherical and uniform, and the average grain size is less than 10 μm, which is smaller than the average particle size of the Co–Cr–W alloy powder (shown in figure 2). This proves that the Co–Cr–W alloy powder was broken during the high-energy ball milling process, and the powder size was reduced from 50 μm to 10 μm when the ball-milling time was extended to 60 h. Besides, it can also be observed from figure 6 that the carbides can form a good interface with the matrix, which can effectively improve the hardness and wear resistance of the alloy.

3.3. Effect of ball-milling time on microstructure and properties

Figure 10 shows the microstructures of the two kinds of alloys prepared by EXPM and ENPM with different ball-milling times. It can be observed that there is no significant difference in phase constituent between the two alloys (based on the contrast of the SEM image), but the size and content have changed. The carbides prepared by...
ENPM are small, and the content is approximately 1.7%–2.0% (volume fraction), while the carbides prepared by EXPM are bigger, and the content is approximately 3.4%–4.4% (volume fraction). The EXPM prepared alloy contains two kinds of carbides, namely small dispersion particles (endogenous) and blocky carbides (exogenous). In addition, with the prolonging of milling time, the size of the carbides in both alloys decreases.

Figures 10(a), (c), (e), (g) show the microstructures of the alloy prepared by ENPM. When the ball-milling time is 24 h, Co-Cr-W alloy powder is sintered after ball milling. The reinforcing phases are mainly in situ
and friction coefficient, respectively. It can be seen that the alloy prepared by EXPM has a higher average hardness and lower friction coefficient.

The indentifi
cation of the phases is based on the contrast of the SEM image, which is discussed on in section 3.2.

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Figure 11. The effect of ball-milling time on the average size and volume fraction of carbides of Co-Cr-W alloy prepared by ENPM and EXPM. (a) average size of carbides; (b) volume fraction of carbides.
corresponding friction coefficient decrease with the prolonging of ball-milling time. However, when the ball-milling time is 72 h, the hardness decreases, and the friction coefficient increases. Besides, it should be noted that there are some differences in the hardness and friction coefficient between each sample, which were prepared at the same ball-milling process. On the one hand, the instrumental uncertainties would cause the measuring errors; on the other hand, the inhomogeneous of the microstructure would also cause errors, which we think is an important reason as the carbides distributed inhomogeneously when the ball-milling time was relatively short (see figures 10(a) and (b)). This would inevitably lead to bigger measuring errors (see figure 12). However, this would not affect the whole trend when analyzing the average value, and the results are relatively convincing.

According to [28], the hardness has a better proportional relationship with the yield strength ($\sigma_{0.2}$), so the hardness can be characterized by $\sigma_{0.2}$. The total strength of an alloy system can be described by a superposition of different strengthening factors $\Delta\sigma_i$ contributing to the total strength [29], which is given by

$$\sigma_{\text{total}} = \sum_i \Delta\sigma_i$$

where $i$ refers to the strengthening mechanism. In the prepared Co–Cr–W alloys, the main strengthening factors are solid solution strengthening ($\Delta\sigma_S$), carbides strengthening ($\Delta\sigma_C$), and grain boundary strengthening ($\Delta\sigma_{GB}$). Based on this model, the total strength of the Co–Cr–W alloys can be expressed as follows:

$$\sigma_{0.2} = \sigma_{\text{Co}} + \Delta\sigma_S + \Delta\sigma_C + \Delta\sigma_{GB}$$

where $\sigma_{\text{Co}}$ represents the Co-based matrix.

Thus, the reason for the difference and evolution of hardness and friction coefficient of the two alloys can be explained by expression (2). In this model, the matrixes of the alloys contain $\gamma$-Co and $\varepsilon$-Co phases. As the FCC structural $\gamma$-Co has more slip systems than that of the HCP structural $\varepsilon$-Co, the $\gamma$-Co should have better plastic property than that of the $\varepsilon$-Co. From this point, the $\varepsilon$-Co may have higher strength than the $\gamma$-Co. As the ENPM prepared alloy has a higher proportion of $\varepsilon$-Co, the $\sigma_{\text{Co}}$ in expression (2) should be higher. However, as 3% WC + 2% Cr$_3$C$_2$ was added to EXPM prepared alloy, the content of W and Cr and the volume fraction of the carbides in the EXPM prepared alloy is higher than that of the ENPM prepared alloy, so the $\Delta\sigma_S$ and $\Delta\sigma_C$ should be higher in the EXPM prepared alloy. Besides, there is little difference between the grain sizes of the two alloys. Still, the added carbides can lead to higher content of carbides on the grain according to the schematic in figure 1, so the $\Delta\sigma_{GB}$ of the EXPM prepared alloy should be higher than that of the ENPM prepared alloy. To sum up, although the first term in expression (2) is higher in the ENPM prepared alloy, the last three terms are much higher in the ENPM prepared alloy, which makes the hardness is higher and the friction coefficient is lower in the EXPM prepared alloy.

With prolonging the ball-milling time, the proportion of different phases and the size of the grain boundary in the two alloys have little changes. Meanwhile, the solid solution elements keep a constant. So the first two and the last terms in expression (2) have little changes as the ball-milling time increase. However, the uniformity of the different phases in the two alloys changes a lot. So we think the uniformity of different phases plays a key role in the evolution of the hardness and friction coefficient of the two alloys.

As it can be seen in this study, in the time range of 0–60 h, the uniformity of the different phases becomes better with prolonging the ball-milling time and the dispersion strengthening effect of different phases becomes enhanced. Therefore, the hardness of the two alloys has increased. Another reason for the increase in hardness is
the formation of the uniformly distributed V₂O₃ particles in the matrices, which may also strengthen the alloys. However, when the ball-milling time is 72 h, the carbides appear to be partially segregated, as can be seen from figures 9(g)–(h). This may lower the dispersion strengthening effect of the second phases. Therefore, the hardness decreases, and the corresponding friction coefficient increase.

As the proper ball-milling time is 60 h, it is adopted for the comparison of the toughness. Figure 13 shows the results of three-point bending experiments. It can be seen the alloy prepared by EXPM has higher absorbed energy than that of the alloy prepared by ENPM. This indicates the added carbides can not only increase the wear resistance but also can increase the toughness (figures 12, 13). This may attribute to the reaction between the added particles and the elements in the matrix. In the process, the added particles consumed the solution-strengthening elements (Ni, Cr, W, etc.) in the matrix (see part 3.4 in equations 5–6) and lowered the brittleness of the matrix.

3.4. Formation mechanisms of the carbides

In the process of high-energy ball milling, the grains grew refining, and carbides became uniform and smaller in size, which indicate both metal powder and carbide powder were broken under the action of ball-milling energy, forming the small-size particles. These particles do not recrystallize or grow up during the sintering process. It is worth noting when the ball-milling time is 24 h, there are many large-size carbides (over 50 µm) in the alloys, and when the ball-milling time is 72 h, the carbides in the alloys is less than 10 µm. This fully proves that M₆C and M₂₃C₆ carbides can be in situ formed during ball-milling process (see figure 6(a)). The equation is as follows:

\[
\gamma - Co + C \rightarrow (W, Co, Cr, Fe)6C \\
\gamma - Co + V + C \rightarrow (Cr, W, V, Fe)23C6
\]

The carbides larger than 10 µm in the EXPM alloy, including the blocky M₆C and the striped M₂₃C₆, are in situ formed by the addition of WC and Cr₃C₂ particles during the process of the ball milling and sintering. The phase transformation processes are as follows:

\[
WC + \gamma - Co \rightarrow (W, Co, Cr, Fe)6C \\
Cr₃C₂ + \gamma - Co \rightarrow (Cr, W, V, Fe)23C6
\]

Therefore, the reinforcing phases M₆C and M₂₃C₆ in Co-Cr-W alloy have two formation mechanisms: one is the in situ endogenous mechanism by phase transformation; the other is the in situ exogenous mechanism by the reaction.

Through comprehensive analysis, it is found the matrix of Co-Cr-W alloys is mainly composed of \(\gamma\)-Co and \(\varepsilon\)-Co at room temperature. However, it has been reported [9–11] the crystal structures of \(\gamma\)-Co and \(\varepsilon\)-Co are FCC and HCP, respectively. The \(\gamma\)-Co is stable at high temperature, while \(\varepsilon\)-Co is stable at low temperature, and the transition temperature of the two phases is 417 °C. As the matrix of the alloy in this work contains many alloy elements such as W, Ni, Cr, V, Fe, etc., they may affect the transformation condition of \(\gamma\)-Co and \(\varepsilon\)-Co. The reported Co-based alloy can be used to analyze the reason, which contains many alloy elements such as W, Ni, Cr, etc., and the matrix only contains the \(\gamma\)-Co [30, 31]. This indicates the alloy elements can lower the transition temperature from \(\gamma\)-Co to \(\varepsilon\)-Co. Therefore, parts of the high-temperature stable phases (\(\gamma\)-Co) are preserved in the cooling process. In addition, after a long time of high-energy ball milling, the activation energy of the phase formation may change, which to some extent changes the transition condition of the two phases.
The characteristic of the matrix is closely related to the distribution of carbides, namely, the ε-Co is distributed around the M₆C, as is shown in figure 10. It is found that compared with γ-Co, the content of W and Cr in ε-Co is lower, and the content of Fe and Ni is higher, while the contents of W and Cr in the carbide are higher, and the contents of Fe and Ni are lower. This indicates that in carbide formation, elements such as W and Cr reacted with C and in situ formed carbide. Therefore, the content of W and Cr in the matrix around the carbide decreases. During the cooling process, as the alloy elements (W and Cr) were consumed by the carbide, the phase transformation driving force of γ-Co to ε-Co increases, so the γ-Co near the carbide changes to ε-Co. It follows then that in Co-Cr-W alloy, the change of element composition is also one of the driving forces to promote the transformation of γ-Co and ε-Co.

4. Conclusions

(1) There are five phases in the carbide strengthened Co-Cr-W alloy prepared by means of endogenous and exogenous particles methods using powder metallurgy technology. The matrix is γ-Co with FCC structure and ε-Co with HCP structure. The reinforcing phases are M₆C and M₂₃C₆, and a small amount of V₂O₃.

(2) Under the same sintering process, by prolonging the ball-milling time, the content of carbides in the Co-Cr-W alloys prepared by EXPM and ENPM remains unchanged. Still the distribution uniformity increases, the grains grow fine, and the hardness increases.

(3) As for the hardness and friction coefficient, there is an inflection point for the ball-milling time. When the ball-milling time reaches 60 h, the volume fraction, distribution, and size of carbides are moderate, and the partial segregation of the two-phase matrix is not obvious, which makes the hardness is the highest and the friction coefficient is the lowest.

(4) In Co-Cr-W alloy, two formation mechanisms account for the formation of carbides: the granular M₆C and M₂₃C₆ carbides are in situ formed during ball milling; the blocky M₆C and stripped M₂₃C₆ are in situ formed by the addition of WC and Cr₃C₂ particles during ball milling and sintering. The precipitation of carbides is one of the driving forces to promote the transformation of γ-Co and ε-Co.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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References

[1] Birol Y 2010 Inconel 617 and Stellite 6 alloys for tooling in thixoforming of steels T. Nonferr. Metal. Soc. 20 1656
[2] Liu R et al 2015 Effects of molybdenum content on the wear/erosion and corrosion performance of low-carbon Stellite alloys Mater. Design. 78 95
[3] Liu R et al 2015 Microstructures and hardness/wear performance of high-carbon Stellite alloys containing molybdenum Metal. Mater. Trans. A. 46 5504
[4] Malayoglu U and Neville A 2003 Comparing the performance of HIPed and Cast Stellite 6 alloy in liquid-solid slurries Wear 255 181
[5] Ahmed R et al 2013 Influence of Re-HIPing on the structure-property relationships of cobalt-based alloys Tribol. Int. 57 8
[6] Kapoor S et al 2013 Microstructure and wear resistance relations of Stellite alloys Inter. J. Adv. Mater. Sci. 4 231 (https://www.researchgate.net/publication/284674237_Microstructure_and_wear_resistance_relations_of_Stellite_alloys)
[7] Liu R et al 2015 Effects of molybdenum content on the wear/erosion and corrosion performance of low-carbon Stellite alloys Mater. Des. 78 95
[8] Liu R et al 2015 Microstructures and hardness/wear performance of high-carbon Stellite alloys containing molybdenum Metal. Mater. Trans. A. 46 5504
[9] Malayoglu U, Neville A and Beamson G 2005 Characterisation of the passive film on HIPed Stellite 6 alloy using x-ray photoelectron spectroscopy Metal. Mater. Trans. A. 393 91
[10] Viennot S et al 2006 Combination fixed and removable prostheses using a CoCr alloy: a clinical report J. Prosthet. Dent. 96 100
[11] Rada I, Li D Y and Llewellyn R 2004 Tribological behavior of Stellite 21 modified with yttrium Wear 257 1154
[12] Hamr S et al 1982 Carbide transformation during aging of wear-resistant cobalt alloys Met. Trans. A. 13 545
[13] Shimizu T, Ikeda Y and Takayama S 1994 (CoCr)1-xM(x)(M = Pt, Ta, W) composite magnetic thin films with admixed SiO2 Adv. Mater. 76 799 (https://www.researchgate.net/publication/300963482_CoCr1-xM(x)_Pt_Ta_W_composite_magnetic_thin_films_with_admixed_SiO2)
[14] Jeshvaghani R A, Shamarian M and Jaberzadeh M 2011 Enhancement of wear resistance of ductile iron surface alloyed by stellite6 Mater. Des. 32 2023
[15] Yang Z Y and Zhou J P 2006 Study on the properties of HVOF Sprayed Co-Cr-W coating China. Surf. Eng. 19 36 (http://www.en.cnki.com.cn/Article_en/CJFDTotal-BMG200602008.htm)
[16] Zhong M L and Liu W J 2002 Microstructure evolution of stellite 6 + WC by high power laser cladding Acta. Metall. Sin. 38 495
[17] Xiong Y et al 2008 Microstructures and properties of laser cladding stellite6/WC China. Surf. Eng. 21 37 (https://xueshu.baidu.com/usercenter/paper/show?paperid=03a3ef4595ad3c16225ab35906a71930&site=xueshu_se&hitarticle=1)
[18] Sciullia E B and Robinsona G M 2008 A study of the effect of wear particles and adhesive wear at high contact pressures Tribol. 255 312
[19] Ma X P and Li C 2014 Effect of superheat temperature for casting and heat treatment on microstructure of CoCrMo alloy J. Mater. Eng. 3 66
[20] You X H et al 2016 Effect of solid solution treatment on microstructure and mechanical properties of hot-press Co-Cr-W alloys Acta. Metall. Sin. 52 161
[21] He B et al 2016 Effects of solution treatment on microstructure and wear-resistant properties of Co-Cr-W alloys Acta. Metall. Sin. 52 248
[22] Wang G G et al 2015 Microstructure and Mechanical Properties of As-cast and Hot-pressed Co-Cr-W Alloys Foundr. Eq. Technol. 2 47 (https://www.zhangguokeyan.com/academic-journal-cn_foundry-equipment-technology_thesis/0201223532205.html)
[23] Liang J Q et al 2017 Effect of sintering temperature on microstructures and mechanical properties of Co-based wear-resistant alloy PM Technol. 35 188
[24] Liu B X et al 2014 Gradient grain distribution and enhanced properties of novel laminated Ti-TiB/ Ti composites by reaction hot-pressing Mater. Sci. Eng. A 595 257
[25] Li S et al 2013 Powder metallurgy Ti-TiC metal matrix composites prepared by in situ reactive processing of Ti-VGCFs system Carbon 61 216
[26] Zhang C et al 2012 Evolution of microstructural characteristic and tensile properties during preparation of TiB/Ti composite sheet Mater. Des. 36 305
[27] Li S et al 2013 Powder metallurgy titanium metal matrix composites reinforced with carbon nanotubes and graphite Compos. A. 48 57
[28] Osada T et al 2013 Optimum microstructure combination for maximizing tensile strength in a polycrystalline superalloy with a two-phase structure Acta Mater. 61 1820-9
[29] Nembach E 1996 Particle Strengthening of Metals and Alloys. (New York: Wiley) p 253
[30] Wang S Y et al 2019 Borides of preferred orientation formed in the transient liquid phase joint of γ′-strengthened Co-base single crystal superalloy Mater. Lett. 246 190
[31] Wang S Y et al 2021 Effect of post-bond heat treatment on the microstructure and high temperature mechanical property of a TLP bonded γ′-strengthened Co-based single crystal superalloy J. Mater. Sci. Technol. 30 244