Preparation of Al$_2$O$_3$/W-Cr composite and its tribology properties

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Abstract. Microstructure and its formation process as well as tribology properties of Al$_2$O$_3$/W-Cr composite prepared by sol-gel and powder metallurgy method were studied in this paper. Results show that the Al$_2$O$_3$ particles can be distributed uniformly in the mixed powders of W-Cr by sol-gel method, and metallurgical bonding between W and Al$_2$O$_3$ particles can also be realized by the bonding action of Cr particles. The wear rate of Al$_2$O$_3$/W-Cr composite increases with the increase of testing load, but the friction coefficient increases firstly and then decreases. When the testing load is 15 N, the friction coefficient reaches the peak value. Wear mechanism of Al$_2$O$_3$/W-Cr composite is dominated by abrasive wear at lower testing loads, but transfer to adhesive wear accompanied with oxidation at high testing loads.

1. Introduction

Seamless steel pipe is one type of circular steel tubes with hollow cross section and no circumferential weld, which is formed by piercing a solid round billet or a steel ingot into a workblank pipe following by cold rolling, cold drawing or hot rolling. Hence, the piercing plug and extruding die inner sleeve are main components that determine the dimension and surface quality of seamless steel pipe. During the production of seamless steel pipe, the extruding die inner sleeve is subjected to high temperature changes (thermal fatigue), larger impact force and friction and wear at high temperature. These hard working conditions seriously decreases the service life of dies, and also affects the production efficiency and economic benefits of enterprises. Although most of the extruding die inner sleeves are made of H13 hot die steel, the its lower wear resistance at high temperature becomes the biggest obstacle [1]. Therefore, developing a new material to replace H13 steel is an very urgent challenge in modern industry.

Tungsten and tungsten alloys are one of the main materials used in high temperature applications, since their high melting point, high strength, low coefficient of thermal expansion and good machinability [2,3]. However, the high embrittlement transition temperatures limits their applications under impact load at high temperature. In order to overcome this problem, tungsten-based composite materials reinforced by particles are considered to be the most prospective way, and the common reinforcements are Al$_2$O$_3$, TiC, ZrC, HfC, SiC, B$_4$C, La$_2$O$_3$, Y$_2$O$_3$, TiB$_2$ and so on [4~17], which can improve the brittleness, hardness, wear resistance and other high temperature properties of tungsten alloys significantly. Among them, Al$_2$O$_3$ particles is one of preferred strengthening particles since its cheap price as well as high hardness and stiffness. Microhardness values can increase significantly from 4.07±0.16 GPa to 5.98±0.31 GPa by adding 2wt% Al$_2$O$_3$ particles W-1%Ni alloy [4]. However, since
there is not reaction or dissolution between W and Al₂O₃ particles, the interfacial bonding between them are always very weak, and then Al₂O₃ particles are easy to fall off from the W matrix and scratch the surface of the contacting component.

In order to achieve a good bonding between tungsten and Al₂O₃ particles, Cr was selected as an additive since it could form solid solutions with both W and Al₂O₃ [18,19]. On this basis, Al₂O₃/W-Cr composite was prepared by the method of sol-gel and hot-pressed sintering, and then its friction and wear properties were investigated.

2. Experiment procedures
Tungsten powder (99.9% purity, 6μm average particle size), chromium powder (99.9% purity, 5μm average particle size) and aluminum nitrate (Al(NO₃)₃·9H₂O, 99.8% purity) were used as raw materials to prepare Al₂O₃/W-Cr composite with 5vol% Al₂O₃ particles, and the operations were as follows. Firstly, Al(NO₃)₃·9H₂O was dissolved into ethanol, and then tungsten and chromium powder were added at a mass ratio of 3:2 and stirred for 1hr. Secondly, NH₃·H₂O was added into the mixed solution drop by drop, until the pH value of the solution reached 8, and then further stirred for 5hrs. Thirdly, the mixed solution was filtered by a Buchner funnel to obtain a viscous mixed wet powder, and then washed with alcohol and filtered for 3 times to obtain viscous mixed sol powder. Fourthly, the mixed sol wet powder was dried at 50 °C for 10 hrs followed by at 200 °C for 10 hrs to obtain sol-gel mixed powder. Finally, the mixed powder was placed in metal mold and pressed into a cylindrical preform with ϕ10 mm × 10 mm under a pressure of 500 MPa, and then sintered at 1500 °C for 2 hrs with a heating rate of 8 °C/min.

The compactness of the composite is expressed in terms of relative density, which is the specific value of actual density to theoretical density. The actual density is determined by the Archimedes drainage method, while the theoretical density is calculated using the formula (1).

\[ \rho_t = \sum \rho_i V_i \]  

where, \( \rho_t \) is the theoretical density of the composite, \( \rho_i \) and \( V_i \) are the theoretical density and volume percentage of each component in the composite.

Microstructures of the composite were observed on OLYMPUS-GX71 metallographic microscope and JSM-6700F field emission scanning electron microscope (SEM). Chemical composition of microzone was performed on an Oxford-type energy dispersive spectrum (EDS) equipped with SEM. Friction and wear properties were carried out on the HT-1000 pin-on-disk type friction and wear tester. The pin with size of 5mm × 5mm × 4mm was made of the Al₂O₃/W-Cr composite, and the disk with size of φ41 mm × 3mm was made of medium carbon steel. The experimental load was selected as 5~20 N, the rotational speed was 400 r/min, and the total sliding distance was about 380 m. The weights of pin sample before and after friction and wear test were weighed on an electronic balance with the accuracy of 0.1 mg, and thus the wear rate was expressed as the volume wear rate per unit load unit distance.

3. Results and discussion
3.1. Microstructure of the composite
Microstructure of Al₂O₃/W-Cr composite is shown in figure 1. It can be seen that the composite consists of some black particles, dark gray grains and a large amount of light gray phase. XRD testing result shows that the main phases of the composite are W, Cr and Al₂O₃, as shown in figure 2. EDS results show that the black particles mainly consists of Al, O and Cr elements, and the content of O (57.55at%) is approximately equal to that in Al₂O₃ compounds (60wt%), as shown in figure 3 and Table 1. Therefore, we can identify these black particles as the solution of Al₂O₃ with Cr, which would be marked by (Al,Cr)₂O₃. The light grey and dark grey phases consist of same elements, viz. W and Cr, but the chemical contents are very different from each other. The main element in the light grey phase is Cr, but that in dark grey one is W. Combining with the XRD patterns, it can be confirmed that the light grey phase is the solution of Cr with W (marked as Cr(W)), while the dark grey one is the solution of W with
Cr (marked as W(Cr)), respectively. On the other hand, no pore or crack can be seen obviously, agreeing well with the high compactness 94.35%.

**Figure 1.** Microstructure of the composite

**Figure 2.** XRD diffraction pattern of the composite

3.2. Microstructure formation of the composite

After ammonia water was dropwise added into ethanol solution of Al(NO₃)₃, it would react with Al(NO₃)₃ by reaction formula (2), and then white flocculent Al(OH)₃ would precipitate.

\[
\text{Al(NO}_3\text{)}_3 + 3\text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 \downarrow + 3\text{NH}_4\text{NO}_3 \quad (2)
\]

Thus, the mix powder after filtering is composed of W powder, Cr powder and Al(OH)₃ powder, as detected by XRD analysis in figure 4. During the subsequent sintering process, Al(OH)₃ powder in the mix powders will be decomposed to form Al₂O₃ particles, Cr atoms diffuses into Al₂O₃ and substitute some Al to form (Al, Cr)₂O₃ ternary compounds, since they have same chemical state. On the other hand, Cr and W can also dissolve into each other, and then form Cr(W) and W(Cr), corresponding to the light grey and dark grey phase, respectively.

**Figure 3.** The point tested by energy spectrum

**Figure 4.** XRD diffraction pattern of the mixed powder before sintering

| Table 1. The composition of each point in figure 3 (EDS) |
|----------------|----------------|----------------|----------------|
| element | weight % | atom % | element | weight % | atom % | element | weight % | atom % |
| Cr      | 59.67    | 83.95  | Cr      | 8.17     | 23.93  | O       | 38.42    | 57.55  |
| W       | 40.33    | 16.05  | W       | 91.83    | 76.07  | Al      | 32.97    | 29.27  |
| W       | 28.59    | 13.18  | Al      | 7.65     | 5.66   | O       | 4.31     | 4.96   |

| D       | Cr      | 17.01  | Al      | 32.64  |
|---------|---------|--------|---------|--------|
| W       | 71.03   | 56.74  | O       | 4.96   |
Figure 5 shows the EDS linear scanning result around the \((\text{Al, Cr})_2\text{O}_3\) particles. It can be found that, there is a high content of Cr in the area corresponding to \((\text{Al, Cr})_2\text{O}_3\) particles and also a gradient of all the detected elements, suggesting a metallurgical bonding between matrix and reinforced particles. This phenomenon indicates that the poor interfacial bonding between W and \(\text{Al}_2\text{O}_3\) can be improved by using the sintering additive Cr powder.

![EDS linear scanning result](image)

**Figure 5.** Result of EDS line scanning (a) scanning position, (b) elements distribution

### 3.3. Friction and wear properties of the composite

The friction and wear properties of \(\text{Al}_2\text{O}_3/W-\text{Cr}\) composite are shown in figure 6. It can be seen that both the friction coefficient and wear rate increase with the increase of loads firstly, but the friction coefficient would be decreased when the load is over 15 N. When the load is small, the contact area between the friction pairs is relatively small, and the raised \(\text{Al}_2\text{O}_3\) hard particles on the composite surface act as a load fulcrum. In this case, the frictional resistance between the friction pairs is small, resulting in a small friction coefficient. With the increase of load, the contact area between the friction pairs also increases, and hence the frictional resistance increases as well, so that the wear rate of the composite will increase.

![Friction and wear properties](image)

**Figure 6.** Relationship among load and friction coefficient, wear rate

When the load further increases to a certain extent, the \(\text{Al}_2\text{O}_3\) reinforcing particles will fall off from the matrix, which would act as abrasive particles existing on the friction surface, resulting in the increase of both friction coefficient and wear rate. At the same time, the increase in load also causes the friction parts to generate more heat, leading to a very high instantaneous temperature (flash temperature) on the interface between friction parts. As a result, oxidation layer may occur on the friction surface, which can act as lubrication for friction[20] and thus decrease the friction coefficient.
Figure 7 shows the morphologies of the worn surface. There are a lot of grooves on the friction surface of the composite, and the larger the load is, the deeper the grooves and the greater the wear rate of the composite would be, suggesting that the wear mechanism at this time is mainly abrasive wear, as shown in Figure 7(a-c). When the load is 20 N, a large number of surface films (oxide film) and plastic deformation appears on the friction surface, but that of grooves decreases. Hence, the dominated wear mechanism of the composite transfers from abrasive wear to adhesive and oxidation wear.

4. Conclusions
The preparation, microstructure formation and friction and wear properties of Al$_2$O$_3$/W-Cr composite are studied in this paper, and the following conclusions can be obtained.

(1) The problem that Al$_2$O$_3$ particles are difficult to be uniformly distributed in W-Cr mixed powder due to the difference in density can be successfully solved by sol-gel method. Metallurgical combination between the W particles and the Al$_2$O$_3$ particles is also realized by adding the sintering aid of the Cr particles.

(2) The wear rate increases with the increase of load under the dry friction condition when Al$_2$O$_3$/W-Cr composite is rubbed with medium carbon steel, but the friction coefficient increases first and then decreases with the increase of load but a maximum value at 15N. The wear mechanism is abrasive wear at low loads and adhesive wear combining with oxidation wear at high loads.

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