Research on ball milling process of Mn powder for ceramic metal welding

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Abstract. The main content of this experiment is to study the optimal ball milling process of Mn powder by controlling the factors such as ball milling ratio, ball milling time and grinding ball size. In the experiment, the Mn powder was ground by wet ball milling method. Ethanol was used as the medium to set different powder: ball: ethanol ratio. The microstructures of Mn were studied by grinding for 6 h, 18 h and 24 h at 400 r/min. The XRD, Scanning Electron Microscope and particle size analyzer were used to analyze the phase, microstructure and particle size of the powder. The results show that the ratio of the crushing rate of material to the time of ball milling are not related. In the initial stage of ball milling, Mn powder was rapidly crushed and refined, but the particle size gradually stabilized after 18 hours. The grinding ball with smaller diameter is slower to crush, but the particle size of Mn powder is more uniform. When the quality of powder: ball: ethanol =1:1.5:1.5, the obtained Mn powder has the finest particle size and uniform particles, which is the best grinding condition. After ball milling, the average particle size of Mn powder is 2.04 μm.

1. Introduction
Alumina ceramics have widely used in electric vacuum devices because of its non-conductive, high hardness and high temperature resistance. In the process of ceramic and metal welding, it is a common process operation to coat the surface of alumina ceramics with molybdenum, manganese and other conductive metal powder [1] to achieve the purpose of modification. The product not only has high temperature resistance, but also has good electrical conductivity, which has a high application prospect in aerospace, energy technology and other industries[2-4].

The activated Mo-Mn method is mainly used in the welding of ceramics and metals. In the process of ceramic metallization, Mn is a kind of very important raw material and is also one of the frontier fields of manganese material research. The particle size of Mn powder plays an important role in ceramic metal sealing. However, high energy mechanical ball milling [5,6] is a common method for powder grinding at room temperature. There are many factors affecting ball milling, such as raw material properties, ball milling strength, ball milling atmosphere, ball milling ratio, ball milling time and ball milling temperature[7-9]. In this paper, the method of obtaining manganese powder with smaller particle size by high-energy ball milling is also a more convenient and clean method than hot processing. The finer the powder, the better the sintering, and the higher the strength of ceramic metal sealing. According to the experimental data, the grinding ball parameters corresponding to the optimal microstructure and sintering strength can be obtained to promote the improvement of Mn powder processing technology and the progress of related industries.
2. Experimental part

Mn powder used in the experiment is analytically pure, purchased from Shaanxi Wenzheng Electronic Technology Co., Ltd., with the average particle size of 9.35 μm and the particle size was analyzed by LS-POP(VI) laser particle size analyzer, as shown in Figure 1.

![Figure 1. Particle size distribution diagram and characteristic parameters of Mn particle size.](image)

The ball milling was carried out under normal temperature and pressure. The aluminum oxide ball mill pot was used with a volume of 300 mL. The average diameter of the big ball and the small ball was 8.38 mm and 5.90 mm respectively. In the experiment, ultra-fine Mn powder, agate balls with different particle sizes and absolute ethanol were added into the ceramic ball mill according to different proportions. The samples were milled by planetary high-energy ball mill. The samples were dried for 6 h, 18 h and 24 h in a constant temperature blast drying oven, and then they were passed through Japanese physics Dmax Ultima. The phase structure (XRD) patterns of the samples were obtained by measuring the X-ray diffraction of the samples with type I X-ray diffractometer. The microstructure of the samples was observed by quanta 250EFG scanning electron microscope at 20 kV.

3. Results and discussion

3.1. Effect of ball milling time

The main mechanism of ball milling is the impact between the high-speed ball and the material to achieve the purpose of crushing materials. At the same time, the length of milling time is bound to affect the quality of materials. Figure 2 (a), (b) and (c) are the SEM images of the samples obtained at 6 h, 18 h and 24 h under the ball milling ratio of $m_{\text{powder}}: m_{\text{ball}}: m_{\text{ethanol}} = 1:1.5:1.5$. The magnification ratio of the three graphs is 3000 times. It can be seen from the figure that the particle size of Mn powder decreases with the time going on, and tends to be stable after 18 h. This is because in the initial stage of ball milling, the Mn powder particles are larger, the momentum generated is also larger, and a lot of energy is released when colliding with the grinding ball[10], which promotes the crushing of Mn powder. After that, with the gradual reduction of particles, the chance of ball catching powder becomes less, and the surface free energy per unit volume increases gradually, which makes it more difficult to further refine the materials. At the same time, the crushing and welding of metal particles are gradually balanced in the process of ball milling, which is also the reason why the crushing rate and time of materials change irregularly in the process of ball milling.
3.2. Effect of ball milling ratio

In ball milling, if there are too many grinding balls, the powder will collide, and if the alcohol is too much, the fluid will be formed. Therefore, it is necessary to set the appropriate ball milling ratio. In Figure 3, the SEM images of samples with different ratios of Mn powder and grinding ball running for 24 h are shown under 3000 times magnification. It can be seen that the particle size of the powder in Figure 3(d)(f)(h) are smaller than that of the others, while the milling effect of (f) is better than that of (d) and (h). Table 1 is obtained after the statistics of the average diameter of Mn powder in the following proportion images.

| Sample | Ball milling ratio / (m\text{powder}: m\text{ball}: m\text{ethanol}) | Average diameter D50/μm |
|--------|---------------------------------------------------------------|-------------------------|
| 1-1    | 2:1:2                                                         | 6.13                    |
| 2-1    | 1:1:1                                                         | 6.45                    |
| 3-1    | 2:1:1                                                         | 4.00                    |
| 4-1    | 2:1:1.5                                                       | 3.59                    |
| 5-1    | 1:1:1.5                                                       | 5.71                    |
| 6-1    | 1:1:1.5                                                       | 2.04                    |
| 7-1    | 1.5:1:1.5                                                     | 4.59                    |
| 8-1    | 1.5:1.5:1                                                     | 3.19                    |
Compared with Figure 3 and Table 1, it can be seen that only when the proportion of ball and ethanol is higher than that of Mn powder, can Mn powder with smaller particle size be obtained. At this time, on the one hand, the chance of collision between Mn powder and grinding ball is increased, while ethanol can fully contact with Mn powder, which reduces the welding between particles, thus making the result of ball milling more ideal and the particle size of Mn powder smaller. The best milling ratio should be \( m_{\text{powder}} : m_{\text{ball}} : m_{\text{ethanol}} = 1:1.5:1.5 \), the particle size analysis diagram and characteristic parameters are shown in Figure 4.

![Particle size distribution diagram and characteristic parameters of particle size with \( m_{\text{powder}} : m_{\text{ball}} : m_{\text{ethanol}} = 1:1.5:1.5 \).](image)

**Figure 4.** Particle size distribution diagram and characteristic parameters of particle size with \( m_{\text{powder}} : m_{\text{ball}} : m_{\text{ethanol}} = 1:1.5:1.5 \). 

### 3.3. Effect of ball size

The results of ball milling are closely related to the properties of grinding balls. In the experiment, agate ball is a natural mineral, mainly because of its high purity, high hardness, can reduce the pollution of materials, and good wear resistance, can improve the rate of ultrafine grinding. Figure 4 is obtained by controlling different ball size. Figure 5 (a), (b) and (c) are the SEM images of samples milled with 8.38 mm diameter agate ball (hereinafter referred to as large grinding ball) with the mass ratio of \( m_{\text{powder}} : m_{\text{ball}} : m_{\text{ethanol}} = 1:1.5:1.5 \) ball milling for 6 h, 18 h and 24 h; and (d), (e) and (f) are the agate balls with a diameter of 5.90 mm (hereinafter referred to as small grinding balls) with the mass ratio of \( m_{\text{powder}} : m_{\text{ball}} : m_{\text{ethanol}} = 1:1.5:1.5 \) ball milling for 6 h, 18 h and 24 h.

![SEM images of Mn powder with different ball size under the same proportion](image)

**Figure 5.** SEM images of Mn powder with different ball size under the same proportion: (a) Large grinding ball 6 h, (b) large grinding ball 18 h, (c) large grinding ball 24 h, (d) Small grinding ball 6 h, (e) small grinding ball 18 h, (f) small grinding ball 24 h.
From Figure 5, it can be seen that the momentum generated is naturally large and the material can be quickly crushed in the initial stage of ball milling due to the large mass of the ball mill. However, due to the small number of large grinding balls under the same mass, the chances of collision with Mn powder are less, so the final particles obtained are larger than those of small ones. In the process of ball milling, the volume of agate ball accounts for about 1/2 of the volume of ball mill pot. Due to the larger area of the small ball and the more Mn powder carried by the ball mill than the large ball under the same mass, there are more chances of collision in the process of ball milling, the material is crushed more fully, and the final Mn powder particles are smaller.

4. Conclusion
In this paper, through controlling the factors of ball milling proportion, ball milling time and ball size, powders under different ball milling conditions were obtained. By comparing the particle size and micro morphology of the materials under different factors, the best ball milling process of Mn powder can be obtained. There is no fixed proportion relationship between grinding rate and milling time. At the beginning of ball milling, Mn powder was crushed and refined rapidly, but the particle size gradually became stable after 18 h. The grinding ball with larger diameter grinds faster, but the particle size distribution of Mn powder is uneven. The optimum mass ratio of \( m_{\text{powder}} : m_{\text{ball}} : m_{\text{ethanol}} = 1:1.5:1.5 \), and the average particle size is 2.04 \( \mu \text{m} \).

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