Development of Mo base TZM (Mo-0.5Ti-0.1Zr-0.02C) alloy and its shapes

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1. Introduction

Refractory metals and their alloys possess high temperature strength, creep resistance, low coefficient of thermal expansion, high thermal conductivity and favourable nuclear properties, which enable them to withstand prolonged exposure to aggressive environments of radiation, temperature, corrosion (gaseous and liquid metal) and stress. These materials have an edge over conventional superalloys as high temperature structural materials and are, therefore, being considered for new generation reactors such as, accelerator driven systems, advanced high temperature reactor, fusion devices [1,2] and reusable launch vehicles [3].

Amongst the high temperature alloys, the refractory metal alloys are the only materials for structural applications beyond 900°C. Molybdenum base alloys such as, TZM, are the most suitable ones amongst the refractory metal alloys for application temperatures up to 1500°C. Amongst the different molybdenum base alloys, TZM (Mo-0.5Ti-0.1Zr-0.02C) is the most suitable one, in terms of yield strength to density ratio, at temperatures above 900°C [4]. In this alloy, small amounts of titanium, zirconium and carbon are added, so as to obtain a coarse distribution of carbides with some titanium and zirconium remaining in solid solution [5]. The high strength of this alloy at elevated temperatures and its excellent corrosion resistance against liquid metals, makes it suitable for application in advanced high temperature nuclear reactors. Other alloys of this class include: TZC (1.2% titanium, 0.3% zirconium, 0.1% carbon), MHC (1.2% hafnium, 0.05% carbon), and ZHM (1.2% hafnium, 0.4% zirconium, 0.12% carbon).

The preparation and fabrication of TZM components is challenging due to its high melting temperature (~2600°C). Of the feasible methods of preparation and fabrication of TZM alloys, viz. (i) aluminothermic reduction of mixed oxides followed by arc or electron beam melting, (ii) component melting and (iii) powder processing, the last route has the advantage of ease of operation, consistency of alloy composition, homogeneity and phase distribution. The present work was taken up with the aim of producing TZM and its components by the powder processing route consisting of the following steps: preparation of pure Mo powder by hydrogen of reduction of MoO₃, preparation of TZM alloy powder from elemental powders by mechanical alloying, compaction of powders into green compacts and sintering for densification. Each of these steps are described in the following sections.

2. Hydrogen Reduction: Preparation of Molybdenum powder

In our investigation, a detailed kinetic analysis of the hydrogen reduction of MoO₃ powder was carried out under isothermal and non-isothermal heating conditions. The reductions were performed with varying percentage of hydrogen (10 to 100%) in the inlet gas mixture containing helium and hydrogen.
The Thermo Gravimetry and Differential Thermal Analysis (TG-DTA) of reduction of MoO$_3$ in hydrogen containing atmosphere shows some interesting facts. Fig. 1A shows, that the reduction takes place in two stages (as obtained from the observed two-stage weight reduction). X ray diffraction (XRD) analysis showed that MoO$_3$ is reduced to MoO$_2$ in the first stage and Mo is obtained from MoO$_2$ in the final stage. The figure shows that the second stage of reduction is affected by the hydrogen content in the atmosphere: it achieves completion at 873°C with 100% H$_2$, it is complete at around 955°C with 50%H$_2$ and is incomplete even at 1100°C with 10% H$_2$. Fig. 1B, on the other hand, shows that the peak temperature for MoO$_2$ formation (first stage) shifts to higher temperature as the hydrogen content of the atmosphere is increased: it is around 642°C when the hydrogen content is 100% and 755°C when it is only 10%. DTA, however, did not show any distinct peak for the second stage of reaction, which could be due to the low enthalpy of the MoO$_2$-Mo reaction.

Isothermal experiments of MoO$_2$-Mo reduction in presence of 100% H$_2$ were carried out at seven different temperatures. The degree of reduction ($\alpha$) with time, Fig. 2, shows the typical sigmoidal shape. Analysis of the data showed that it followed the Johnson, Mehl, Avrami and Kolmogorov model of reaction kinetics:

$$ g(\alpha) = \left[ -\ln(1-\alpha) \right]^{n/2} = kt $$

(1)

Where, $n$ is Avrami exponent, $t$ is time, and $k$ rate constant. It is observed that $n$ varied from 1.5 to 2 with increase in temperature of reduction, while the activation energy of for the isothermal reduction is 136 kJmol$^{-1}$.

Fig. 3 shows the SEM micrographs of powders obtained by the reduction of MoO$_3$ in pure hydrogen atmosphere for 150 minutes at six different temperatures. The MoO$_2$ powder used in these experiments had an average size of 3.25μm and a rod or acicular morphology. At 625°C, the powder was only partially reduced, the micrographs showing irregularly shaped Mo particles, platelets of the intermediate phase, MoO$_2$, and rod shaped particles of unreduced MoO$_3$. At 655°C, the reduction was complete, but the Mo particles showed significant amount of porosity and edge cracks. With increasing temperature of reduction, porosity and cracks reduce...
and edges of individual particles start rounding off till a near equiaxed shape is obtained at 865°C. Finally, at 900°C, spherical Mo particles were obtained that are completely devoid of edge cracks and porosity.

Based on these studies, the optimum conditions for producing Mo by hydrogen reduction of MoO$_3$ were determined to be: controlled heating up to 900°C followed by an isothermal holding for 2.5 hrs in a flowing atmosphere of pure hydrogen. Large quantities of molybdenum powder have been successfully produced using these optimized conditions.

3. Mechanical Alloying: Preparation of TZM alloy powder

Mechanical alloying is a technique that allows production of homogeneous materials starting from blended elemental powder mixtures. Here, the repeated welding and fracturing process during milling tools leads to a gradual alloying of the elemental powders. The aim of the present work was to determine the optimum conditions for the production of TZM alloy powders by mechanical alloying.

The Mo powder produced by hydrogen reduction was mixed thoroughly with pure titanium, zirconium and graphite (C) powder of required quantity and of nearly similar size range. The powder mixture was milled in a planetary ball mill with 10mm diameter WC balls (3:1 balls to powder weight ratio) for varying periods of time up to 120 hours at a constant milling speed of 400 rpm.

XRD patterns of the starting powder mixture and mechanically alloyed powder are shown in Fig.4. As the amount of Ti and Zr was very low in the powder mixture, its XRD pattern shows reflections of only bcc molybdenum. On the other hand, mechanical alloying expectedly results only in the marginal shift of bcc reflections, as Ti, Zr and Mo have similar atomic sizes. The gradual broadening of the reflections with milling time is due to refinement of crystallite size and accumulation of lattice defects. However, there was no significant increase in peak broadening beyond 60 hours of milling.
A confirmation that alloying had been achieved during mechanical milling was obtained from Transmission Electron Microscopy (TEM) of powders milled to 60 and 120 hours. Fig. 5 shows that the microstructure consists of fine second phase particles distributed uniformly within a bcc matrix. Analysis of the ring diffraction patterns obtained from selected areas of the powder indicated the formation of the orthorhombic \((\text{Mo}_{0.72}\text{Ti}_{0.28})\text{C}\) phase. The presence of complex carbides along with a slight shift of XRD reflections is evidence enough of the successful creation of the TZM alloy by mechanical alloying.

The particle size of powders measured by Scanning Electron Microscopy (SEM) was found to reduce with milling time, from about 730nm to about 230nm. However, there was not much of reduction of particle size between 60 h and 120 h of milling as steady-state equilibrium was probably attained: in this situation a balance is achieved between the rate of welding and the rate of fracturing. Smaller particles are able to withstand deformation without fracturing and tend to be welded into larger particles, the overall tendency driving very fine and very large particles towards an intermediate size [6].

4. Sintering of TZM powder

Sintering is a thermally activated process that leads to densification. Isothermal sintering studies at nine different temperatures between 1000 to 1800°C were conducted on compacted pellets of TZM powders. Fig. 6, which presents the densification behavior of the pellets as a function of time, shows that the relative density varies with time in a nonlinear manner during the initial stage of sintering. There is a spurt in the rate of densification at around 1400-1500°C, the maximum relative density of 0.97 being obtained at sintering temperature of 1800°C. It must be mentioned that very little densification is obtained at sintering temperatures below 1300°C.

In order to understand the grain growth behaviour of TZM during sintering, pellets of both pure Mo and TZM alloy powders were sintered at 2000°C for 10 minutes. The microstructures of the sintered pellets, obtained as orientation maps using Electron Back-Scattered Diffraction (EBSD), are shown in Fig. 7. The role of the complex carbides in restricting the grain growth in TZM alloy is obtained from the fact that the grain size of Mo is 8.12μm and that of TZM is only 3.36μm. The carbides also shift the recrystallization temperature to higher temperatures and improve the creep behaviour.
5. Hot Isostatic Pressing

Techniques best suited for achieving near theoretical density of powders are: Hot Isostatic Pressing (HIP), spark plasma sintering, explosive compaction, pressure-less sintering, explosive compaction and hot pressing. Of these, HIP is the most promising for producing uniformly dense fine grained material. In this study, TZM alloy powder was consolidated using Cold Isostatic Pressing (CIP) into green compacts of 15mm diameter and about 20mm length. The compacts were then pre-sintered at 950°C for 2 hours under hydrogen flow for removing traces of oxygen and vacuum encapsulated in thin stainless steel tubes. The capsules were then placed inside a HIP chamber and isostatically compacted at varying argon gas pressures of up to 350 bar at 1250°C for 4hours. It was found that density better than 99.9% of the theoretical value (10.16 g/cc) was achieved by HIP. TEM analysis of the HIPped material, Fig.8, shows uniform dispersion of second phase precipitates of 40 to 100 nm size, dispersed in the matrix of equiaxed grains of 1 to 1.5 μm. The ring diffraction patterns obtained from selected areas show the formation of the hexagonal (Mo$_{0.54}$Ti$_{0.46}$)C, and the orthorhombic (Mo$_{0.72}$Ti$_{0.28}$)C complex molybdenum-titanium carbides. The high pressure and temperature resulted in dense materials free of pores.

6. Shape fabrication

Based on the study of powder consolidation and sintering, an attempt was made to prepare TZM alloy tubes. The green tubes were produced from the mechanically alloyed TZM powder by CIP at an optimized compaction pressure of 250 MPa. A specially designed cylindrical mould with matching end plugs having the provision to hold a polished SS tapered rod 25mm diameter was specially designed. The SS rod was polished and tapered for easy removal of compacted green tubes. A mechanical vibrator was used to fill the powder around the SS rod within the rubber mould. Multistage sintering of the green tubes was done in a resistance type graphite-heating furnace. The green tubes were initially heated slowly to about...
1000°C under hydrogen atmosphere to remove any absorbed or adsorbed oxygen from previous processing stages. The final stage of sintering was conducted at 1800°C for 2 hours at a vacuum level of $10^{-5}$ mbar obtaining a density of about 0.97 of theoretical value. Finally, TZM alloy tubes of 50 mm length, 22 mm ID and 27 mm OD were prepared from the sintered pre-forms by conventional single-point machining. Fig. 9 shows the green compact, the sintered pre-form and the machined tube produced from mechanically alloyed TZM powders. The detailed flow sheet of the process is presented in Fig. 10.

Based on results of a study on the hot deformation of TZM alloys, it is envisaged that extrusion of sintered tubes at 1300-1400°C would be suitable for making tubes of larger dimensions. Finally, it should be mentioned here that a halide activated pack cementation technique has also been successfully developed, for incorporating a silicide based coating on the inner or outer surfaces of these TZM tubes, for improved high temperature oxidation resistance.

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7. References


