Synthesis and Characterization of W\textsubscript{80}Ni\textsubscript{10}Mo\textsubscript{10} alloy produced by mechanical alloying

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Abstract. The present study aims at synthesis and characterization of nanostructured W\textsubscript{80}Ni\textsubscript{10}Mo\textsubscript{10} (wt. %) alloy produced by mechanical alloying (MA). Elemental powders of tungsten (W), nickel (Ni), molybdenum (Mo) were subjected to mechanical attrition in a high energy planetary ball-mill using chrome steel as grinding media and toluene as a process control agent. The crystallite size and lattice strain of the nanostructured powders at different stages of milling (0 h to 20h) was calculated from the X-ray diffraction patterns (XRD). The crystallite size of W in W\textsubscript{80}Ni\textsubscript{10}Mo\textsubscript{10} powder was reduced from 100 µm to 55 nm at 10 h and further reduction to 40 nm at 20 h of milling with increase in lattice strain of 0.25% at 20 h of milling. The lattice parameter of tungsten showed initial expansion up to 0.03% at 10 h of milling and then contraction up to 0.04% at 20 h of milling. The scanning electron microscopy (SEM) also showed mixed morphology of W\textsubscript{80}Ni\textsubscript{10}Mo\textsubscript{10} powders consisting spherical and elongated particles after 20 h of milling. SEM analysis also revealed that particle size reduced from 100 µm to 2 µm with an increase in the milling time from 0 to 20 hours. The dark-field Transmission Electron Microscopy (TEM) observations revealed that the crystallite size of W in milled W\textsubscript{80}Ni\textsubscript{10}Mo\textsubscript{10} alloy is in good agreement with calculated crystallite size from XRD.

1. Introduction
Tungsten is a refractory metal that possesses high melting point (3410°C) and excellent mechanical strength at elevated temperature, highest density of all engineering materials (19.3 g/ml) and tensile elastic modulus of 411 GPa. Therefore it is desired for applications in electrical, electronic, nuclear and space vehicle equipment [1]. On the other hand tungsten suffers from relatively poor fabricability and high ductile-brittle transition temperature. In order to improve the properties and to increase the spectrum of applicability, much effort has been directed towards the development of tungsten alloys in recent years. The work is essentially centered on the goals such as to improve fabricability, particularly at elevated temperatures and to lower the ductile brittle transition temperature of W based alloys. As a result of increasing demand for higher and better mechanical properties, amorphous and nanocrystalline tungsten alloys have attracted enormous attention in recent years [2, 3]. Mechanical properties of nanostructured materials are known to be improved by the refinement of microstructures by mechanical alloying which is a convenient solid state synthesis alternative to melt spinning and similar rapid quenching techniques to develop crystalline and amorphous alloys [4]. Among the various solid state methods, high-energy ball milling has gained quite popularity in recent years.

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because of its simplicity, ease scale up production, high productivity, relatively inexpensive equipment, and applicability to a wide variety of materials [5].

Present investigation aims at synthesis, characterization and optimization of the process parameters of the current W$_{80}$Ni$_{10}$Mo$_{10}$ alloy produced by mechanical alloying (MA) route.

2. Materials and methods
A planetary ball mill (Fritsch Pulverisette P5) was used to mill elemental W, Ni, Mo powder at a mill speed of 300 r.p.m using chrome steel as grinding media and ball to powder weight ratio of 10:1. Milled samples were taken out after 1, 5, 10, 15, 20 h for characterization purpose. The details of the selected alloy and milling parameters are presented in the table 1.

| Composition          | Grinding Medium | Ball to powder weight ratio | Mill Speed (rpm) | Milling Duration (h) | Milling Medium |
|----------------------|-----------------|-----------------------------|------------------|----------------------|---------------|
| W$_{80}$Ni$_{10}$Mo$_{10}$ | Chrome Steel     | 10:1                        | 300              | 20                   | Toluene       |

A high resolution X-ray diffractometer (Make: Rigaku Japan, Model: Ultima IV) was used to record the X-ray diffraction pattern (XRD) of the mechanically alloyed powders at different stages of milling using Cu-$k_a$ radiation ($\lambda$=1.541874 Å). The record was matched with the JCPDS data bank to track the evolution of phases during mechanical alloying [6]. The crystal size and lattice strain was calculated by determining the peak position and broadening of peak from the X-ray diffraction pattern [7]. The lattice parameter was calculated from the X-ray diffraction pattern after stripping of K$_{a2}$ of XRD pattern using precise lattice parameter calculation method [7]. The d values of the high angle diffraction peaks were extrapolated against the function cos$^2$ (θ)/sin (θ), cos$^2$ (θ)[6], to yield the precise measure of d at cos (θ) tending to 0. It was found that cos$^2$ (θ) function gave best possible fit. The morphology and particle size of the mechanically alloyed (MA) powders at different stages of milling was observed under a scanning electron microscope (SEM) (Make: JEOL, Model: JSM-6084LV). The elemental compositional distribution of milled W$_{80}$Ni$_{10}$Mo$_{10}$ powder was analyzed by the energy dispersive X-ray (EDX) analysis attached with SEM. Crystallite size of nanostructured W in mechanically alloyed W$_{80}$Ni$_{10}$Mo$_{10}$ powder at 20 hr was detected by transmission electron microscope (TEM) (Make : JEOL, Japan, Model- JEM 2100). Selected area diffraction (SAD) patterns were obtained to identify the crystal structure using appropriate aperture and tilt.

3. Result and Discussion
3.1. X-ray Diffraction (XRD) analysis of milled powders
The XRD patterns of milled W$_{80}$Ni$_{10}$Mo$_{10}$ powder at different milling times (1, 5, 10, 15, 20 h) are displayed in figure 1. The patterns show continuous broadening and reduction in the intensity of the peaks, thus evidencing refinement of crystallite size of W with increase in milling time. It is evident from figure 1 that Ni and Mo undergo into solid solution in the W matrix with increase in milling time. Reduction in crystallite size and plastic strain buildup is attributed to the increase in full-width at half-maximum with increasing milling time [8]. Peak broadening analysis was done with the help of Scherrer equation after elimination of contributions from the strain and instrumental error [6].
Figure 1. XRD pattern of W$_{80}$Ni$_{10}$Mo$_{10}$ alloy milled for 20 h.

The variation of crystallite size and lattice strain is shown in figure 2. The crystallite size is 40 nm at 20 h of milling for W$_{80}$Ni$_{10}$Mo$_{10}$ composition. Recent result shows that crystallite size of W based alloys can be brought down to 30 nm at 20 h of milling using tungsten carbide as grinding media [1]. The higher percentage of size reduction in case of tungsten carbide grinding media is attributed to higher hardness of tungsten carbide than chrome steel [1].

Figure 2. Variation of crystal size and lattice strain of W with milling time in W$_{80}$Ni$_{10}$Mo$_{10}$. 

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The variation of lattice parameter of W with milling time in W$_{80}$Ni$_{10}$Mo$_{10}$ alloy during mechanical alloying is shown in figure 3. It is evident that initially the lattice parameter of W expands up to 0.03% at 10 h and then contracts up to 0.04% at 20 h of milling. This is due to the fact that the initial expansion of lattice parameter of W is attributed to the negative hydrostatic pressure exerted by the formation of nano-crystallites during mechanical alloying. Pabi et al. has recently reported that a significant expansion of Nb lattice during ball milling of pure Nb [9]. On the other hand, the alloying elements Mo and Ni undergoes to form the substitutional solid solution with W, as their atomic radius is marginally lower than that of atomic radius of W which leads to contraction of the lattice after 10 hours of milling [10]. Initially up to 10 hours of milling the reduction in crystallite size is predominant whereas from 10 to 20 hours of milling formation of solid solution (by alloying of Mo and Ni with W) dominates over crystallite size reduction.

3.2. Scanning Electron Microscope (SEM) analysis of milled powders

The SEM micrographs in figure 4 illustrate the change in particle morphology and size from ~100 µm to ~2 µm at different milling time. The W, Ni and Mo particles consist of spherical shape at 0 h which changes to elongated shape after 20 h of milling. The elongated nanoparticles at 20 h of milling are not conducive for flowability due to large interparticle friction therefore responsible for poor green densification property.
Figure 4. SEM images of powder morphology of W$_{80}$Ni$_{10}$Mo$_{10}$ alloy after different milling times: (a) 0 h, (b) 1 h, (c) 5 h, (d) 10 h, (e) 15 h, and (f) 20 h.

The EDX spectrum of as milled W$_{80}$Ni$_{10}$Mo$_{10}$ powder at 20 h of mechanical alloying is reported in figure 5 which confirms the presence of predominant element W and also minor elements Mo and Ni.

Figure 5. EDX spectrum of W$_{80}$Ni$_{10}$Mo$_{10}$ powder milled for 20 h.

3.3. Transmission Electron Microscope (TEM) analysis of milled powder at 20 h

Bright field TEM image along with corresponding SAD pattern of W$_{80}$Ni$_{10}$Mo$_{10}$ milled powder at 20 h is shown in figure 6 (a) and (b) respectively. It reveals that the formation nano-crystalline phase at 20 h of milling with size varying from 30 to 40 nm and it is in reasonable good agreement with the result obtained from XRD analysis (figure 2). The SAD pattern consists of continuous rings which denote the presence of fine polycrystallites. Figure 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 0.22...
nm for (110), 0.15 nm for (200), and 0.09 nm for (222) respectively. The results of the interplaner spacing \((d)\) values are matching with the standard values of BCC-W from JCPDS data files.

Figure 6. TEM image of \(W_{80}Ni_{10}Mo_{10}\) powder milled at 20 h: (a) Bright field TEM image and (b) corresponding SAD pattern.

Conclusion
From the details synthesis and structural characterizations of the present alloy, the following conclusions can be drawn:

- Mechanical alloying is an effective route for synthesis of \(W_{80}Ni_{10}Mo_{10}\) alloy powder.
- Crystallite size of tungsten in \(W_{80}Ni_{10}Mo_{10}\) gradually decreases with increasing milling time and it records 40 nm at 20 h of milling have been calculated by using Scherrer formula from the XRD patterns.
- The lattice parameter of tungsten initially expands upto 0.03% at 10 h and then contracts upto 0.04% at 20 h of milling.
- The apparent particle size of powders gradually reduces from 100 µm (manually blended) to 2 µm (20 h) by SEM analysis of milled powders.
- The presence of nanocrystalline BCC-W phase with 30-40 nm in size at 20 h of milling is confirmed from the bright field TEM image and corresponding SAD pattern.

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