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A study of molybdenum addition on W-Ni-Fe based heavy alloys sintered with spark plasma sintering

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Abstract. Tungsten heavy alloys comprising tungsten, nickel and ferrous were modified, where molybdenum was added in varying weight proportions keeping the ratio of Ni: Fe (8:2) constant. The powders were mixed in a high-energy ball mill and were further fabricated using the spark plasma sintering (SPS) method at a peak temperature of 1000°C with heating rate of 100°C/min. The details of the microstructure and mechanical properties of these various alloy compositions were studied. With the increasing weight composition of the Mo in the alloy, the relative density of the alloy increased with a significant improvement in all the mechanical properties. The yield strength (YS), ultimate tensile strength (UTS) and hardness improved significantly with increase in the proportion of Mo; however, a reduction in elongation percentage was observed. The maximum strength of 1250 MPa UTS was observed in the alloy with a Mo proportion of 24%. The heavy alloy unmixed with Mo has shown distinct white and grey regions, where white (W) grain is due to tungsten and grey region is a combinatorial effect of Ni and Fe. Upon addition of Mo, the white and gray phase differences started to minimize resulting in deep gray and black 'C'-phase structures because of homogenization of the alloy. The main fracture mode found during this investigation in the alloys was inter-granular mode.

Key words: tungsten heavy alloys, sintering, mechanical properties, fracture modes.

1. Introduction

The current research is focused on developing the heavy alloys with enhanced mechanical properties, inter-relationship, and microstructures. There is a need for alloys with improved and enhanced ballistic properties, and with kinetic energy penetration ability for defeating the armor materials which secure and protect the battle tanks [1]. Tungsten heavy alloys are generally adopted in parts production, i.e. in production of parts which are typically exposed to high temperatures such as in welding electrodes, and to withstand heavy wear damages such as in bearing bars, extension shacks, grinding and turning spindles etc. The other advantages of the tungsten heavy alloys include their ability of shielding and collimating X-rays and gamma radiations, high electric and thermal conductivity, vibration dampening and resistance to corrosion. The alloys that are used for commercial purposes such as manufacturing of above mentioned parts, generally contain about 90–98% tungsten and other remaining 2–10% as nickel in combination with either iron or copper as the binding phase. Other applications of the tungsten alloys include usage in making inertia kits, in producing counter-balance weights for platforms in air-crafts, in production of cranks of race cars, making ammunition, building armor with anti-piercing capabilities, producing medical and sports equipment etc [2–6]. Tungsten exhibits highest melting point of all the heavy metals at 3422°C. Hence, the production of alloys containing tungsten has become essential and are synthesized using the technique of powder metallurgy. The desired density in the alloy can be achieved by applying liquid phase sintering (LPS) technique in synthesizing tungsten heavy alloys [5, 7–10]. The production of parts with larger cross-sectional area usually prefers copper (Cu) containing alloys [11]. The hardness of the Cu containing alloys is higher compared to Fe added alloys. The main difficulty is sintering the alloy to full density. The significant advantage of alloys which contain copper is that they are non-magnetic in nature. Using any of the mixing method of powder the elemental metal powders can be easily mixed [12]. During the process of sintering, when the powders of metals are compressed under heat, the temperature of hydrogen for the cleaning purpose is raised to 1000°C not considering the effect of atmosphere. The time taken for sintering varies from few minutes to several hours depending upon size of the final product. When the alloys are shaped in molds, the sintering procedure helps the alloys to be free of carbon remnants and lubricants. The most significant role in production of alloys is played by sintering [13, 14]. In an ideal W-Ni-Fe alloy, the binding rate between the Ni and Fe should be in the ratio of 1.5 and 4. The decrease in the Ni content from this ratio (Ni:Fe – 1.5:4) would make the alloys brittle and not fit for commercial use. Although heating of the metals involved in sintering can compress the metallic powders, it is not enough to bind them properly into one alloy. An increase in the binding rate of metals during sintering will result in proper binding of different metals into one alloy [15, 16]. The tungsten heavy alloy synthesized by liquid phase sintering technique has two phases, particulate body centered cubic (BCC) lattice and continuous face centered cubic (FCC) lattice matrix. Therefore, the chemistry and mechanical properties of the alloy are influenced by thermo-mechanical processing [17]. To improve the

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mechanical properties of a tungsten heavy alloy, the addition of different metals is done. For example, metals like cobalt (Co), molybdenum (Mo), tantalum (Ta), rhenium (Re) are chosen to improve the mechanical and structural properties of a classical tungsten heavy alloy; resulted in increased strength of the alloy [18–23]. However, not at all times, the addition of metals has influenced in a positive way. For example, addition of chromium (Cr) had a negative effect on the properties of the conventional tungsten heavy alloy. The reason being, Cr increased the porosity of the alloy by forming inter-metallic barriers. The addition of the Co has been widely used in researches as its addition improves both the strength and the ductility [24]. Upon analyzing the available data and information, Mo and Co were found ideal in making new tungsten based heavy alloys (W-Ni-Fe) with 90% W. The production of the alloys was done using the liquid phase sintering (LPS), followed by swaging for attaining greater strengths exceeding 1500 MPa. These alloys undergone further heat treatment involving the treatment of solution in atmosphere and in partial vacuum at 100–1200°C finally followed by quenching. The main purpose of the heat treatment here was imparting ductility by decreasing the formation of inter-metallic barriers and eliminating the segregation of the various interfaces leading to the impaired properties [25]. In this study, molybdenum was added to tungsten heavy alloys to improve the mechanical properties to make them suitable for nuclear applications.

2. Experimental procedure

The raw materials; W, Ni, Fe, and Mo used in this study were obtained in powder form from Sigma-Aldrich with a purity of greater than 99.5%. These powders were mixed in varying proportions. Through all the mixtures, proportion of Ni and Fe was constant at 8 and 2 percent respectively while varying only proportions of W and Mo. The mixtures used in making the alloys were listed in Table 1, where Mo proportion varied from 0 to 24 percent on a gradient of 6 percent. While the W proportions varied from 66 to 90 percent on a gradient of 6 percent. The composite powders of the W alloys were kept in planetary high-energy ball mill, QM-2SP20. The weight ratio between the balls to powder was maintained at 5:1, and cemented carbide was used as the grinding medium. The speed of the ball mill was set at 260 rpm and the milling was carried out for 40 hours in an inert Argon (Ar) gas atmosphere. The SPS equipment

Table 1
Composition of various samples in wt. percentages

sample	W (%)	Ni (%)	Fe (%)	Mo (%)
W-8Ni-2Fe-0Mo	90	8	2	0
W-8Ni-2Fe-6Mo	84	8	2	6
W-8Ni-2Fe-12Mo	78	8	2	12
W-8Ni-2Fe-18Mo	72	8	2	18
W-8Ni-2Fe-24Mo	66	8	2	24

used in the experiment was SPS-825 spark plasma sintering system. The mixture of powders was condensed using SPS for 8 minutes under a pressure of 30 MPa at a peak temperature of 1000°C with heating rate of 100°C/min. The samples were then cooled down to room temperature and finally taken out from the furnace for the study. The compositions of different mixtures of powders used for making the alloys are shown in Table 2.

Table 2
Characteristics of powder used in the experimental study

Characteristics		W	Ni	Fe	Mo
Powder Shape		irregular	spiky	spherical	irregular
Apparent Density (g/cc)		4.9	2.3	3.10	3.5
Tap Density (g/cc)		6.4	3.2	3.50	4.0
Flow rate, 50g (s)		Non-flowing	Non-flowing	5.5	—
Particle size (μm)	D_{10}	2.1	3.7	1.4	4.4
	D_{50}	4.3	11.0	7.0	8.2
	D_{90}	6.3	31.8	19.0	14.6
Theoretical Density (g/cc)		19.25	8.91	7.86	10.22
Purity		>99.9	>99.9	>99.9	>99.9

2.1. Spark plasma sintering. All the experiments were conducted in a SPS 825 system, which was manufactured by Sumitomo Coal Mining Co. Ltd, Japan. This system produces 12 electric pulses in 2 periods allowing a final pulse sequence of 12:2. The sintering chamber was emptied and evacuated to less than 6 Pa. The system has 30.4 mm internal diameter and has a 15 mm thick wall. The characteristics of the different metal powders used for making alloys are listed in the Table 2 below.

Measured amounts of the metal powders for the alloy are mixed and were added to sintering equipment and the pulses were passed through the graphite die. The temperature attained was from the optical pyrometer during the whole experiment and was aimed on a hole which was further placed inside the female die. Hence, there was a difference between the measured temperatures of die and the powder bed. There temperature difference was found within the current evaluation between pyrometer and powder compact, which was calculated to be less than 50°C. The preset heating program controlled heating from room temperature till 600°C and the process of heating was completed within the time to 4 minutes. After the temperature raised from 600°C various heating schedules were utilized. The composite powders were sintered in the furnace of SPS for 8 minutes under a pressure of 30 MPa at the temperature of 1000°C while temperature was increased at a rate of 100°C/min. The holding time of the objective temperature was set to 0 minutes, which means as the temperature reached this point the supply in the current was stopped, and the suppression of the applied stress shuts off finally allowing the specimens or the samples to be cooled. The relative sintered density

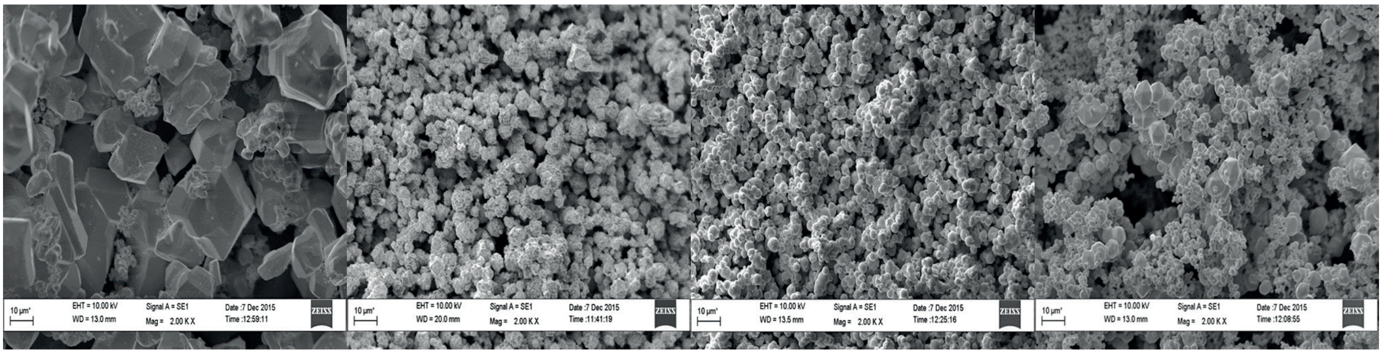

Fig. 1. SEM images of powders used in experiments

values are tabulated in Table 3. Then the samples were further polished and grounded for removing the graphite contamination which was present on the surface. Using the Archimedes method, the density of the sintered mixture was calculated. On dividing the apparent volume mass by the theoretical value, final relative density was obtained. The samples were taken and investigated using XRD, SEM with EDAX and tested for mechanical properties

Table 3
Relative sintered density with varying compositions of Mo

Mo and W Composition 8%Ni &2%Fe (constant)		Relative Sintered Density (%)
Mo%	W%	
0	90	80.84 ±2.14
6	84	84.61 ±1.97
12	78	86.34 ±1.85
18	72	93.12 ±2.78
24	66	94.25 ±1.58

3. Results and discussion

The microstructures of all the samples were studied using SEM, and the correlation between the structure and chemical composition was verified by EDAX. EDAX gave a clearer picture on the diffusion pattern of different metals in these heavy alloys, and change in the pattern upon addition of Mo in varying proportions. The physico-mechanical properties like the hardness, YS, UTS of the samples was studied by standard ASTM methods. Upon increase of Mo proportion in the alloys, a significant increase in YS, and UTS was observed. However, not much change was observed in hardness, and reduction in elongation length was observed upon increased addition of Mo.

3.1. Densification. With the aid of spark plasma sintering method, the densification of powders and sintering are achieved at a faster rate as the heating rates are high. In this experimental study, the powders are heated at a very high heating rate of 100°C/min, and the solid-state sintering induces cohesion between the powders before complete melting occurs. The temperature is considerably low in SPS as compared to microwave sintering [28]. The grain growth on sintering is manifested with finer grains and thus makes it feasible for the Mo to diffuse through the matrix increasing the relative density of the alloys. The solubility of tungsten in Ni is good. The diffusion of W in Ni-Fe-Mo matrix is attained at the lower temperatures in SPS, and as a result the relative sintered density (RSD) is increased with the content of Mo in the metal matrix. It is also seen from EDS study in Fig. 3 that the Mo dissolved in the Ni-Fe matrix leads to increased density of the alloys, and the cohesion between tungsten particles is high with SPS. The relative sintered density values of the alloys with addition of Mo in the W-Ni-Fe matrix are summarized in Table 3. The maximum relative density of the alloys in this study is attained with 24% of Mo as shown below in Table 3.

3.2. Microstructure study. The optical and SEM images were shown in Fig. 2. The figure shows the microstructure images of the optical microscope at a magnification of 500× and of SEM with a magnification at 2000×. Mo was added to the W-Ni-Fe alloys at different weight proportions and sintered by SPS at 1000°C. Initially, in Mo free composition, it is observed that the boundaries between tungsten and matrix of nickel and ferrous are clearly visible and not much of tungsten is thoroughly diffused in Ni and Fe (Fig. 2a). The white region within the SEM image shows tungsten, and grey region constitutes of Ni and Fe. By adding Mo in the weight ratio of 6–24% keeping the weight proportions of Ni and Fe unaltered at 8 and 2 percent respectively, it is observed that the diffusion of tungsten and molybdenum in the Ni-Fe metal matrix is significant (Fig. 2b–e). The homogenization of the metal matrix is noticed with addition of Mo. This phenomenon is also verified by EDAX, and the greater diffusion of white and grey regions resulting on deep gray structures is observed at a Mo concentration of 24% (Fig. 3). It is observed that adding molybdenum results in reduction of sharp borders across white and grey structures for deep grey diffused homogenized matrix. The

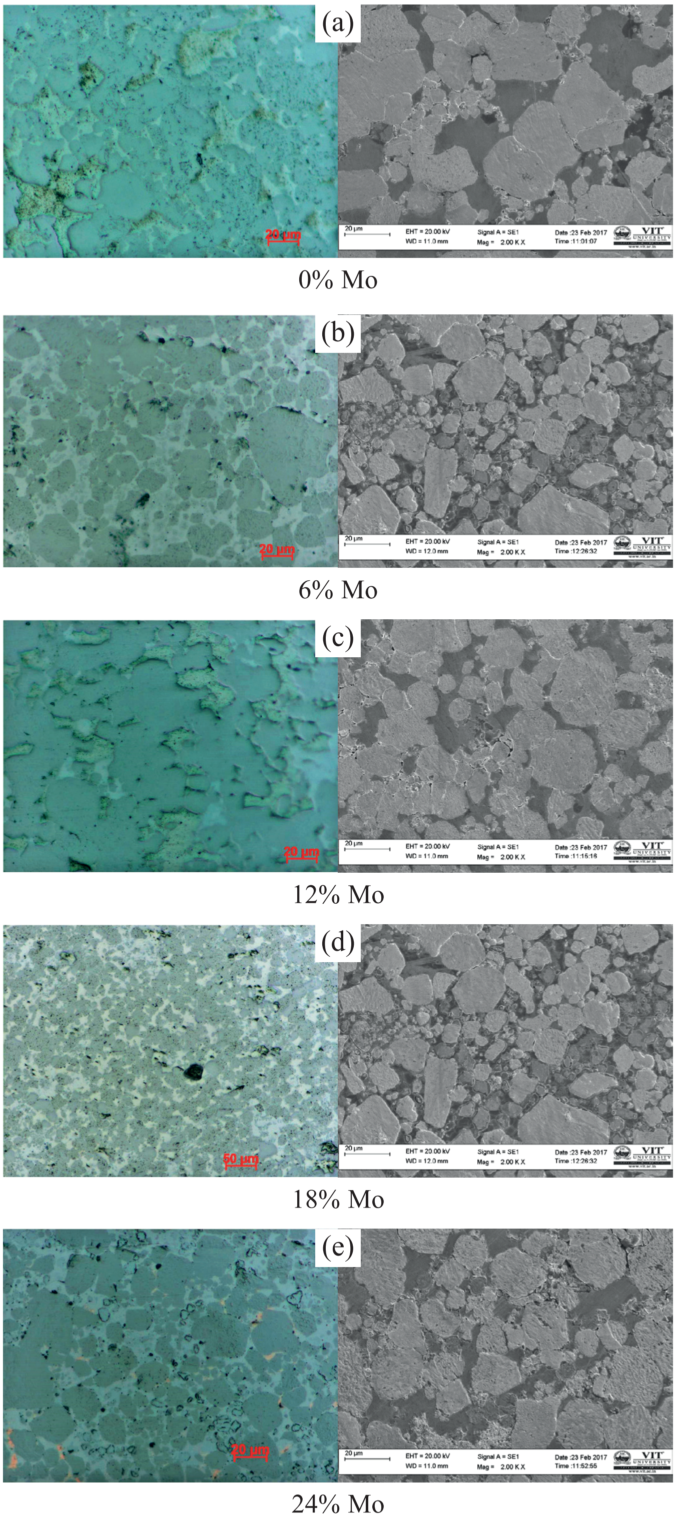

Fig. 2. Microstructure of alloyed samples with various Mo proportions. Corresponding reduction is in W, where Ni-Fe levels are constant (optical microscopy and SEM)

SEM images of microstructure of the alloys help in analyzing that the strength of the alloy increases with addition of molybdenum. The parameters of microstructure such as tungsten grain size, solid volume fraction, contiguity and the solubility of W in the binder phase reveal that these parameters influence the mechanical properties of the alloy. The existence of the deep grey structure is due to the presence of the 'O' content that might be produced due to oxidation of powders of Fe by water and oxygen. The grey structure keeps on increasing as the content of Mo keeps on increasing (Fig. 2).

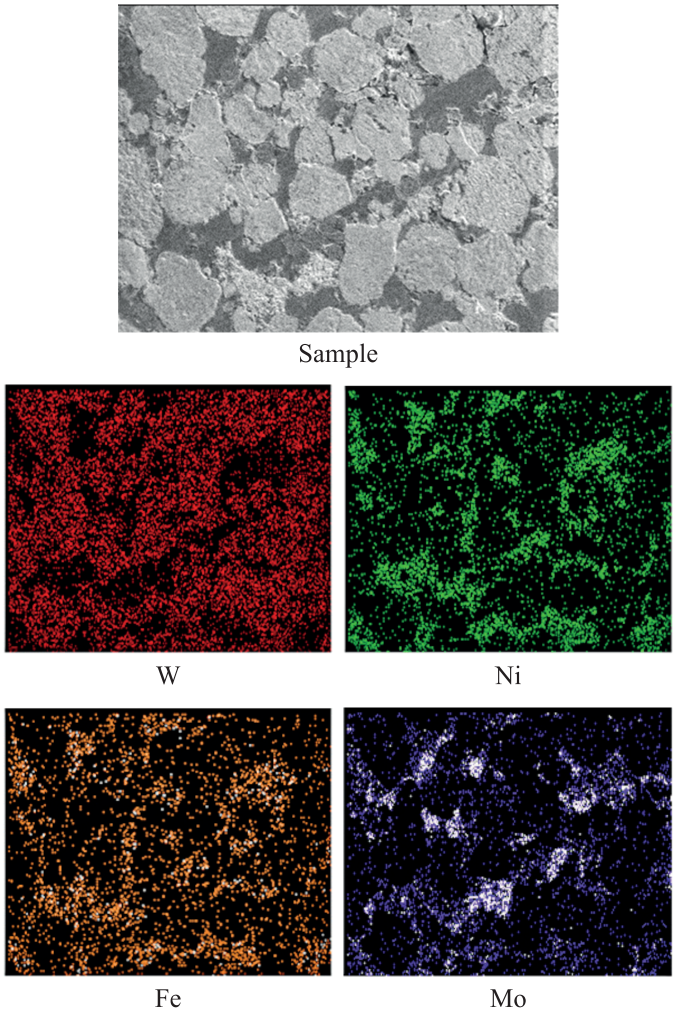

Fig. 3. EDAX analysis of W-Ni-Fe-Mo with 24% Mo

3.3. Mechanical properties. To study the mechanical properties, tensile tests and the micro-hardness tests were conducted and the results are summarized in Table 4. It is evident from the

Table 4
Mechanical properties with the different composition of Mo

Molybdenum composition (%)	YS (MPa)	UTS (MPa)	Elongation (%)	Hardness (HRA)
0	586 ±3	975 ±5	28	63 ±2
6	784 ±2	1025 ±3	22	65 ±4
12	825 ±4	1120 ±2	14	68 ±1
18	950 ±6	1160 ±4	05	72 ±3
24	998 ±8	1250 ±5	02	75 ±2

results that the hardness is not much influenced by addition of Mo to the alloys as there is only a diminutive increase in hardness. The maximum hardness attained is 75 HRA with 24% of Mo in the alloys. This is because solubility of Mo in the matrix does not increase hardness as the hardness of tungsten is very high and significant. However, it is noticed from the results that the percentage of elongation is reduced dramatically, and this can be attributed to the poor ductility of Mo. The heating rate is quite high in SPS when compared to conventional and microwave sintering. This swift heating refines the grains without coarsening much, thus enabling the heavy alloys in attaining superior mechanical properties. The strength of the alloys is significantly affected by the heating rate during sintering process. This influences the microstructure by grain growth refinement, and in bonding of W with the metal matrix.

The results of the tensile properties revealed that the strength of the alloys increased in tandem with the increase in Mo proportions from 0–24%. The alloy samples also exhibited an increasing trend in yield strength, UTS and hardness upon increasing Mo, and elongation percentage which is an attribute of ductility. Ductility is the only parameter that has shown a reverse trend on increasing Mo proportions.

The hardness is changed because of the micro-pores. The yield strength also increases and is related to the W grain. This data further suggests that the composite powders sintered by SPS in a high-energy ball mill at low temperatures such as 1000°C result in smaller white grains in the alloy representing higher hardness. It is analyzed from SEM microstructure and EDAX studies that the diffusion of Mo in Ni-Fe matrix along with W displayed in light grey resulted in high-tensile strength to the alloy (Fig. 3).

3.4. Fractography. The surfaces of the alloy samples were analyzed by SEM for fractures, and an attempt was made to correlate the increase in tensile properties to the fractures formed. The fractures are generally formed as a result of increase in brittleness and loss of ductility. On observing the surface of the alloy with no Mo, it is understood that Ni-Fe forms the matrix and W stays apart from the matrix resulting in fractures. With increase in the Mo proportions, it is observed that Mo blends into the matrix resulting in smaller 'W' regions and more fractures (Fig. 4). This thus results in high fractured surfaces on increasing Mo, and therefore high tensile strength, hardness and reduced ductility can all be correlated. The highest tensile strength of 1250 MPa was achieved with 24 Wt% of Mo in the alloy, and hardness was 75 HRA which is associated with more brittle cleavage fractured surface. It can therefore be stated that alloying of W heavy alloys with Mo is much useful in increasing the tensile strength to a higher magnitude making them feasible to use in nuclear applications at elevated temperature.

4. Conclusion

In the current study, the fabrication of the fine grain alloys was performed successfully using the SPS method at a comparative low temperature of 1000°C. The size of the particles was same

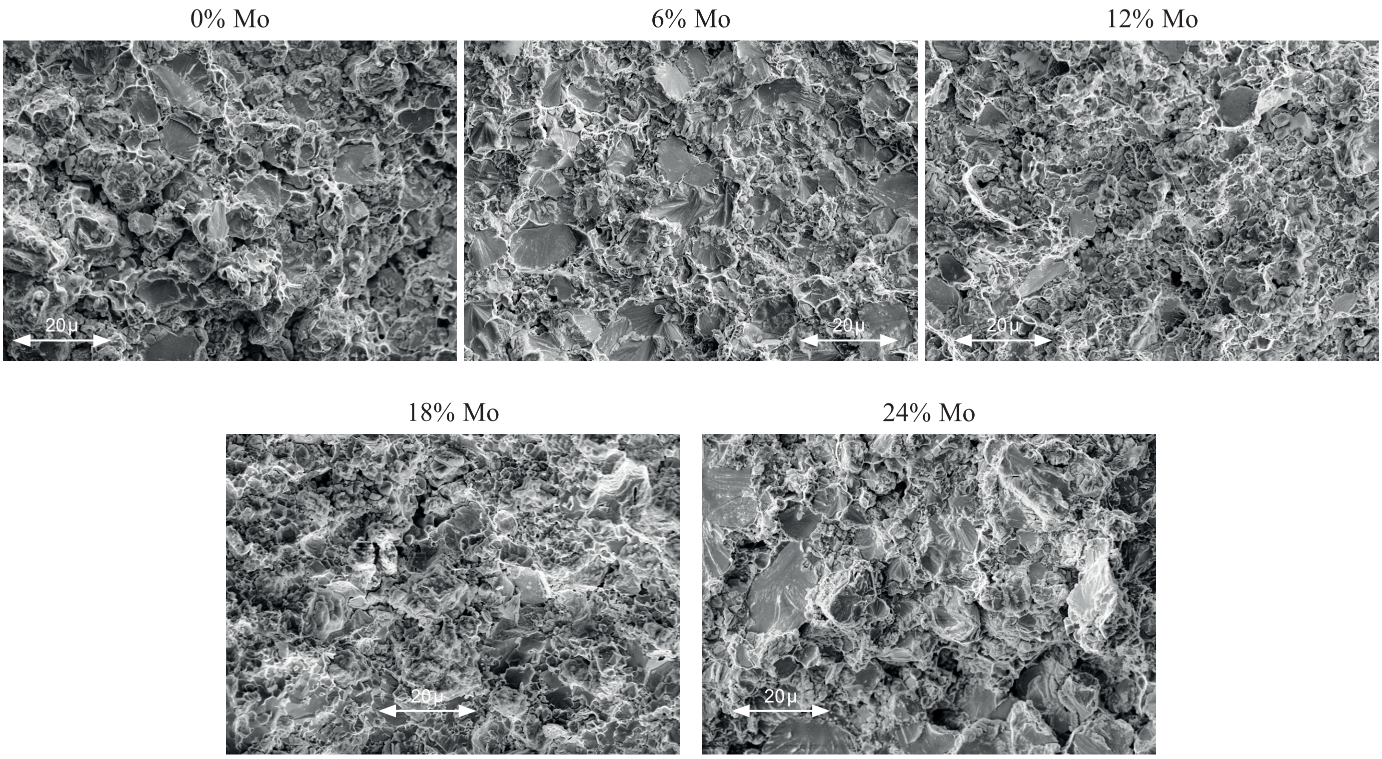

Fig. 4. SEM images of fracture surface of samples tested for tensile strength

for all the compositions. The diffusion of Mo in Ni-Fe matrix is higher order leading to high densification giving higher relative sintered density. With varying weight ratios of Mo in the W-Ni-Fe alloys, the mechanical properties are affected considerably. The process is very swift as the heating rates are high in SPS compared to conventional and microwave sintering as the sintering in SPS occurs in solid state. The increase of Mo in the heavy alloys resulted in the increase of the YS and the UTS significantly, whereas the diminutive improvement in hardness is observed. The percentage of elongation in the Mo added alloys decreased considerably because the Mo exhibits inferior ductility, and that SPS employs heating at a faster rate. The fractured surface is the combination of ductile fracture and brittle cleavage, and the region of brittle cleavage increased with addition of Mo. The elevated tensile strength of the alloys along with hardness is useful in nuclear applications and radiation shielding

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References

[1] C.L. Chen and C. L. Huang, "Milling media and alloying effects on synthesis and characteristics of mechanically alloyed ODS heavy tungsten alloys," *Int. J. Refract. Met. Hard Mater.*, 44, 19–26 (2014).
[2] Y. Jin, S. Cao, J. Zhu, et al., "Gradient structure induced by molybdenum in 90W–Ni–Fe heavy alloy," *Int. J. Refract. Met. Hard Mater.,* 43, 141–146 (2014).
[3] H.J. Ryu, S.H. Hong, and W. H. Baek, "Microstructure and mechanical properties of mechanically alloyed and solid state sintered tungsten heavy alloys," *Mater. Sci. Eng. A*, 291, 91–96 (2000).
[4] S.G. Caldwell, "Heat Treatment of tungsten alloys, *Int. Powder Metall.,* 39, No. 7, 43–51 (2003). 63
[5] S.J. Park, J.L. Johnson, Y. Wu, et al., "Analysis of the effect of solubility on the densification behavior of tungsten heavy alloys using the master sintering curve approach," *Int. J. Refract. Met. Hard Mater.,* 37, 52–59 (2013).
[6] L. Ding, D.P. Xiang, Y.Y. Li, et al., "Effects of sintering temperature on fine-grained tungsten heavy alloy produced by high-energy ball milling assisted spark plasma sintering," *Int. J. Refract. Met. Hard Mater.,* 33, 65–69 (2012).
[7] H. Ibrahim, A. Aziz, and A. Rahmat, "Enhanced liquid-phase sintering of W–Cu composites by liquid infiltration," *Int. J. Refract. Met. Hard Mater.,* 43, 222–226 (2014).
[8] H. Liu, S. Cao, J. Zhu, et al., "Densification, microstructure and mechanical properties of 90W–4Ni–6Mn heavy alloy," *Int. J. Refract. Met. Hard Mater.,* 37, 121–126 (2013).
[9] J. Zhu, S. Cao, and H. Liu, "Fabrication of W-Ni-Fe alloys gradient structures", *Int. J. Refract. Met. Hard Mater.,* 36, 72–75 (2013).
[10] N.K. Caliskan, N. Durlu, and S. Bor, "Swaging of liquid phase sintered 90W–7Ni–3Fe tungsten heavy alloy," *Int. J. Refract. Met. Hard Mater.,* 36, 260–264 (2013).
[11] J.W. Noh, E.P. Kim, H.S. Song, et al., "Matrix penetration of W–W grain-baundaries and its effect on mechanical properties of 93W–5.6Ni–1.4Fe heavy alloys," *Metall. Trans. A*, 24, No. 11, 2411–2416 (1993).
[12] J.J. Dunkley, *Powder Metallurgy, Metal Handbook*, ASM International Publ., 7, No. 9, 111–112 (1998).
[13] A. Upadhyaya, "Processing strategy for consolidation tungsten heavy alloys for ordnance applications," *Mater. Chem. Phys.,* 67, 101–110 (2001).
[14] S.H. Hong and H.D. Ryu, "Combination of mechanical alloying and two-stage sintering of 93W–5.6Ni– 1.4Fe tungsten heavy alloy," *Mater. Sci. Eng. A*, 344, 253–260 (2003).
[15] J. Liu and R.M. German, "Rearrangement densification in liquid-phase sintering," *Metall. Mater. Trans. A*, 32, 3125–3131 (2001).
[16] A. Mondal, A. Upadhyaya, and D. Agrawal, "Effect of heating mode and sintering temperature on the consalidation of 90W–7Ni–3Fe alloys," *J. Alloy Compd.*, 509, 301–310 (2011).
[17] Y. Sahin, J. Powder Technol. (2014) 764306.
[18] R. Cury, F. Issartel, J.M. Joubert, and H. Couque, Powder Metall. 56 (2013) 347.
[19] Penrice TW, Bost J. U.S. Patents. 1988; Patent no. 4762 559.
[20] Stuitje P, Harkema, Taal C, U.S. Patents 1995; Patent No. 5,462,576.
[21] A. Bose and R.M. German, Metall. Trans. A. 19A (1988) 3100.
[22] T. Xinglong, L. Bangyi, et al., Trans. Nonferrous Metals Soc. China 14 (4) (2004) 747.
[23] L. Wensheng, M.A. Yunzhu, and H. Baiyun, Bull. Mater. Sci. 31 (1) (2008) 1–6.
[24] D.V. Edmonds and P.N. Jones, Metall. Trans. A. 10A (1979) 289.
[25] G. Nicolas, US Patents. 1990; Patent no. US4938799 A.
[26] A. Kumari, M. Sankaranarayana, and T.K. Nandy, On structure property correlation in high strength tungsten heavy alloys, International Journal of Refractory Metals & Hard Materials 67 (2017) 18–31.
[27] A. Mondal, D. Agrawal, and A. Upadhyaya, Microwave Sintering of Refractory Metals/alloys: W, Mo, Re, W-Cu, W-Ni-Cu and W-Ni-Fe Alloys, *Journal of Microwave Power and Electromagnetic Energy, 44 (1),* 2010, pp. 28–44.
[28] W. Liu, Y. Ma, and Q. Cai, "Consolidation of MA W-Ni-Fe Alloyed Powder by Microwave-Assisted Sintering," *Materials Sciences and Applications*, Vol. 2 No. 6, 2011, pp. 609–614.