Refinement of the Secondary Phase Structure in Molybdenum-Based Refractory Alloys Achieved Through Mechanical Milling

Haolong Liu[1], Ning Li[1]
State Key Laboratory of Materials Processing and Die & Mould Technology, and School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China
*Corresponding address: e-mail: d202180439@hust.edu.cn

Abstract: This study investigates the impact of mechanical milling on the ~~microstructural properties~~ microstructure of TZM alloy prepared via powder metallurgy. Increasing milling time significantly reduces the size of doped particles in the green bodies, due to the breakdown of larger particles during the milling process. The size of doped particles in the green body milled for 8 hours was reduced by 38% compared to that in the green body pressed from unmilled powder. Sintered samples show a significant decrease in the size of second-phase particles and grain size with increased milling time. The grain size decreased from 9.45 μm in the sample prepared from unmilled powder to 6.89 μm in the sample prepared from powder milled for 8 hours. This grain refinement is attributed to the overall reduction in powder particle size and the pinning effect of refined second-phase particles**.**

Keywords: TZM alloy； Powder metallurgy； Ball milling

1 Introduction

TZM molybdenum alloy exhibits superior specific strength at temperatures above 1000K. It possesses high mechanical strength and creep resistance at high temperatures (1373K), and its low thermal expansion coefficient combined with high thermal conductivity minimizes thermal stress during rapid heating and cooling, ensuring the working dimensions of the mold remain unchanged. Therefore, molybdenum alloy molds can meet the long-term, high-temperature (1373K), and high-load usage requirements that traditional mold materials cannot satisfy. [1,2].

TZM alloy, composed of Mo-Ti(0.4~0.55)-Zr(0.06~0.12)-C(0.01~0.04), benefits from the addition of alloying elements titanium (Ti) and zirconium (Zr), which not only contribute to solid solution strengthening but also help to purify the grain boundaries. These elements form fine second-phase particles within the molybdenum (Mo) matrix, which pin dislocations and grain boundaries, thereby refining the grains. This allows TZM ~~molybdenum~~ alloy to achieve solid solution strengthening, grain refinement strengthening, and second-phase particle strengthening simultaneously[3-6].

In this work, the second-phase particles in TZM alloy prepared by powder metallurgy were significantly refined through mechanical milling.

2 Experimental procedure

The material preparation method is powder metallurgy. The raw powders used are TiH_2 powder, ZrH_2 powder, graphite powder, and molybdenum powder. First, the raw powders are mixed in a three-dimensional mixer for 10 hours at a speed of 30 revolutions per minute (rpm). Then, the mixed powder is ball milled for 2, 4, and 8 hours, with a ball-to-material ratio of 1:1, at a speed of 200 rpm. The milling medium consists of 3 mm ZrO_2 balls, and the milling jar is made of stainless steel. To minimize the ~~increase in~~ oxygen content in the powder, the entire milling process is carried out under argon protection. The mixed powder was compacted into green bodies using cold isostatic pressing at 280 MPa. The green bodies were then sintered at 1900°C for 4 hours.

The microstructural analysis was performed using a Leica DM2700 M optical microscope and a Phenom XL G2 desktop scanning electron microscope. The powder particle size was measured using a Mastersizer 3000 laser particle size analyzer.

3 Result and discussion

Microstructural analysis of green bodies

The SEM images shown in Figure 1 illustrate the distribution of doped particles (black) and molybdenum powder particles (white) in the green bodies of TZM alloy prepared with different milling times. The size of doped particles in the green bodies significantly decreases with increased milling time. This reduction is attributed to the further breakdown of large particles in the mixed powder during the milling process. As shown in Table 1, the D_{50} of powder particles decreases from 13.3 μm to 6.8 μm. Due to the varying degrees of fragmentation of the doped powders, different sizes and distributions are observed. The specific particle size distribution of the doped particles in the green body is depicted in Figure 2. The doped particle size in the green body prepared by 8 hours of milling is reduced by 38% compared to that in the green body pressed from unmilled powder.

Microstructural analysis of sintered samples

Figure 3 presents the optical micrographs of the microstructure of sintered TZM alloy prepared with powders milled for different durations. The black particles within the white molybdenum matrix are second-phase particles formed during sintering. It is clear that with increasing milling time, the size of the second-phase particles in the sintered alloy significantly decreases. Furthermore, the grain size also shows a decreasing trend, from 9.45 μm in the sample prepared from unmilled powder to 6.89 μm in the sample prepared from powder milled for 8 hours. This grain refinement is attributed to the overall reduction in powder particle size due to milling, as each powder particle forms an initial grain during sintering. The finer the powder, the finer the initial grains. Additionally, the refined second-phase particles hinder grain growth during the sintering process. The combined effect of these factors results in smaller grain sizes.

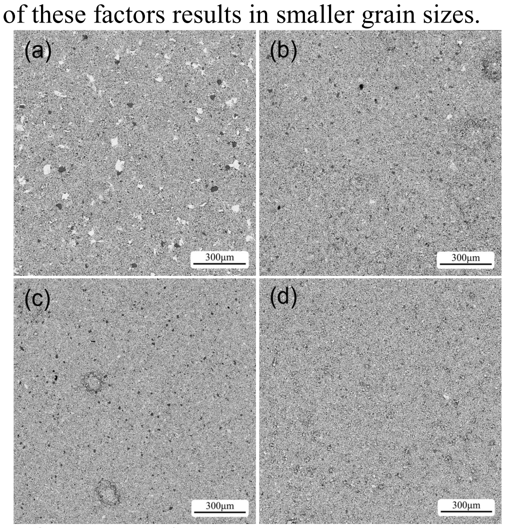

Figure 1. SEM images of doped particles distribution in TZM alloy green bodies with different milling times:(a) 0h.(b) 2h.(c) 4h.(d) 8h.

Table 1. Laser particle size analysis of powders with different milling times

Ball milling time(h)	0	2	4	8
D_{50}(μm)	$13.3_{\pm0.6}$	$8.3_{\pm0.7}$	$7.8_{\pm0.4}$	$6.8_{\pm0.5}$

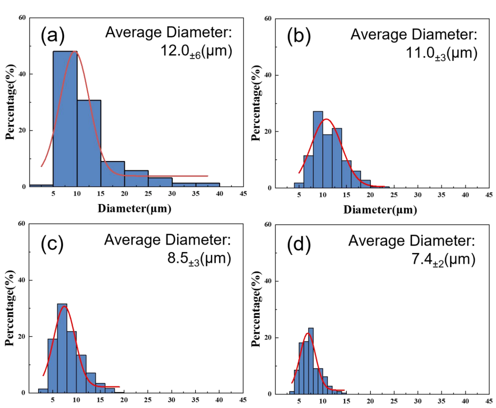

Figure 2.Particle size distribution of the doped particles in TZM alloy green bodies with different milling times:(a) 0h.(b) 2h.(c) 4h.(d) 8h.

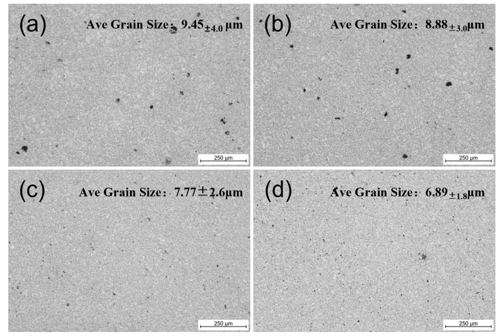

Figure 3. Optical micrographs of second phase distribution in TZM alloy as-sintered samples with different milling times:(a) 0h.(b) 2h.(c) 4h.(d) 8h.

4 Conclusion

The microstructural analysis of TZM alloy green bodies and sintered samples demonstrates that mechanical milling effectively refines the size and distribution of doped particles. With increased milling time, the D50 of powder particles significantly decreases, resulting in finer doped particles in the green bodies. This refinement continues through the sintering process, leading to smaller second-phase particles and reduced grain size. The combined effects of reduced powder particle size and the pinning action of refined second-phase particles hinder grain growth, resulting in smaller grains. These finer grains enhance the material's strength through grain refinement strengthening. Thus, mechanical milling is a critical process for optimizing the microstructure and overall performance of TZM alloy.

References

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