Effect of Hydrogen sintering on phase, mechanical property and High temperature response of Nanostructured W-60 at. % Cr Defense alloy

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Abstract: Nanostructured W_{40}Cr_{60} alloy was produced by mechanical alloying (MA) of elemental tungsten (W), chromium (Cr) powder in a high energy ball-mill followed by compaction at 250 MPa pressure and hydrogen sintering at 1500°C for 5 h. The evolution of phase and microstructure of the milled powder and consolidated alloy was investigated by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). The crystallite size of W in W_{40}Cr_{60} powder reduced from 100 µm at 0 h to 29 nm at 20 h of milling and lattice strain increases to 0.51% at 20 h of milling. The lattice parameter of tungsten shows initial expansion of lattice upto 0.22% at 5 h of milling and contraction of lattice upto 0.25% at 20 h of milling. The TEM observation revealed that the observed crystallite size (~20 nm) agrees well the measured crystallite size from XRD. Maximum solid solubility of 5.4 at. % Cr in W has been achieved at 20 h of milling. Hardness and Elastic Modulus of sintered W_{40}Cr_{60} alloy are less compared to pure tungsten. Maximum wear depth and compressive strength of 54.33 µm and 914 MPa respectively is achieved in sintered W_{40}Cr_{60} alloy. Oxidation behavior of the sintered W_{40}Cr_{60} alloy is also studied at 800°C for 15 h. Comparative study on the oxidation resistance of W, W_{70}Cr_{30} and W_{40}Cr_{60} alloy has been carried out to understand the high temperature behavior of pure W and W-Cr alloy. The research work shows encouraging results in terms of enhanced hardness and oxidation resistance as compared to recent study on nanostructured W-Cr alloys.

Keywords: Mechanical alloying, Lattice parameter, solid solubility, Hardness, Strength; Oxidation.

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1. Introduction

Tungsten (W) is a promising candidate for electrical, electronic, nuclear and space vehicle applications due to unique characteristics of high melting point (3410°C) and excellent mechanical strength at elevated temperature and the highest density of all engineering materials (19.3 g/ml) with tensile elastic modulus of 411 GPa at 20°C [1,2]. However, high ductile-brittle transition temperature limits the wide spectrum of application of W. Development of W based alloys results in improved fabricability, and lowering of the ductile brittle transition temperature. As a result of increasing demand for higher and better mechanical properties, amorphous and nanocrystalline tungsten alloys have attracted enormous attention in recent years [3,4]. Mechanical alloying is a convenient solid state synthesis alternative to melt spinning and similar rapid quenching techniques to develop amorphous and nanostructured alloys [5,6]. Among the various solid state method the attractive prospect of high-energy ball milling in recent years is due to its simplicity, ease scale up production, high productivity, relatively inexpensive equipment, applicable to synthesize a wide variety of alloys including supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures and amorphous alloys and enhancement of solid solubility than other non-equilibrium processing technique such as rapid solidification [6].

The strong possibility of the formation of volatile oxide on tungsten surface at high temperature causes serious shortcoming with respect to its application. Consequently, the formation of protective and adhere coating on tungsten surface is necessary for its high temperature application. Alloy addition in pure tungsten improves the feasibility of high temperature applications [7]. Solid state sintering of W and W based alloy demands sintering temperature in excess of 2400°C. Consolidation of W and W based alloy at this high temperature is restricted due to cost and inability to sinter complex shaped materials [8, 9]. Recent study shows that the sintering temperature of pure W can be brought down to ~1800°C from the conventional 2700°C by making the W-powder nanostructured prior to sintering [10]. Present investigation aims at synthesis and characterization of W-Cr alloys and lowering the sintering temperature of W-Cr alloys by making the powders nanostructured by prior mechanical alloying (MA).

2. Experimental methods

A planetary ball mill (Fritsch Pulverisette-5) was used to mill elemental W and Cr powder (~99.5 pct pure) with nominal composition of W$_{40}$Cr$_{60}$ (at.%) having initial particle size of 100-200 µm at a mill speed of 300 r.p.m using tungsten carbide (WC) balls (10 mm diameter) as grinding media and ball to powder (BPR) weight ratio of 10:1. Toluene was used as a process control agent (PCA) to control the excessive welding and agglomeration during milling. Milled powder samples were taken out at an interval of 0, 1, 3, 5, 7, 10, 15, 20 h and characterization the powder samples were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM).

A high resolution X- ray diffractometer (Philips, X’ pert pro) was used to record the X-ray diffraction pattern (XRD) of the mechanically alloyed powder using Co-k$_{\alpha}$ radiation ($\lambda$=1.790607 Å). The record was matched with the JCPDS data bank to track the evolution of phases during mechanical alloying. The crystal size and lattice strain were calculated by
determining the peak positions and broadening of the X ray diffraction pattern by using Williamson and Hall method [11].

The lattice parameter was calculated using Nelson–Riley extrapolation method [12] by incorporating three strong XRD peaks of milled powders. Nelson–Riley function for each peak has been evaluated by using the equation as provided below.

\[
\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} = \text{(1)}
\]

The values were fitted linearly in a straight line and extrapolated to y-axis. The point of intersection on y axis provides the actual lattice parameter value. The dislocation density \(\rho_d\) of the milled powders was calculated as below:

\[
\rho_d = 2\sqrt{3} \frac{\varepsilon^{1/2}}{D \times b}
\]

where \(b\) is the burgers vector of dislocations and \(b = (a\sqrt{3})/2\) for the bcc structure, \(D =\) crystallite size, \(\varepsilon =\) lattice strain, \(a =\) cell parameter= lattice parameter [13-15].

Solid solubility of Cr in W can be calculated using Vegard’s formula as :

\[
(1 - x)a_1 + x a_2 = a
\]

where \(a_1\) and \(a_2\) are the lattice parameter of the pure solvent and solute element, respectively, \(a\) is the lattice parameter of the solid solution alloy and \(x\) is the solid solubility [16]. The values of \(a_1\), \(a_2\) and \(a\) has been calculated from the interplanar spacing \((d)\) and respective diffraction plane of X-ray diffraction peak of solute, solvent and solid solution alloy.

The morphology of the mechanically alloyed (MA) powders as well as surface topography of the sintered sample was observed under a scanning electron microscope (SEM).

A transmission electron microscope (JEOL, JEM 2100) with accelerating voltage of 200 KV, and lattice resolution of 0.14 nm was employed to observe the crystallite size in mechanically alloyed powders of \(W_{40}Cr_{60}\) using bright field imaging technique. Selected area diffraction (SAD) pattern was used to identify the crystal structure.

The \(W_{40}Cr_{60}\) powder milled for 20 h were subjected to compaction in an automatic hydraulic press using 250 MPa pressure for 5 minutes. Sintering of the compacts of \(W_{40}Cr_{60}\) was carried out at 1500°C for 300 min (5 h) under flowing hydrogen atmosphere in a continuous pusher type sintering furnace.

Sintered density was evaluated using the density measurement kit (Sartorius, 215S) by Archimedes’s principle as below [17, 18]:

\[
\rho_s = \frac{W_a}{W_{sat} - W_{susp}} \times \rho_w \text{ gm/cm}^3 \text{ (4)}
\]

Where \(W_a\) is weight of the sintered sample in air. \(W_{sat}\) is the weight of the sample with all the open porosity saturated with water, \(W_{susp}\) is the weight suspended in water. \(\rho_w\) is the density of water. The sinterability was evaluated from the percentage ratio of density of the sintered sample to theoretical density of the sintered sample.
A nanoindenter (MTS System Corporation, Nanoindentation® XP) was employed to measure the hardness and elastic modulus of sintered W<sub>40</sub>Cr<sub>60</sub> alloys. The compression test was carried out at room temperature using Instron-SATEC KN600 machine to determine the maximum compressive strength of the sintered samples. A ball on plate wear tester (Ducom, TR-208-M1) was used to measure the wear depth with respect to sliding distance traversed by the indenter on the sample. The load, time and sliding speed during wear test was kept at 20 KN and 10 mins and 25 rpm respectively. Sliding distance can be measured by using the following equation.

\[
\text{Sliding Distance (S. D)} = \left( \frac{R}{60} \right) \times t \times 2\pi r
\]  

(5)

where \( R \) is the number of rotation per minute traversed by the indenter on sample surface, \( t \) is the time in sec, \( r \) is track radius (4 mm) measured from the center of the sample to the track.

Oxidation behavior of the sintered products at 800°C for 15 hours was studied in muffle furnace (Fig. 2). The furnace temperature was calibrated by Pt-Pt+13%Rh thermocouple. For Oxidation study initial weight and dimension of the sample was recorded. Sample was placed inside the alumina crucible and taken out from the furnace at an interval of 30 min, weighed and placed inside the furnace. Weight change per unit area as a function of time was measured to investigate the oxidation kinetics of the alloys. Sample exposed to 15 h of oxidation in air was characterized by XRD.

3. Results and discussions

3.1. XRD Study of milled powder

The XRD patterns of W<sub>40</sub>Cr<sub>60</sub> powder at 0 to 20 h of milling are displayed in the Fig. 1. The patterns show continuous broadening and reduction in the intensity of the peaks, thus evidencing refinement of the crystallite size of W by ball milling. The crystallite size is 29 nm after 20 h of milling for W<sub>40</sub>Cr<sub>60</sub> composition. Similar trend is also reported in recent literatures [19, 20]. The variation of solid solubility with milling time for W<sub>40</sub>Cr<sub>60</sub> alloy is displayed in Fig 2. The maximum solubility of Cr in W was measured as 5.4 at. %.

![Fig. 1. XRD pattern of W<sub>40</sub>Cr<sub>60</sub> alloy milled for 20 h.](image1)

![Fig. 2. Variation of Solid solubility of Cr in W with milling time.](image2)
The variation of lattice parameter of W with milling time in W$_{40}$Cr$_{60}$ alloy is shown in Fig. 3 (a) which illustrates initial expansion of lattice upto 5 h of milling and contraction of the lattice from 5 h to 20 h of milling. The initial expansion may be attributed to the negative hydrostatic pressure exerted by the nano-crystals. Recent report shows a significant expansion of Nb lattice with crystal size refinement during ball milling [21]. Similar behavior has been reported in recent literature [22]. Cr (atomic radius: 0.166 nm) act as a substitutional element [23] in W (atomic radius: 0.193 nm) causes softening of the W lattice which leads to contraction of the lattice afterwards. The rate of diffusion of Cr atom in W lattice is slower upto 5 h of milling as in the initial period of milling severe deformation dominates over the atomic diffusion which leads to sharp increase in dislocation density (Fig. 3(b)). The atomic diffusion of Cr sharply increases after 5 h of milling as the diffusion distance between particles attain to a critical limit to drive stress assisted diffusion mechanism. The dislocation density increases sharply with increase in the milling time from 0 to 10 h, whereas marginal increase in dislocation density is found with increase in milling time from 10 to 20 h (Fig. 3(b)). The sharp increase in dislocation density at 10 h of milling is attributed to the substantial decrease in crystallite size. The rapid rate of increase in dislocation density drops beyond 10 h of milling due to diffusion of Cr atom in W lattice which dominates the crystallite size reduction.

![Fig. 3. Variation of a) Lattice parameter of W b) dislocation density in W$_{40}$Cr$_{60}$ alloy with milling time.](image)

3.2. SEM Study

The SEM micrograph in Fig. 4 (a) illustrates that of W and Cr particles mostly possess irregular spherical shape before initiation of milling (0 h). The irregular and spherical particles are strain hardened and fractured at 20 h of milling (Fig. 4(b)). Recent report suggests that nanoparticles at 20 h of milling are not beneficial for flowability due to large interparticle friction which results in poor green density (density before sintering) [22].
SEM micrograph of powder morphology of W_{40}Cr_{60} alloy milled for a) 0 h b) 20 h.

SEM micrograph of sintered W_{40}Cr_{60} (Fig. 5(a)) evidences almost fully dense alloy and no pores or cracks has been found in the sample. The phases are identified by Energy Dispersive spectroscopy (EDS) analysis (Fig. 5(b)) of the sintered product. No traces of oxygen have been found by EDS analysis as sintering is carried out in hydrogen atmosphere. All the residual oxygen has been removed as moisture by reacting with hydrogen thereby eliminating any presence of brittle oxides. Traces of oxygen during mechanical alloying can deteriorate the mechanical properties of sintered alloy where sintering has been carried out in vacuum or Argon atmosphere as vacuum environment or Argon is unable to remove any presence of oxide before sintering. Therefore hydrogen sintering proves to be fruitful in terms of achieving better mechanical properties as compared to vacuum or Argon purged sintering [20].

TEM Study of milled powder

Fig. 6 (a) and (b) displays bright field TEM image with corresponding SAD pattern of W_{40}Cr_{60} milled powder at 20 h respectively. TEM image reveals the formation of nano-crystalline phase at 20 h of milling with size varying from 20 to 30 nm. Continuous rings of SAD pattern are attributed to the formation of fine polycrystallites. Fig. 6 (b) reveals the presence of (110), (200), (222) planes of W after the indexing of SAD pattern. The calculated interplaner spacing (d) values of BCC-W are 0.20 nm for (110), 0.15 nm for (200), and 0.091 nm for (222) respectively.

3.3. TEM Study of milled powder

Fig. 5 (a). SEM micrograph b) corresponding EDS pattern of sintered W_{40}Cr_{60} alloy milled for 20 h and sintered at 1500°C for 5 h.
The interplaner spacing \((d)\) derived from SAD pattern matches well with the standard values of BCC-W of JCPDS data files.

Fig. 6. TEM image of \(W_{40}Cr_{60}\) powder milled at 20 h: (a) Bright field TEM image and (b) corresponding SAD pattern.

3.4. Sinterability study

Sinterability is the percentage ratio of sintered density to the theoretical density of a material. The variation of sinterability of sintered \(W_{40}Cr_{60}\) alloy at different compaction pressure is displayed in Fig. 7. The sinterability increases with increase in compaction pressure. Maximum sintered density of 92% has been achieved at 20 h of milling by using 250 MPa compaction pressure. The increase in sintered density with increase in pressure can be attributed to the reduction of pore size to a greater extend which enhances the sintering kinetics. X-ray diffraction study of sintered \(W_{40}Cr_{60}\) sample at different milling time (Fig. 8) shows no new phase or intermetallic formation during sintering, thereby eliminating the possibility of deleterious effect of any undesirable phases on mechanical properties of sintered \(W_{40}Cr_{60}\) alloy.

Fig. 7. Sinterability of \(W_{40}Cr_{60}\) milled for \(W_{40}Cr_{60}\) different pressure and sintered at 1500°C for 5 h.

Fig. 8. X-ray diffraction of sintered sample milled for different time and sintered at 1500°C for 5 h
3.5. Hardness and Elastic Modulus study

The hardness and the elastic modulus of the sintered W\textsubscript{40}Cr\textsubscript{60} alloy was measured by the nanoindenter, and the results are shown in Fig. 9 (a), (b) respectively. The average hardness and elastic modulus for W\textsubscript{40}Cr\textsubscript{60} is 8.23 GPa and 318 GPa respectively. The hardness and elastic modulus of W\textsubscript{40}Cr\textsubscript{60} is lower than the reported values of nanostructured W milled for 20 h [24] as Cr addition softens the W lattice as evident from Fig. 2 (a).

![Fig. 9 (a) Nanoindentation hardness and (b) Elastic modulus of W\textsubscript{40}Cr\textsubscript{60} milled for 20 h and sintered at 1500°C for 5 h.](image)

3.6. Wear and Compression study

Fig. 10 displays the variation in wear depth with sliding distance traversed by the indenter on the sample surface for W\textsubscript{40}Cr\textsubscript{60} alloy. The wear depth shows an increasing and decreasing profile due to non-homogeneity of hardness and composition throughout the cross section of the sample. Fig. 11 shows the stress strain curve of the sintered sample under compressive loading at room temperature using a strain rate of 10\textsuperscript{-1}/min. It is evident from Fig. 11 that sintered W\textsubscript{40}Cr\textsubscript{60} alloy shows maximum compressive strength of 914 MPa. Recent report also shows a similar trend of compressive behavior of W based alloy [25].

![Fig. 10. Variation of Wear depth for W\textsubscript{40}Cr\textsubscript{60} milled for 20 h and sintered at 1500°C for 5 h.](image)  
![Fig.11. Compressive stress strain curve of sintered W\textsubscript{40}Cr\textsubscript{60} alloy.](image)
3.7. Oxidation Study

Fig. 12 (a) shows the oxidation kinetics of W<sub>40</sub>Cr<sub>60</sub> alloy at 800°C for exposure time up to 15 h. The results show that for W<sub>40</sub>Cr<sub>60</sub> the oxidation rate marginally decreases however recent reports suggest that increase in oxidation rate in case of W and W<sub>70</sub>Cr<sub>30</sub> is due to formation of porous WO<sub>3</sub> scale which leads to rapid diffusion of oxygen into the base metal [24]. The decrease in the rate in case of W<sub>40</sub>Cr<sub>60</sub> can be attributed to the loss or healing of some low melting eutectic scale. Formation of protective layer of Cr<sub>2</sub>O<sub>3</sub> and CrWO<sub>3</sub> is evident from the XRD study of W<sub>40</sub>Cr<sub>60</sub> alloy (Fig 12(b)). The above investigation suggests that higher percentage of chromium is effective in providing protective coating to the base metal at elevated temperature. The present investigation suggests that W<sub>40</sub>Cr<sub>60</sub> alloy is more oxidation resistant than recently investigated W or W<sub>70</sub>Cr<sub>30</sub> alloy [24].

![Weight change as a function of exposure time for the oxidation of W<sub>40</sub>Cr<sub>60</sub> alloy at 800°C](image)

![XRD pattern of the oxide phase formed on the surface of W<sub>40</sub>Cr<sub>60</sub> alloy after exposure at 800°C for 15 h in air.](image)

Fig.12. (a) Weight change as a function of exposure time for the oxidation of W<sub>40</sub>Cr<sub>60</sub> alloy at 800°C [1] [Ref. 24] (b) XRD pattern of the oxide phase formed on the surface of W<sub>40</sub>Cr<sub>60</sub> alloy after exposure at 800°C for 15 h in air.

4. Conclusions

Contraction of W lattice occurs after 5 h of milling due to the formation of solid solution (alloying of Cr in W lattice). Solid solubility of Cr in W is more pronounced after 5 h of milling due to progressive attainment of shorter diffusion distance results in enhanced stress assisted atomic diffusion. Dislocation density increases sharply upto 10 h of milling and minimal increase after 10 h of milling due to rapid inter-diffusion of Cr in W which dominates over severe deformation beyond 10 h of milling. No cracks or new phase formation was observed in sintered W<sub>40</sub>Cr<sub>60</sub> as evident from XRD or SEM analysis. Oxygen was not found in the sintered sample as sintering was carried out in hydrogen atmosphere which removes any presence of oxygen. Lower hardness and Elastic modulus of nanostructured W<sub>40</sub>Cr<sub>60</sub> alloy than nanostructured W revealed that addition of Cr softens the W matrix. Oxidation study reveals that higher percentage (60 at. %) of Cr addition is sufficient to provide resistant coating on W<sub>40</sub>Cr<sub>60</sub> alloy at elevated temperature as compared to recently investigated pure W and W<sub>70</sub>Cr<sub>30</sub> alloy.
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