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Studies on the synthesis of a Mo-30 wt% W alloy by non-conventional approaches

S.P. Chakraborty*, S. Banerjee, Gopal Sanyal, V.S. Bhave, Bhaskar Paul, I.G. Sharma, A.K. Suri

Materials Group, Bhabha Atomic Research Center, Trombay, Mumbai-400085, India

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ABSTRACT

In the present study, alternate routes for the synthesis of a single phase Mo–30 wt% W alloy were pursued to surmount the limitations experienced in conventional technique. The process essentially consists of preparation of active Mo and W powders by H₂ reduction of the respective oxide intermediates through multiple processing steps and then converting those pure powders into Mo–30 wt% W alloy by mechanical alloying technique (MA) at RT under Ar atmosphere in a high-energy planetary ball mill. The structural evolution of the alloy from the milled powders at different interval of time was studied by X-ray diffraction (XRD) and phase corresponding to Mo–30W alloy was confirmed. The broadening of peaks in XRD pattern was due to crystallite refinement during milling towards the formation of the designated alloy. A high rate of densification for MA powder was achieved during sintering between 900°C and 1200°C and density close to theoretical density was attained. The microstructure of sintered alloy exhibited uniform, polyhedral grains with average grain size of about 3 μ m. The morphological evolution of ano sized crystallites with polyhedral shapes. The crystallites were initially arranged in clusters which later on got distributed uniformly with the progress in milling time. The average crystallite size of MA powder was found to be 7.3 nm after 25 h of milling.

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1. Introduction

Molybdenum (Mo) base refractory alloys are characterized by high strength at elevated temperature, excellent corrosion resistance against molten metal's and high melting temperature. These alloys are capable of working at much higher temperature than conventional nickel-based super alloys because of having higher thermal conductivities with appreciably lower thermal gradients and thermal strains. Amongst the various Mo-base alloys, Mo-30 wt% W alloy has gained its prominence in missile and aerospace applications for having high melting temperature (~2832°C) that can withstand erosion or incipient melting of rocket nozzles at higher propellant combustion temperatures. The Mo-30 wt% W alloy is also a promising structural material for hightemperature nuclear reactor (HTR) applications for its elevated temperature strength and excellent chemical inertness in presence of corrosive molten zinc and lead. According to the W-Mo binary phase diagram as depicted in Fig. 1, it is interesting to note that W forms continuous solid solution with Mo in full phase field, which implies that Mo (or W) elements completely dissolve in the remaining bcc W (or Mo)-based phase. As W is added to Mo, the alloy is gradually strengthened by the mechanism of substitutional solid

solution strengthening. Addition of 30 wt% W in Mo increases the capability of the alloy to retain strength at a temperature in excess of 1700 °C. The Mo–30 wt% W alloy is also readily machinable and capable of forming into a variety of wrought shapes including round bars, sheets and plates as well as simple assemblies [1,2].

Mo-30 wt% W alloy is commercially prepared by vacuum arc melt-casting route technique. However, this method is expensive and highly energy intensive in view of using high temperature and high vacuum for melting. Moreover, due to large variation in the melting temperatures of Mo (2610 °C) and W (3410 °C), the alloying components do not mix well leading to their segregation. As a result, the final alloy is obtained as inhomogeneous mass. Repeated crushing and melting steps are required till a homogeneous alloy is formed. However, such exercise is time consuming and expensive. Mechanical alloying is basically a solid-state powder processing technique where no elaborate energy intensive steps of high temperature and high vacuum are required. Synthesis of the alloy is carried out by milling the elemental powders in simple experimental set up of different kind of mills, e.g. attrition, planetary, centrifugal, etc. The elemental powders are repeatedly fractured and cold welded during the process of milling leading to alloying. Homogenized alloy or composite metal powders with controlled and fine microstructure can be produced by this process [3–5].

In the present investigation, alternative approaches were employed to synthesize Mo-30 wt% W alloy to overcome the difficulties experienced in conventional melting technique. In this

^{*} Corresponding author. Tel.: +91 22 25593931; fax: +91 22 25505151/19613. *E-mail addresses*: spc@barc.gov.in, spc.barc@gmail.com (S.P. Chakraborty).

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Fig. 1. Binary phase diagram of Mo-W system.

context, high pure Mo and W powders, the starting components for the preparation of Mo-30 wt% W alloy, were freshly prepared in the laboratory from their respective oxide intermediates by H₂ reduction following multiple processing steps. Since these powders are highly susceptible to oxidation, and their respective oxide intermediates are also highly unstable and sensitive to different temperatures, hence, achieving these elements in their pure state is a very difficult task. Therefore, elaborate experimental campaign was carried out in order to establish an optimized experimental condition to maximize the powder yield. The freshly prepared powders were then used in place of commercially available expensive powders of Mo and W with higher oxygen content to synthesize the alloy. The designated alloy was then synthesized from as-reduced Mo, W powders at room temperature by employing mechanical alloying technique in a planetary ball milling system under Ar atmosphere. The mechanically alloyed powder was subsequently consolidated by powder metallurgical technique such as compaction by cold isostatic pressing and sintering. Structural evolution of the as-milled powder was established by X-ray diffraction (XRD) analysis. The effect of sintering temperature and powder characteristics on densification behavior was studied. The morphology of the as-milled powder after different hours of milling was investigated by scanning electron microscope (SEM) observations.

2. Experimental

2.1. Preparation of materials

The starting materials used for the synthesis of Mo–30W alloy are W and Mo metal powders. These powders were freshly prepared in laboratory by reduction with H_2 of the respective oxides. The as-reduced active metal powders were then used for mechanical alloying. The reduction process involving conversion of WO₂ and MoO₂ into respective metal powders was carried out in a resistance heating furnace with horizontal retort, as shown in Fig. 2. The charge materials were kept in a clean Mo boat at the centre of the retort. A number of experiments were conducted on 100 g scale by varying temperature, time and H_2 flow rate. The best yield for W was achieved at a temperature of around of 850 °C and for Mo at 700 °C within 2 3 h. The flow rate of H_2 was maintained approximately at 250–300 l/min. Prior to sending H_2 gas, the inside chamber of the furnace was flushed with Ar till moisture and air were completely driven out. H_2 gas after use was burnt at the exit to convert into H_2O .

The as-reduced powders of Mo and W with a purity of around 99.9% and average size of 5 and 10 μ m, respectively were mechanically alloyed in a planetary ball mill for a period of 25 h to synthesize Mo–W alloy of composition Mo–30 wt% W. The Mo and W powders were thoroughly blended in their desired ratio and a total charge of 100 g of Mo+W powder mixture corresponding to the composition of Mo–30 wt% W was filled in the milling chamber of the high energy ball mill. The chamber was made up of stainless steel bowl, internally lined with hard layer of tungsten carbide The bowl after filling the charge, was air tightened with 'O' ring fitted lid and was then purged with high purity Ar gas during milling operation. Subsequently, milling was performed with ball to powder weight ratio of 10:1 using 10 mm dia hard balls of W carbide. The rotation speed was set at 250 rpm. Milling time intervals were set to 5, 10, 15 and 25 h, respectively. The experimental parameters used in performing the mechanical alloying were described in Table 1.

2.2. Characterization

Milled powders were taken at regular intervals of time for structural analysis. Structural analysis of the as milled powders was carried out by X-ray diffraction technique using Cu K α radiation ($\lambda = 1.54$ Å) at a tube rating of 40 kV and 30 mA in a commercial powder X-ray diffractometer (Seifert 3003 T/T). The extent of alloying was determined qualitatively by monitoring the relative intensities of the Mo, W and MoW peaks. As-milled powders were subsequently cold pressed into columned



Fig. 2. Horizontal heating furnace used for the preparation of Mo, W powders.

Table 1

Planetary ball milling parameters.

Parameters	Value
Mill capacity	1 l (250 ml for each bowl)
Container material	304 stainless steel with W carbide lining
Speed of rotation	300 rpm
Ball diameter	8 mm
Charge to ball ratio (w/o)	1:10
Total charge	200 g
Atmosphere	Toluene

green compacts having 6 mm dia and 10 mm length with the application of pressure of 300 MPa. The shrinkage profile of the sample was studied by carrying out sintering in a vertical thermal mass analyzer (TMA) [Setsys Evolution TMA 1600, SETARAM] instrument with no load conditions. The sample was heated at a heating rate of 10 °C per minute up to a set temperature of 1300 °C and isothermally held for 1 h at that temperature. The powder processing technique such as cold isostatic pressing (CIP) was applied to study the consolidation behavior of the mechanically alloyed powders and parent powder mixture. Prior to CIP, the as-milled and parent mixture powders were tightly filled inside flexible silicon rubber moulds and then encased in surgical gloves. The encased moulds containing the samples were subsequently put inside the coIP using water pressure of 3000 bar. Sintering of the samples were carried out in the horizontal furnace as described in Fig. 2 under gas mixture of Ar +H₂ at the temperature range of 600–1500 °C.

Green densities of the samples were measured using the geometrical dimensions. Density after sintering was measured both by Archimedes principle and geometrically. The hardness of the sintered specimen was measured by a micro hardness tester. The morphology of the as-milled powder and sintered compacts were observed in a scanning electron microscope.

3. Results and discussion

3.1. Preparation of W powder

The starting materials for the preparation of W in general are ammonium paratungstate (APT), tungstic acid or tungsten blue. In the present study, tungstic acid (H₂WO₄) was chosen as the starting material because ultimately chemically defined oxide, WO₂ can be obtained from it for the preparation of W powder by subsequent H₂ reduction. WO₂ being a stable oxide, unwanted formation of other suboxides can be avoided during H₂ reduction. Hence, as-received tungstic acid was thermally decomposed initially to prepare yellow oxide, tungstic anhydride (WO₃) by heating it in air at 250 °C for 3 h. WO₃ was then converted into the brown oxide, WO₂ by H_2 reduction at 720 °C. The brown oxide was finally mixed with a fresh charge of yellow oxide, WO₃ for W metal production at 860 °C. The overall reduction process of tungstic anhydride (WO₃) to W by H₂ can be summarized as a three-stage process. These stages can be differentiated by following set of chemical equations. The operating conditions were judiciously adjusted finally to attain W powder as per the following reactions:

$$2WO_3 + H_2 \Leftrightarrow W_2O_5 + H_2O \tag{I}$$

 $W_2O_5 + 3H_2 \Leftrightarrow 2WO_2 + H_2O \tag{II}$

$$WO_2 + 2H_2 \Leftrightarrow W + 2H_2O$$
 (III)

As these reactions are reversible in nature, each stage of the above reactions therefore was guided by the equilibrium constant as given below:

$$K_{\rm P} = \frac{P_{\rm H_2O}}{P_{\rm H_2}}$$

where P_{H_2O} is the equilibrium partial pressure of water vapor; P_{H_2} the equilibrium partial pressure of H_2 . The respective equilibrium curves are shown in Fig. 3. It is observed that every next stage requires a higher temperature and greater H_2 content in the gas mixture. Accordingly, the experiments were conducted.



Fig. 3. Equilibrium curves for the reduction of W oxides by H_2 .

3.2. Preparation of Mo powder

As-received high-grade molybdenite (MoS_2) concentrate powder containing 50–53% Mo value was used as a source for MoO_2 . The concentrate was roasted in air to convert it into MoO_3 as per the following equation:

$$MoS_2 + 3.5O_2 = MoO_3 + 2SO_2$$
 (IV)

The roasting temperature was not allowed to exceed $650 \,^{\circ}$ C, else the MoO₃ will be melted due to local overheating and high volatility. A dynamic flow of air was maintained during roasting in order to avoid any localized overheating and also to convert any sulphorous residue present in the molybdenite concentrate into SO₂ as the roasting temperature was kept low. The vapor pressure of MoO₃ varied significantly with temperature as is evident from Table 2. The reduction of Mo trioxide to Mo metal involved three-stage reduction as indicated below

$$2MoO_3 + H_2 = MO_2O_5 + H_2O$$
 (V)

$$Mo_2O_5 + H_2 = 2MoO_2 + H_2O$$
 (VI)

$$MoO_2 + 2H_2 = MO + H_2O$$
(VII)

Since, MoO₃ might partially melt at 500–600 °C and the reaction is easy to carry out, hence to avoid such occurrence, the first step was carried out at 450 °C. The second step was carried out at 1000 °C because this reaction requires more elevated temperature and lower water vapor contents in the gases. The MoO₃ was then reduced by H₂ to prepare MoO₂ [6,7].

Table 2
Variation of the vapour pressure of molybdic acid, MoO3 with temperature.

	Temper	Temperature (°C)							
	650	800	900	1000	1100	1150			
P(mm Hg)	0.05	10.1	53.9	198.3	476.2	760.0			



Fig. 4. XRD pattern of thermally decomposed tungstic acid to obtain WO₂.



Fig. 5. XRD pattern of H₂ reduced WO₂ to obtain W powder.

3.3. XRD analysis

The XRD plot at Figs. 4 and 5 confirmed the formation of WO_2 and W in the product after thermal decomposition of tungstic acid. Similarly, Figs. 6 and 7 confirmed the formation of MOO_2 and Mo as per the chemical reactions in equation nos. (VI) and (VII). Fig. 8



Fig. 6. XRD pattern of H₂ reduced MoO₃ to obtain MoO₂.



Fig. 7. XRD pattern of H₂ reduced MoO₂ to obtain Mo powder.

demonstrated the structural evolutions of as-milled powder in the form of XRD patterns at different time intervals. Formation of Mo-W phase was affirmed after 5 h of milling by the appearance of Bragg reflections corresponding to (200), (110) and (211) crystal planes. As the milling progressed, the initially sharp diffraction peaks were getting broadened and reduced in intensity because of increase in atomic level strain due to crystallite size refinement and structural disorder accumulation processes that occurred during alloying of Mo and W. These features originated from the repeated fracturing and alloying of the particles. XRD patterns further showed that elemental Mo and W powders gradually transformed into Mo–30 wt% W alloy at the expense of Mo and W [8]. The crystallite size of the as-milled powders at different duration of time was measured from the corresponding XRD plots by using Scherrer equation,

$$\tau = \frac{\kappa \lambda}{\beta \cos \theta}$$

where τ is the mean crystallite dimension, *K* (=0.94) is the shape factor, λ is the X-ray wavelength, typically 1.54Å, β is the line broadening at half the maximum intensity in radians, and θ is the



Fig. 8. XRD spectra of the powder milled in Ar at various milling times.

Table 3	
The calculation for determining crystallite size for all duration of milli	ış

	Hours of n	Hours of milling							
	5	10	15	20	25				
θ (°)	40.31	40.45	40.31	40.43	40.45				
$\beta_{1/2}$ (°) τ (nm)	0.72 12.287	1.23 7.196	1.1 8.042	1.19 7.437	1.22 7.255				

Bragg angle [9,10]. The average crystallite size after 25 h of milling was determined to be around 7.3 nm. Table 3 shows the calculation for determining τ for all duration of milling.

3.4. Milling studies

The particle size distribution of as-reduced Mo and W powders was depicted in Fig. 9 which indicated that the particle size of starting Mo and W powders was available in the range of around 20–30 μ m. It is clearly seen that with the progress of milling, the initial crystallite size of Mo–30W alloy rapidly decreased during MA process and got converted into nanocrystalline powders after a span of 25 h of milling. The variation of crystallite size with the progress of milling was presented in Fig. 10. This plot was constituted using Scherrer equation based on the line broadening data of XRD analysis of as-milled powders. It can be seen from the plot that the reduction in size of the milled powder progressed linearly with time. Under the influence of repeated fracturing by mechan-



Fig. 9. Particle size distribution of Mo, W and Mo-30W powders.



Fig. 10. Variation of crystallite size during milling as a function of time.



Fig. 11. Effect of sintering on shrinkage rate and profile as a function of time.

ical alloying coupled with hard and brittle nature of Mo and W powders, the transformation of micron size particles into nano size range was rapid and easy. The average crystallite size after 25 h of milling was evaluated to be 7.3 nm as described above.

3.5. Compaction and sintering

The shrinkage behavior of hydraulically pressed MA powder was evaluated by conducting an isothermal sintering study at 1300 °C for duration of 1 h as depicted in Fig. 11. The profile has demonstrated the occurrence of an appreciable shrinkage during sintering equivalent to around 13.5 wt% indicating good sinteribility of the MA powder. In general, refractory metals and alloys possess high melting temperature and brittle characteristics. Consequently, these materials respond to slow sintering kinetics. Hence, conventionally, in order to accelerate the sintering process, the sintering temperature of refractory metal and alloys is kept very high, in the order of 1800–2000 °C with longer duration in comparison to super-alloys and other variety of high strength materials. However, prolonged duration of soaking at high sintering temperature may induce oxidation and significant grain growth [11]. In the present case, Mo-30W alloy processed by MA is already in a high state of energy with higher surface area which is favorable attributes for sintering. In the present investigation, a combination of mechanical alloying and isostatic pressing were applied to the samples prior to sintering. Obviously, this strategy influenced positively on the rate of densification and sintering temperature as described below.

The green densities of cold isostatically compacted samples prepared from the parent powder mixture and mechanically alloyed powder were 76% and 64% respectively of the theoretical density (12 g cc^{-1}) . Although the MA powder was having much smaller particle size (10 nm) as compared to the parent powder (5–10 μ m), however, it produced lower green density as the particles were hard and brittle. Fig. 12 represents the densification behavior of both types of samples during sintering between 600 and 1500 °C for 6 h in reducing atmosphere. Because of the lower particle size, the rate of densification of the MA powder compact was much higher in the intermediate temperature range (900-1200 °C). This could be attributed to the availability of higher specific surface area and faster inter grain boundary diffusion in this temperature range. The sintering kinetics was much slow beyond this temperature for both the cases. A maximum sintering density of 99% TD was achieved for MA powder at the highest sintering temperature of 1500 °C. The average knoop hardness value measured at 0.98 N (100 g) load for sintered pellet was 400 HK as compared to 270 HK for arc consolidated alloy. Higher hardness of Mo-30W alloy was



Fig. 12. Effect of sintering on shrinkage rate and profile as a function of time.

due to crystallite refinement, lattice distortion and formation of fine-grained microstructure during mechanical alloying. This high hardness value was quite comparable with other high strength Mo based alloys [12].

3.6. SEM characterization of milled and sintered powder

The SEM images corresponding to the MA powder at 5, 10, 15, 20 and 25 h of milling time were presented in Figs. 13-17, respectively. According to SEM micrograph at Fig. 13, particles of Mo and W together have formed several large clustering consisting of smaller micro-welded particles. Cold welding was the predominant mechanism at this stage. As the milling time progressed to 10 h, work hardening led to the fracturing of the particles and the particle size was reduced proportionately with decrease in the overall volume of the particulate mass. This was demonstrated in Fig. 14. The phenomenon of welding and fracturing with simultaneous alloying continued as the milling progressed to 15 h. This has resulted in further reduction in size of the particles along with the total volume as can be seen from Fig. 15. As the milling time was increased to 20 h, the alloying was found to be the predominant stage. Due to alloying, the alloyed particles were dissociated from the cluster and rearranged themselves in a new fashion. This was depicted in Fig. 16. After 25 h of milling, it was observed that the particles again formed cluster of finer crystalline grains as demonstrated in



Fig. 13. SEM micrograph showing powder morphology after 5 h of milling.



Fig. 14. SEM micrograph showing powder morphology after 10 h of milling.



Fig. 15. SEM micrograph showing powder morphology after 15 h of milling.

Fig. 17. The average crystallite size was determined to be around 10 nm which was in close approximation with the value evaluated by using Scherrer equation.

The SEM micrograph of sintered Mo–30 wt% W alloy in Fig. 18 revealed formation of uniform granular structure with polyhedral shapes and well defined grain boundaries. The grains were observed to be in close association with each other with hardly any pores seen indicating good sintering. The average grain size was 3 μ m. Excellent solid-state diffusion of Mo and W into each other was responsible for nearly pore free structure [13].



Fig. 16. SEM micrograph showing powder morphology after 20 h of milling.



Fig. 17. SEM micrograph showing powder morphology after 25 h of milling.



Fig. 18. SEM micrograph of sintered Mo-30 wt% W alloy.

4. Conclusion

Present investigation demonstrates technical feasibility of synthesis of a Mo–30 wt% W alloy from freshly prepared active Mo and W powders by mechanical alloying technique. Nanostructured alloy powders of average crystallite size of ~7.3 nm with polyhedral shape were achieved after 25 h of milling in Ar. The structural analysis of the milled powder by XRD confirmed the formation of Mo–30 wt% W solid solution alloy phase via crystallite refinement. SEM micrographs revealed the morphological details related to the mechanism of alloy formation. Faster sintering kinetics for MA powder was observed between 900 and 1200 °C. SEM study of sintered samples revealed the presence of a granular structure with good solid-state bonding.

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