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Short Communication

Preparation of nanostructured high-temperature TZM alloy by mechanical alloying and sintering

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ABSTRACT

Mechanical milling proceeded by sintering was used to synthesize nanostructured temperature-resistant TZM alloy. Milling under Ar for different times (1, 2, 3, 5, 10, 15, 20, 25, and 30 h) and sintering at 1500, 1600 and 1700 °C for 30, 45, 60 and 90 min resulted in increasing of low-energy grain boundaries (LEGBs) and dispersion of TiC and ZrC with a size of ~65 nm in the matrix near LEGBs. Morphology and grain size of the products were determined from scanning electron microscope (SEM) images and X-ray diffraction (XRD) patterns, almost precisely. Optimum density of nanostructured TZM alloy ~9.95 ± 0.01 g/cm^3 was achieved by sintering at 1700 °C for 90 min.

1. Introduction

TZM alloy shows unique properties like creep strength, resistance to recrystallization and softening as compared to the elemental molybdenum, high corrosion/erosion resistance, low thermal expansion, good heat-conduction, exceptional high-temperature stiffness and strength, thermal compatibility with other materials such as copper and Ti–6Al–4V alloy and stable physical and mechanical properties over a wide range of temperatures [1–10]. Nominal composition of TZM is Mo–0.5Ti–0.08Zr–0.02C (wt.%) [1,2]. It is applicable in nuclear and aerospace industries for making high-temperature dies, fusion-reactor diverter components and missile combustion chambers [1–6,8].

TZM alloy can be fabricated either by powder metallurgy (PM) or by vacuum arc melting (VAR) and electron beam melting (EBM) methods [1,4,5,8,11–13]. Information on production and characterization of nanostructured TZM alloy is very limited. Dispersion of nano-sized carbides and its effects on mechanical and physical behavior of TZM alloy are non-existent. Abe et al. have tried to disperse the nano-sized particles in 9Cr–3 W–3Co–VNb and 9Cr–2 W–VNbTi heat resisting steels [14,15]. Optimum creep strength combined with adequate solid solution strengthening has been acquired by this dispersion process. It has been shown that the grain growth and the structural failure can be inhibited by formation of fine titanium and zirconium carbides at the grain boundaries of the TZM alloys [16–18]. Low-angle boundaries (LABs) have been shown to display improved physical, mechanical and chemical properties relative to the high-angle boundaries (HABs) existing generally in the samples [19–21].

Mechanical alloying proceeded by sintering of elemental powders was employed in this research to extend low-angle grain boundaries, to increase the dispersion of carbides within the LABs and production of nanostructured TZM alloy. Effect of the milling time as well as the sintering time and temperature on crystallite size was rigorously investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for characterization of the produced samples.

2. Experimental procedure

Molybdenum, titanium and zirconium powders with a minimum purity of 99.99% and particle sizes of less than 2 μm were mixed with highly pure activated carbon powder having a particle size of 44 μm and then dry-milled in a planetary ball mill (PM400, Germany) under an Ar atmosphere for 1, 2, 3, 5, 10, 15, 20, 25 and 30 h. High purity of 99.999% argon gas was used in the ball-milling steps. The milling cup was made of stainless steel. It contained the mixture of stainless steel balls and powder with a ball to powder weight ratio (BPR) of about 10:1. To prevent iron contamination due to the stainless steel balls and milling jar during the milling step, a pre-milling for about 100 h was accomplished. Tablets sizing ø13 × 5 mm were made of nanostructured and microstructured powders by compaction at 300 MPa pressure. The tablets were heated up with a heating rate of 5 °C/min to 1500, 1600 and 1700 °C and isothermally sintered under purified Ar for 30, 45, 60 and 90 minutes. The etching solution was 1 g CrO_3 (BDH) + 1 ml H_2SO_4 + 500 ml water and the etching time was about 30 s. The Archimedean method was used to measure the density of

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the sintered samples. Fe total of milled powders was determined by atomic absorption spectroscopy (AAS, Perkin Elmer 3110). Morphology, particle size and microstructure of the sintered specimens were studied by X-ray diffraction (XRD, Powder Metallurgy 9920/50, Philips, Holland) having Cu Kα radiation of 0.15405 nm wavelength and scanning electron microscope (SEM, VEGA, TESCAN Czech Republic).

3. Results and discussion

The XRD patterns of the mechanically alloyed Mo–0.5Ti–0.08Zr–0.02C (wt.%) powders are given in Fig. 1. As is seen, the XRD graphs exhibit three well-defined sharp peaks, altogether. Among these peaks, the tallest one confirms the existence of the elemental molybdenum and two fairly short ones verify titanium and zirconium carbides. These peaks indicate that there is no significant amount of crystalline species like titanium and zirconium. The XRD patterns given in Fig. 1 indicate that by increasing the milling time, the carbide peaks broaden until they resemble a nearly amorphous phase at t = 30 h.

Fig. 2 shows the SEM images of the as-received and the dry-milled TZM powder after 30 h. As is illustrated in Fig. 2 and determined by the wall to wall tool of a scanning electron microscope, the average particle size is about 1.5 μm for as-received Mo powder and ~60 nm for 30 h dry-milled under argon powder, moreover ~500 nm for agglomerated clusters of milled powders. TZM powders may be contaminated with materials such as iron eroded from the milling media of stainless steel. Fe total of milled powders was determined by atomic absorption spectroscopy (AAS). The iron content of milled powders is presented in Fig. 3. It can be observed that iron contamination increases continuously from 100 ppm for 5 h to about 400 ppm for 30 h of milling time. The maximum iron content of powders milled for 30 h is approximately 400 ppm, however. The effect of milling time on the average particle size of the TZM powder is shown in Fig. 4. Patently, it can be seen that the average particle size of the TZM powder becomes lower than 100 nm, after milling for 30 h.

Synthesis and preparation of temperature-resistant TZM alloy by mechanical milling proceeded by sintering route have also been reported by other researchers, and their results showed that formation of nano-carbides during mechanical alloying leads to refine the particle size of the TZM alloy [22,23]. Density change of the microstructured and the nanostructured TZM alloys is shown against

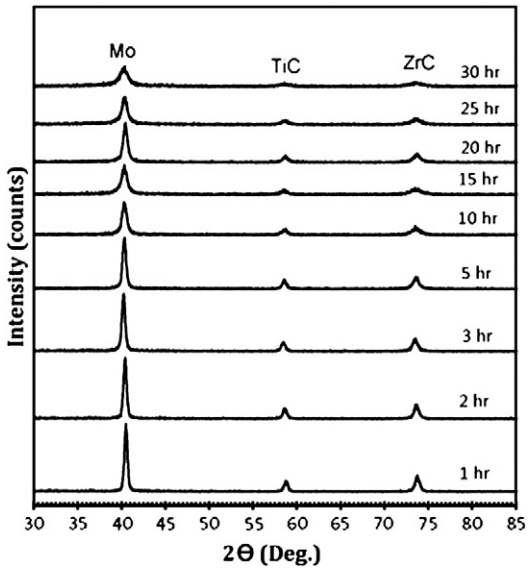

Fig. 1. XRD patterns of the TZM powders ball-milled under argon for 1, 2, 3, 5, 10, 15, 20, 25 and 30 h.

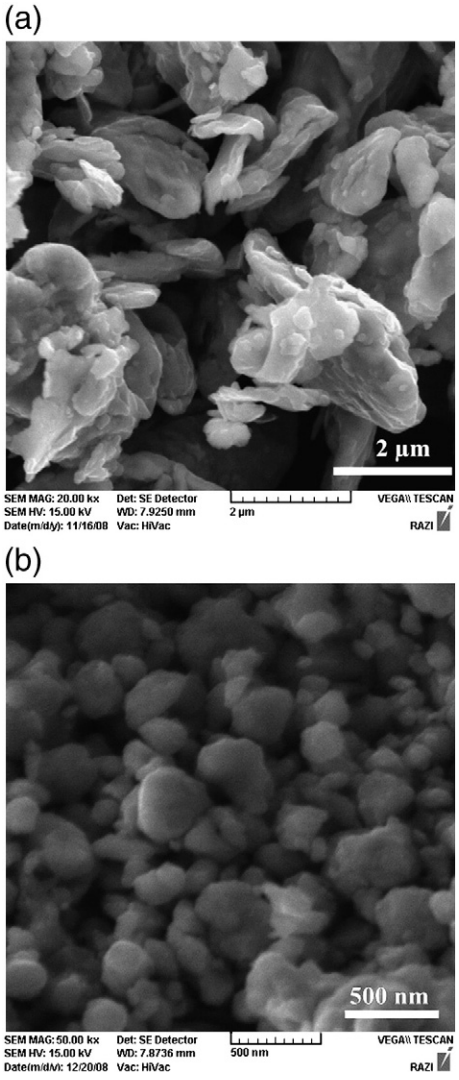

Fig. 2. SEM image of TZM powder mixture (a) as-received and (b) dry-milled for 30 h.

the sintering time and temperature in Fig. 5. These plots demonstrate remarkable differences between nanostructured and microstructured samples. Higher densities are observed at higher sintering temperatures and longer sintering times (e.g. 1700 °C and 90 min). Greater densities of the nanostructured tablets can be attributed to the higher sintering temperatures. Hence, any change from microstructured to nanostructured TZM, results in a denser tablet. Optimum density can

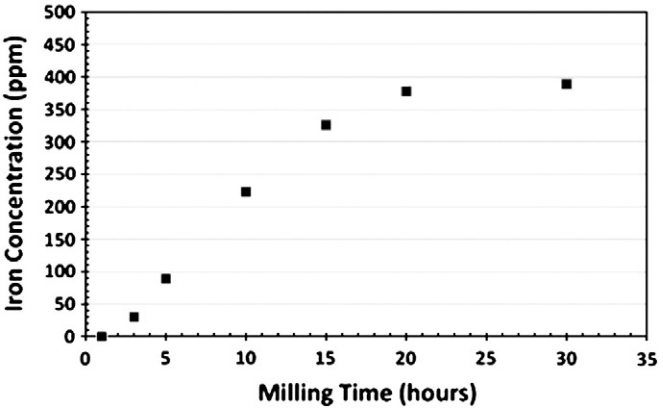

Fig. 3. Iron concentration of TZM milled powders with respect to the milling time.