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Formation of surface coating on milling balls during milling of Cr powders①

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[Abstract] The formation regularity of surface coating on milling balls during milling of Cr powders was investigated, revealing that the plastic deformation of the balls surface plays an important role in the formation of coating and that the stronger affinity between the powders and the balls is a necessary pre-condition for the coating. The size of Cr powders, the coating thickness and the microhardness vary consistently with milling time during milling. At initial milling stage, the powder size decreases, while the coating thickness and the microhardness increase, however, after milling for 24 h, they all change slightly with prolonged milling, indicating a dynamic equilibrium between the powders cold welding and crashing, i. e. an almost equal rate for the powders attaching to and breaking off the milling balls.

[Key words] coating; milling balls; plastic deformation; microhardness
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1 INTRODUCTION

New materials, such as dispersion strengthened alloy, amorphous and intermetallics, can be obtained by mechanical alloying which shows a promising application prospect[1~8]. During alloying, a strong interaction takes place between powders and milling balls and even the balls themselves, accompanying with cold welding and refinement, part of the powders are absorbed on the surface of the balls and the walls of the vessel[9,10]. Because the coating forms during ball milling, there inevitably exists close relationship between the properties of the coating and the alloying mechanism. In order to investigate the formation regularity of the coating on milling balls, we chose one single Cr powders to mill.

2 EXPERIMENTAL

The Cr powders with the purity no less than 99% and the grain size of 53 μm were chosen as raw materials, and were put into ball milling vessels. After evacuating the vessels and back filling with argon to prevent oxidation, the powders were milled in a QM-ISP planetary ball miller. The balls are GCr15 bearing steel with the diameter of 10 mm. The rotation velocity of the miller is 150 r•min^{-1}, and the mass ratio of the balls to the raw materials is 10∶1.

The microstructures of the coating were examined by optical microscopy, JXA-840 scanning electron microscopy (SEM), and the hardness was measured by Type-M microsclerometer.

3 RESULTS AND DISCUSSION

During mechanical alloying, the powders undergo a dynamic process of cold welding and crashing, giving rise to the initial increment of the granularity and to the reduction afterwards and further to a stable value[11]. However, the granularity of Cr powders decreases rapidly when ball milling begins, and upon prolonged milling, the reduction rate of the granularity becomes slower, as shown in Fig. 1. Fig. 2 reveals the variation of coating thickness on milling balls during milling. It is obvious that the coating thickness increases quickly at the initial stage of milling, and gradually tends to a comparatively stable value. From Fig. 1 and Fig. 2, the variations of powder granularity and coating thickness decrease after milling for 24 h, demonstrating that a dynamic equilibrium of cold welding and crashing is reached, namely the rate for the powders cold welding on the balls approximately equals that of the powders separating from the balls thereafter. Fig. 3 is the Cr coating on the surface of bearing steel balls after milling for 96 h. The coating is compact and distributes uniformly with a thickness of 5~7 μm and excellent erosion-resistance. When the coating was etched by the solution of 3% nitric acid and 97% alcohol, a bright layer can be observed. Fig. 4 is the SEM morphology and the line-distribution of elements Cr and Fe in the coating. It can be seen that the coating binds tightly with the matrix and that there is a density gradient of Cr and Fe around the boundary. By measurement, the coating contains 8.2% (mole fraction) of Fe, while the matrix around the boundary, 3.11% (mole fraction) Cr. During milling, the kinetic energy from the milling balls transforms largely into heat energy, resulting in the rise of temperature of the system. At the early stage of milling, the mutual collision be-

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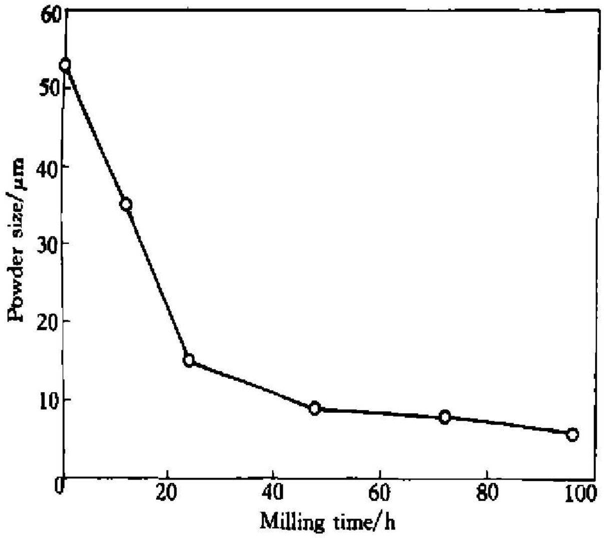

Fig. 1 Variation of size of Cr powders with milling time

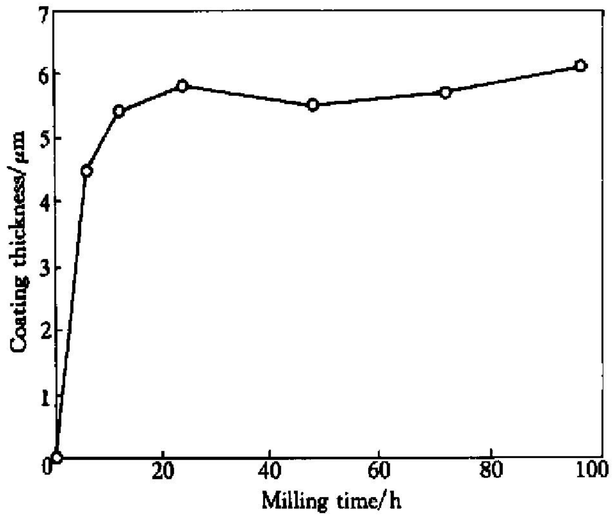

Fig. 2 Variation of coating thickness of bearing steel balls with milling time

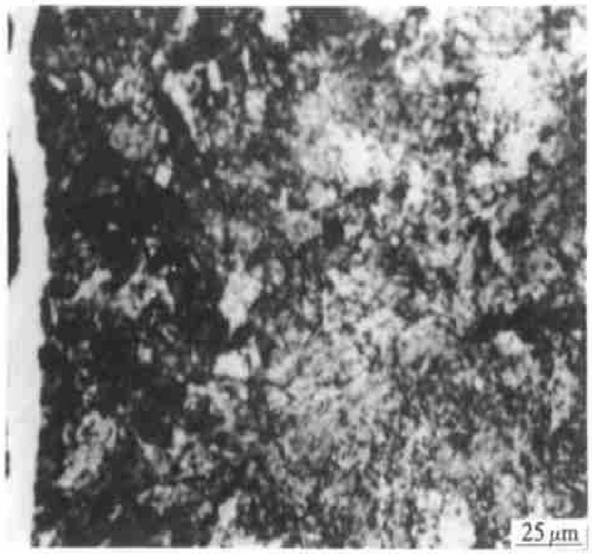

Fig. 3 Metallographic structure of Cr coating on surface of bearing steel milling balls

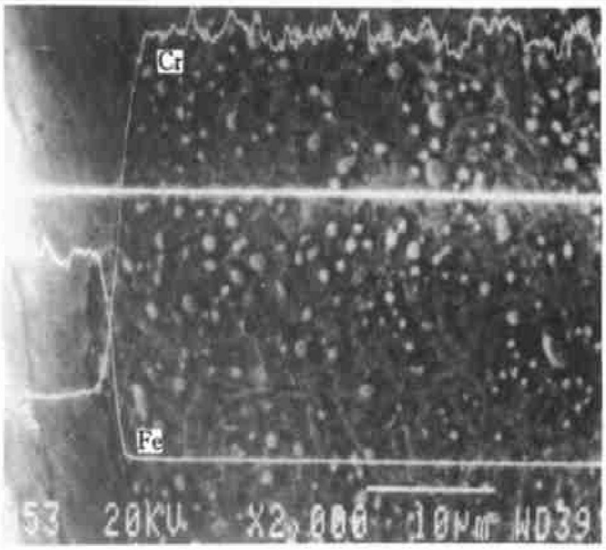

Fig. 4 SEM microstructure of Cr coating on bearing steel milling balls and line-distribution of elements Cr and Fe

tween the balls and powders gives rise to abrasion of balls surface, which is responsible for the increment of Fe in the coating. Upon further milling, cold welding take place due to the collision, accelerating the diffusion of Cr into the matrix from the coating and Fe into the coating from the matrix.

It is known that the specific surface energy of the powders is very high, the congregation and absorption of the powders on the balls and vessel walls is a process during which the free energy falls. The uninterrupted strong collision of the balls promotes the binding between the powders and the balls. Meanwhile, the powders absorbing on the balls undergo severe plastic deformation and become brittle owing to work hardening, they are liable to peeling off and falling off the balls when subjecting to further collision. It is easy for these desquamated powders to be refined continuously during mechanical alloying. However, the surface activity of the balls improves after the desquamation. Also the dislocations and lattice distortion produced by large deformation during the collision between the balls and the powders and the balls themselves, enhance the activity of the powders and the balls. These factors are greatly helpful for the binding between the powders and the balls. Thus the plastic deformation of the balls surface is one of the important reasons for the formation of coating. The balls with good plasticity can be deformed severely, resulting in the micro accidented surface, which is favorable to the powders filling in the hollows with the help of the mechanical force and cold welding on the balls. With the progress of milling, the powders cold welds constantly on the balls till the coating is thick enough and the balls surface is smooth enough, hereafter, the rate for the powders coldly welding on the balls almost equals that of the powders separating from the balls.

To verify the conclusion that the plasticity of the balls promotes the formation of coating, we put some low-carbon steel balls into the milling vessels. The milling condition is the same as that for the bearing steel balls. Fig. 5 shows the variation of the coating thickness on the low-carbon steel balls with milling time. It can be seen that the thickness of the coating increases markedly by comparison with that on the bearing steel balls, and the increasing rate of the coating becomes slower with further milling. Nevertheless, the thickness of the coating increases continuously during the whole milling process. Fig. 6 is the metallograph of the coating on the low-carbon steel balls after milling for 96 h. The coating is about 60~80 μm in thickness but with worse compactness and more holes and cracks. A concomitant phenomenon is the severe deformation on the low-carbon steel balls. It is just the plastic deformation of the balls that reinforces the absorption of the powders and the formation of the coating.

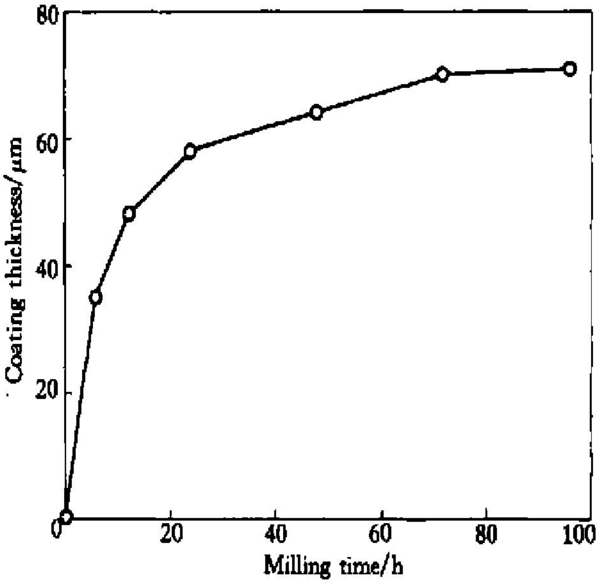

Fig. 5 Variation of coating thickness on low-carbon steel balls with milling time

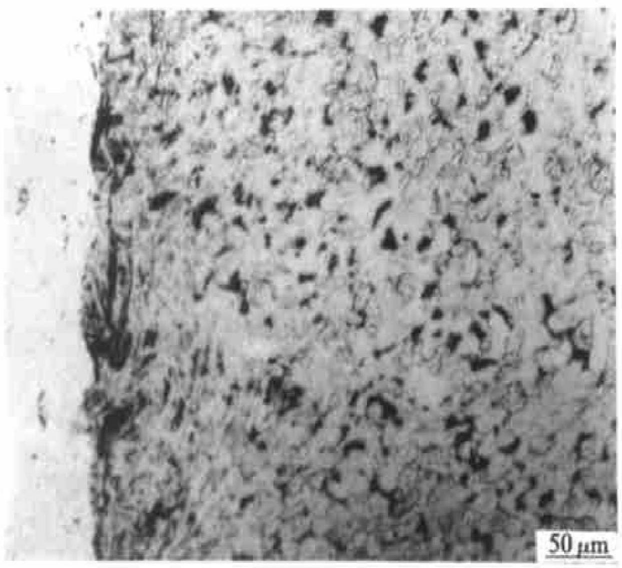

Fig. 6 Metallographic microstructure of Cr coating on low-carbon steel balls

In addition, the stronger binding force between the Cr powders and the milling balls is the necessary pre-condition for the formation of the coating. Owing to the identical structure and the similar atom size, Cr and Fe can form infinity solid solution. So Cr powders can form coating on the bearing steel balls or low-carbon steel balls during milling. However, although Cu has good plasticity, it can hardly solve with Fe under equilibrium state and forms no compound, even if the Cu powders were subjected to ball milling for 96 h, no apparent coating could be examined on the surface of the bearing steel balls or low-carbon steel balls.

The addition of graphite or other organic substances will markedly affect the formation of the coating. Because of the lower surface tension of graphite or organic substances than metal powders, they can adhere easily to the surface of the powders and the balls, which makes the powders not contact with the balls mutually[12]. Moreover, the adhesion of graphite or organic substances to the balls surface may still lead to the decrease of surface energy, as well as to the decrease of the driving force for the powders adhering to the balls. Accordingly, it is difficult to form coating on the surface of balls with the existence of graphite and organic substances.

Fig. 7 is the variation of the microhardness of the coatings on the bearing steel and low-carbon steel balls with milling time. Obviously, the microhardness of the coating increases with milling time, after milling for 24 h, the variation becomes gently, which agrees well with the regularity of the granularity and the coating thickness. At the initial

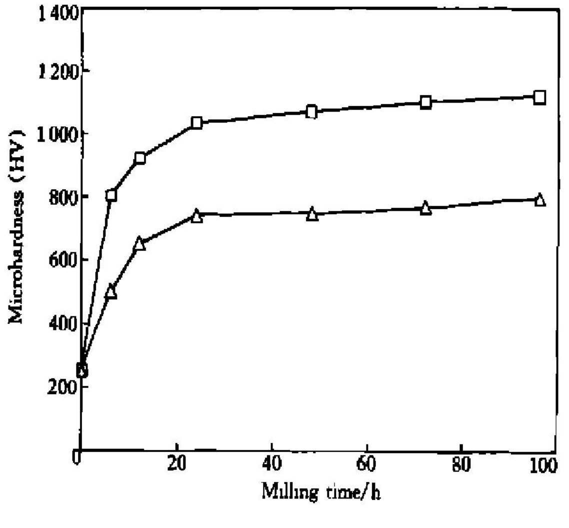

Fig. 7 Variation of microhardness of Cr coating on bearing steel and low-carbon steel balls with milling time

□ —Bearing steel ball; △ —Low carbon steel ball stage, the coating is worse in compactness but still with better plasticity and low hardness. With the increment of milling time, the coating work hardens and the compactness improves, giving rise to the promotion of hardness. After milling for 24h, a dynamic equilibrium may reaches and the microstructure does not change largely any longer, leading to a slight variation in hardness. From the experiment result, the coating hardness on the bearing steel balls is higher than that on the low-carbon steel balls, because the coating on the low-carbon steel balls is thicker and with a lower compactness.

4 CONCLUSIONS

1) During ball milling, the granularity of Cr powders, the thickness and the microhardness of the coating on the milling balls have the identical regularity with milling time. At initial milling stage, the powder size decreases, while the coating thickness and the microhardness increase, however, after milling for 24h, they all change slightly with prolonged milling, indicating a dynamic equilibrium between the powders cold welding and crashing and an approximate equal rate of the powders attaching to and breaking off the milling balls.

2) The plastic deformation of the surface of the milling balls is an important factor for the formation of the coating, and the stronger binding force between the powders and the balls is the necessary precondition.

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