UDC 669.275:621.762.5

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Tungsten heavy alloys with molybdenum, Y_2O_3 and lanthanum. A review

The consolidated results of studies of tungsten doping with various metals and compounds (Ni, Fe, Cu, Mo, Y_2O_3, La_2O_3) are presented, the advantages of doping with regard to its conditions, microwave and plasma sintering techniques are shown. It has been found that the mechanical properties of tungsten are significantly improved by the addition of the above elements. The resulting heavy fame tungsten can be used to protect against nuclear radiation.

Keywords: *tungsten, sintering, microstructure, microhardness, tensile strength, yield strength, elongation, viscosity, molybdenum, lanthanum oxide, yttrium oxide.*

INTRODUCTION

The Swedish expression tungsten is the beginning of the component name Tungsten as tung sten in Swedish alludes to substantial stone. The tungsten element has the compound image W, allocated after its German name Wolfram. In spite of the fact that viewed as a rare colourful metal, its supplies are plentiful in territory of China and in North America. Tungsten has the most noteworthy liquefying point (3420 °C) and least thermal coefficient of expansion among all metals. Current Tungsten heavy alloys (WHAs) are regularly ternary or quaternary arrangements. The primary WHA created in 1938 was a W–Ni–Cu combination. The ternary alloy has its limitations to utilize them special areas of defence, military and nuclear applications. For quite a few years, the W–Ni–Fe ternary has turned into the industrial standard for industrial applications, synthesized by powder metallurgy techniques with enhanced mechanical properties for a given W content. Beginning with essential W–Ni–Fe system, property and characteristic sets can be modified for particular end applications. The sintered hardness of WHA is moderately low at 24–29 HRC.

For unique applications requiring more noteworthy hardness without post-sinter distortion, components like Mo, partially settled zirconium (PSZ), Yttrium balanced out zirconium, Lanthanum, Y_2O_3, and so forth can be utilized as an alloying elements [1–5]. In liquid stage sintering, Mo dissolution acts in reducing W, bringing about an incredibly refined W grain size [6]. Alloying with PSZ improves the mechanical properties of tungsten by lessening the hardness and bringing down flexible fragile move temperature. Addition of Y_2O_3 to Tungsten heavy alloys helps in enhanced properties, high strength in particular at elevated temperature of 800 °C. WHAs with addition of the above elements display a remarkable combination of mechanical properties of high quality at high temperatures, high elasticity and sturdiness. Customary WHAs are manufactured by liquid stage sintering of powders with high purity, the 90–98 wt % of pure W and remaining of Fe and Ni results in WHA generation. Substantial combinations containing under 90 wt % of W are not ordinarily accessible because of liquid phase sintering (LPS). This will prompt two functional problems: 1 – disturbance of shape control due to LPS and 2 – non consistency of thickness because of gravitationally incited settling of the denser, strong W phase inside the liquid closure during sintering. In spite of the fact that WHAs have been created with 99 % W, it is uncommon to discover WHA being used with a W content surpassing 97 wt %. The little measure of liquid phase during LPS significantly hinders pore disposal, moderating the generation rate for completely thick sintered parts.

Production of Tungsten Heavy Alloys

There are numerous conceivable creation advances exist which might be utilized for particular applications, essentially all assembling forms utilize the customary powder metallurgy (P/M) approach of press and sinter. Powder metallurgy approach is applied for two essential reasons, the high melting temperature of W (3420 °C) blocks the use of a dissolve and cast approach for practical difficulties, constraints on liquefy control, and the boiling of alloying components. Besides, P/M gives economy through the capacity to frame net shape parts or close net shape components. The basic role of P/M creation is to hold however much shape detail as could reasonably be expected in oversize tooling which represents both the volumetric changes as a result of compaction of powder during squeezing and from progressive densification. The tungsten metal powder utilized as a part of tungsten overwhelming composites is delivered by H_2 decrease of an oxide of the parent metal. The utilization of powders of high purity is basic for accomplishing high mechanical properties in the sintered state. Chosen metal powders are weighed to create the right combination detailing and subsequently blended in a pivoting shell sort blender. Shell sort blenders are regularly fitted with a fast instigator which helps in powder de-agglomeration and mix homogenization. Cold isostatic compacting (CIC) permits the use of dry mixed powder, and is utilized at whatever point conceivable because of flexibility, economy, effortlessness, and resultant green quality of the compacted part. CIC uses particularly molded elastomeric tooling, permitting squares, pieces, poles and even empty barrels in a similar press cycle. The deformable tooling is not fit for giving definite geometric frame, with the end goal that parts squeezed utilizing CIC normally require either green forming in the squeezed state or machining to the required setup once sintered. Any extreme material evacuation is done in the as-squeezed state because of financial matters of recuperation.

Sintering of Tungsten Heavy Alloys

Powder compacts are presented to sintering process in a H_2 environment heater, as appeared in Fig. 1. Feasible generation of WHA segments most of the time utilizes steady pusher-sort heaters so that such plans offer high amount rates and are equipped for astounding sintered quality. As the temperature of alloy increases, the metal oxide layer on each metal molecule is decreased by the receptive H_2 air, surrounding water vapor as a response item. Ideal heating rate is controlled by part segment thickness, with huge segments requiring slower heating to evade surface pore before the de-oxidation process. Cluster sort metallurgical heaters are perfect for the sintering of expansive parts requiring moderate temperature gradients. Thermally enacted surface dissemination drives between molecule neck arrangement in the region of 1000 °C, rearrangement of particles and moderate densification happen as this procedure proceeds. As the temperature rises to 1400 °C, the part will have attained full thickness while still in the solid state. Contingent upon beginning pressed thickness, direct shrinkages up to 20 % may happen. In spite of the fact that it is conceivable to accomplish full thickness with handling for additional time in solid state condition, resultant mechanical properties would be too low. The solidus temperature for tungsten alloys is reliant on the blend of lower liquefying temperature components. Any remaining porosity is practically eliminated in the sintering process. LPS is performed 30 °C or more over the solidus temperature of the compound, as this extra temperature advances a more prominent volume part of liquid cover stage to shape through expanded Tungsten solvency, subsequently supporting spheroidization of the W.

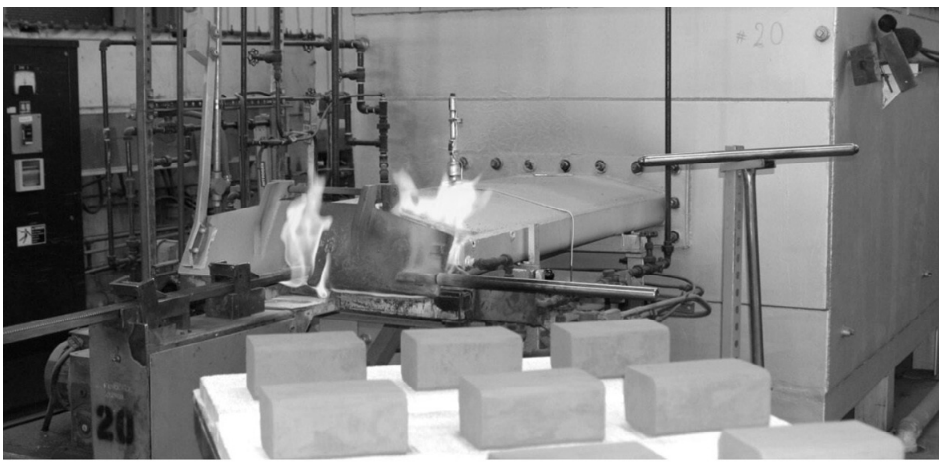


Fig. 1. Compacted WHA samples sintering in H_2 environment.

Post Sintering Process

There are numerous applications that require more prominent mechanical properties in some application driven angle, either more prominent flexibility and sturdiness or more noteworthy quality and hardness along with strength where high stresses are developed. In such cases, handling is required in the wake of sintering. For upgrade of quality, shape transformation is fundamental as there are no known transformational fortifying components in customary WHA frameworks. With legitimate post-sintering, WHAs can be handled for most extreme flexibility surpassing 40 % stretching or for greatest quality levels surpassing 1700 MPa with related hardness up to 50 HRC. Tungsten, similar to iron in the ferritic state, has a BCC crystal structure. It correspondingly displays vulnerability for hydrogen embrittlement. The sintering is done in a furnace under the control of H_2 environment, WHAs provided in the as-sintered business state have mechanical properties constrained by the nearness of interstitial H. While this is not a problem for different mass property WHA applications, it is not an alluring condition for material that will be utilized as a part of stress applications or for dynamic applications that are prone to impact damage. Hydrogen embrittlement of WHA can be basically dispensed by a post-sinter heat treatment in vacuum or inactive gas environment that give adequate heat activation to release H, enormously lessening the interstitial H substance of the material to a low ppm level.

Cooling of WHAs from Sintering Temperature

The mechanical properties of Tungsten heavy alloys are greatly effected by rate of cooling from sintering temperature. Many experimental studies to analyze the influence of cooling rate from sintering temperature above 1400 were able to give a relationship between physico-mechanical properties and the rate of cooling, in order to find the optimum cooling rate of alloys as per the engineering requirements. Andreiev [7] conducted experiments and investigated how the cooling rate influences the mechanical properties of WHAs with W–7Ni–3Fe as it is the most used composition of the alloys in the current use of engineering. Andreiev used samples of 50 mm diameter and 100 mm long for the investigations, sintered them in a hydrogen atmosphere heating to a temperature 40° above its liquid phase temperature. The rate of cooling was controlled by certain mechanism in the range of 8 °C/min and 0.3 °C/min. The effect of cooling rate on the properties of WHAs are shown in the Table 1.

Table 1. Ultimate tensile strength with different cooling rates for 90W–7Ni–3Fe alloy [7]

Cooling rate from liquid phase temperature, °C/min	Ultimate tensile strength, N/mm^2
8	300
3	320
0.3	400

It is also important to understand that the WHAs are matrix microstructures and these structures when heated to high temperatures in liquid phase sintering, undergoes a plastic-viscous flow. This phenomenon is explained by Andreyev [8] through his experimental investigations. He conducted experiments on Tungsten heavy alloys with 89 % Tungsten and remaining of Ni and Fe with the composition ratio of Ni/Fe being 7/3. The blanks were made of the above compositions in different cross sections and investigations were done to understand the viscoplastic flow in them. Big blanks having a diameter 40 mm and length 300 mm were sintered by passing them through furnace at controlled speed of 3 mm/min, where the liquid phase sintering temperature is 1450 °C. As the blanks are of big size, it was keen to understand the distortion of the blank over its length and also cross sectional-wise is due to high temperature and speed of travel. This distortion due to plastic-viscous flow in the microstructure matrix of WHAs can be a minimized by Spark Plasma sintering which heats and adjusts the temperature gradient according to the density.

Properties of Tungsten Heavy Alloys

WHAs with 90–95 % of Tungsten have commendable blend of malleable properties (elasticity till 1000 MPa and percent lengthening 30 %), and high density of 17000 to 18000 Kg/m^3. Because of high thickness of compounds, WHAs find extensive variety of applications such as center of gravity (CG) agent, kinetic energy penetrators (KEP), radiation shields, vibration damping applications, and so forth. Microstructure of WHAs influence their properties and these properties of WHAs can be changed by controlling the size and the volume part of the W grains [6], and furthermore by monitoring the quality of the W/grid interface [9, 10]. A generally higher strength, energy and elongation (883 MPa, 29 J and 10 %) were accounted for 95W–5(Ni/Fe) composite, when a higher interfacial holding quality exists between fastener stage and W grains [11]. A high quality of interfacial holding decreases cleavage break of W grains and flexible crack of the grid [10, 11]. The interface quality between W grains and the lattice is administered by the purity of W powder, grain size and grid arrangement to an extensive degree. Arrangement of combinations additionally influence the mechanical properties of WHAs, where W–Ni–Cu base overwhelming compounds have exceptionally mediocre properties contrasted with W–Ni–Fe base composites [12]. The WHA properties are to a great extent reliant on the extent of W matter and Fe/Ni or Ni/Cu proportion [13, 14]. According to Song et al., the WHAs with Fe/Ni proportion 1:4 shows best mechanical properties [11]. It was accounted for by German and Bourguignon that the ideal Ni/Fe proportion as 7:3 [2]. By decreasing the measure of Tungsten to 90 % in the WHAs, it is noticed that there is noteworthy change in a tensile strength and furthermore lengthening of the sintered WHAs. Bose and Kapoor tested WHAs with 92.5W–(Ni–Fe–Co) and observed when these are deformed up to 95 % showed an exceptional tensile strength of 1720 N/mm^2 with 16 % of elongation [14]. Bose and Kapoor additionally revealed that Tungsten substantial composites doped with Re and Mo had demonstrated change in yield strength. The mechanical properties of W–Ni–Co composites with proportion of Ni to Co in the range of 2 and 9 are much better contrasted with W–Ni–Fe alloys [15]. Liu et al. [16] demonstrated that the higher measure of Mo when added to WHAs prompts weakness due to the precipitation stage. Rhenium enhances the properties of WHAs, but it is costly and constrained in use [14]. On nitty gritty investigation of the science, microstructure and mechanical properties of WHAs, appropriate combinations of compositions were composed. These combinations are WNC1 (95W, 3.5Ni and 1.5Cu), WNC2 (96W, 3Ni, 1Cu) and WNF (91W, 7Ni, 1.5Fe, 0.5Co) delivered by customary powder metallurgy. Good tensile properties are achieved by WNF composites whereas WNC2 alloys have poor tensile properties (Table 2) [26].

Table 2. WHAs properties from the literature [26]

Alloy	Grain size, μm	Densification, %	Tensile strength, MPa	Elongation, %
WNC1	60	98.4	660±10 (deformation rate 1/s)	3
WNC2	70	98.4	660±12 (deformation rate 1/s)	3
WNF	30	99.4	1000±20 (deformation rate 1/s)	20

TUNGSTEN HEAVY ALLOYS WITH MOLYBDENUM

Customary WHAs with W, Ni and Fe powders included with metal powder of Molybdenum is raw material. Powders of W, Mo, Ni, and Fe with purity higher than 99.5 % and particle size is around 1–3 microns. The powders were blended at a mass proportion of 88:2:7:3 (W:Mo:Ni:Fe) [25]. QM-2SP20 planetary high energy ball mill is utilized in which tungsten powder is set where the ball to powder weight proportion of 5:1 is kept up and a WC cemented carbide ball was utilized as the pounding media [25]. As W and Mo are components of the same VIA gathering, their lattice parameters are close which empowers the blending procedure easily. Mo which is commercial and non-radioactive, decreases the dissolving point by which the refinement of grains in compound happens [25]. Figure 2 shows the sintering temperature impact on the relative thickness of the W–2Mo–7Ni–3Fe combination utilizing the HEBM in SPS method. Expanding the sintering temperature from 1000 to 1200 °C, there is moderate fall incline in relative density. In the wake of escalating the sintering temperature to 1250 °C, the relative density starts to rise. The relative density of W combinations does not exceed 90 %. In the HEBM process, the scraped area between the crushing ball and factory port gives numerous impurities to the powders, and the dynamic powders in the position are more inclined to retain gases. Due to this the WHAs cannot attain full density. Plenty of research has been done on W–Ni–Fe substantial compounds with Molybdenum. The instrument of precipitation of intermetallic mixes in W–Mo–Ni–Fe alloys is researched by Lin [27]. The grain development system of WHAs with various measures of Molybdenum are studied by Hsu [28]. The mechanical properties yield strength, hardness and ultimate tensile strength of W–Mo–Ni–Fe compounds are enhanced by expanding the Mo and magnificent mechanical properties are come about with sufficient Molybdenum, however a lot of Mo can bring about fragility.

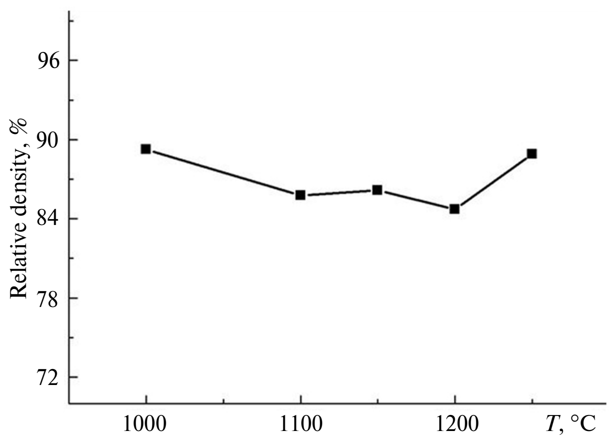


Fig. 2. Sintering temperature vs relative density of W–2Mo–7Ni–3Fe alloy [23].

It is obvious from the Fig. 3 that the intensity of diffraction pinnacle of W rises with increase in temperature [25]. It is likewise seen that there is no critical change in the diffraction top width with a rise in temperature. A weak diffraction top shows up at 1000 and 1100 °C and it vanishes when the temperature surpasses 1150 °C. The SEM pictures of W–2Mo–7Ni–3Fe appeared in Fig. 4 are sintered by Spark Plasma Sintering (SPS) at various sintering temperature. The grain development of the Tungsten in the composite are partitioned into three stages [23]. At 1000–1100 °C, the measure of W grain is little in the scope of 1.5 μm. Between 1150–1200 °C, the grain size is somewhat bigger in the scope of 2 to 2.5 μm. At 1250 °C, the W grain has noteworthy development, yet the size infrequently surpasses 5 μm. Contrasted with customary sintering procedures which has a liquid stage temperature of 1500 °C [29], the HEBM processed powders sintered by SPS is a viable method to have fine grain structure (less than 5 μm)of amalgams at lower temperature. The W–2Mo–7Ni–3Fe composite is a blend of white W-grains, dark γ-(Ni, Fe, W, Mo), restricting stage, grey W-rich structure and deep-grey W-rich structure which are noted with 1, 4, 2 and 3 in Fig. 4, *e* [25].

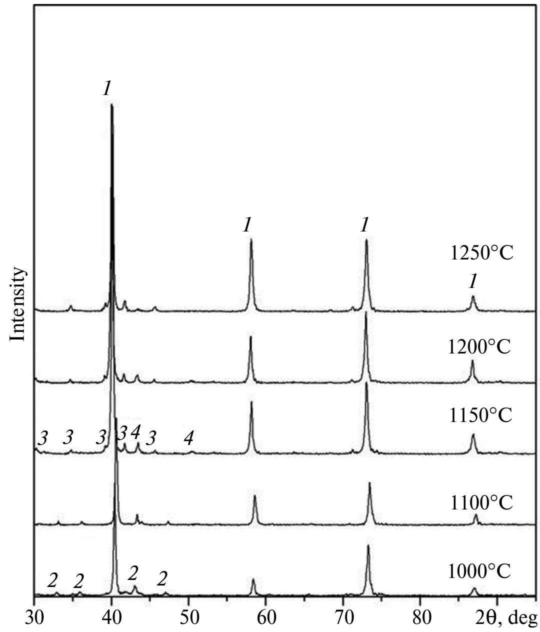


Fig. 3. SPS sintered W–2Mo–3Fe–7Ni alloy XRD patterns at various temperatures [25]: *1* – W; *2* – Mo_6Ni_6C; *3* – Ni_2W_4C; *4* – (Fe, Ni).

Kemp [30] examined the microstructural development, the grain development active procedure of W–Mo–Ni–Fe alloys. Between the W–Mo grains and the lattice stage, Kemp [30] investigated the microstructural advancement and the kinetics of grain development of W–Mo–Ni–Fe alloys. He noticed that the furnace cooling, another intermetallic stage hastened in the interfaces between the W–Mo grains and the framework stage, and changed the mechanical properties. Be that as it may, its correct synthesis and structure were not distinguished. It was additionally noticed that the intermetallic stage couldn't be wiped out through regular heat treatment.

Precipitation in Tungsten Heavy Alloys with Molybdenum

Lin and Hsu [31] inspected two diverse Tungsten alloys with arrangement of W–8Mo–7Ni–3Fe and W–22.4Mo–7.8Ni–3.4Fe. The powders which were blended and mixed in a plastic jug for around 16 h are utilized as a part of these compounds and recorded in Table 3 [31].

The powders in the Table 2 are blended altogether to shape and afterward sintered in a tube furnace presenting to heat treatment for oxide lessening and densification. During the heat treatment, hydrogen environment is kept up until the most recent 10 minutes with isothermal holding, and a short time later it is changed to argon during furnace cooling. Figure 5 demonstrates the W–8Mo–7Ni–3Fe example BEI picture which is isothermally held at 1773 K for 5 min and surface cooled.

Table 3. Composition of metal powders used for experimental work [31]

Metal powder	W	Mo	Ni	Fe
Purity, %	99.95	99.8	99.8	97.8
Average particle size, μm	2.5	4	5	4
Tap density, g/cm^3	2.8	2.2	4.7	4.3
Impurities	O	Si, Fe, Sn	C, O, Fe	N, C, O

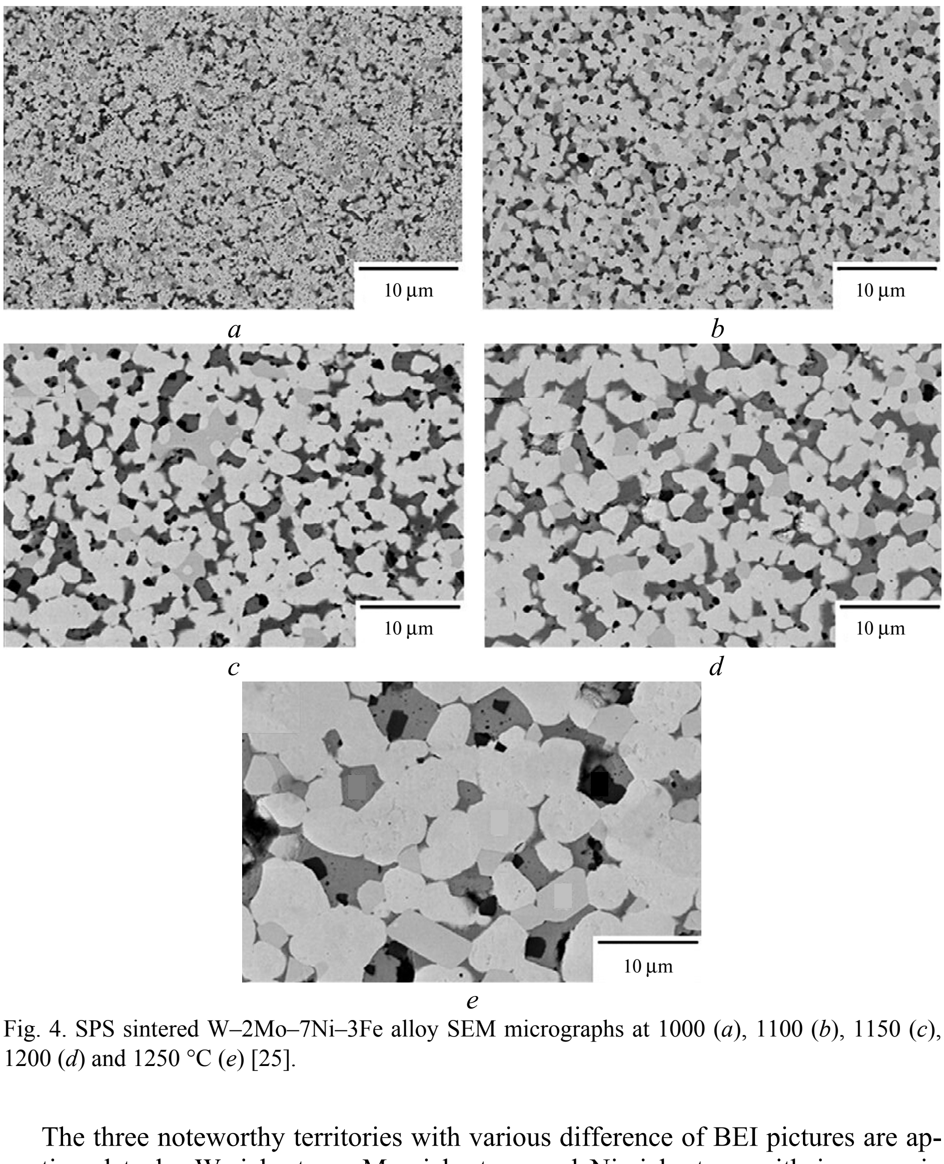
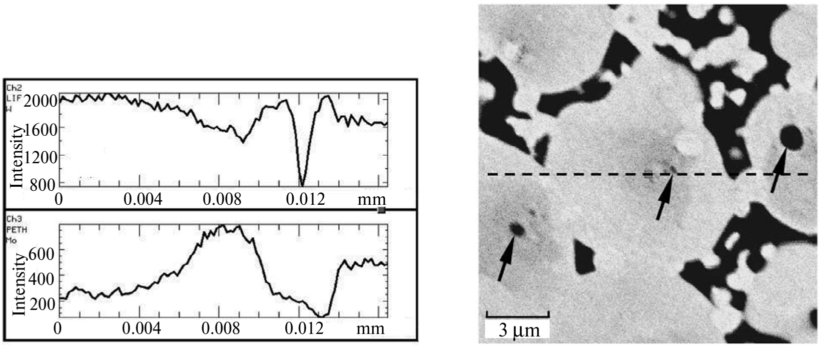


Fig. 4. SPS sintered W–2Mo–7Ni–3Fe alloy SEM micrographs at 1000 (*a*), 1100 (*b*), 1150 (*c*), 1200 (*d*) and 1250 °C (*e*) [25].

The three noteworthy territories with various difference of BEI pictures are apportioned to be W-rich stage, Mo rich stage and Ni rich stage with increase in darkness. This figure has indicated both shape anomalies and bimodal size circulation of grains [31]. Test examinations on both W–8Mo–7Ni–3Fe and W–22.4Mo–7.8Ni–3.4Fe alloys have uncovered that the Mo coefficient in the network surpassed that of W by a factor of 2.6. In light of the perception by Lin and Hsu [31], it is obvious that the little amount of Mo addition in the matrix phase reduces the W composition significantly.



a *b*

Fig. 5. W–8Mo–7Ni–3Fe specimen's BEI image (*b*) and line scanning (*a*) which is isothermally held at 1773 K for 5 min and cooled in a furnace. W–Mo grains packets of matrix phase are indicated by arrows [31].

Consolidation of Properties of WHAs with Molybdenum

Considering the standard proportion of Ni/Fe in WHAs, it is obvious from the research that Mo included in WHAs enhances the mechanical properties vitally. The trial estimations of quality and hardness with % elongation are appeared in Table 4 [42]. As examined before, the outcomes from the experiments carried out by German clearly demonstrates that the mechanical properties of WHAs improve with increment in Mo and in the long run the % elongation diminishes. However the hardness qualities are not impacted much with change in Mo content.

Table 4. Properties of tungsten heavy alloys with Mo from research [42]

Additive Mo, wt %	Ni/Fe ratio	Yield strength, N/mm^2	Tensile strength, N/mm^2	Elongation, %	Hardness, HRA
0	7/3	534	923	30	63
0	8/2	551	918	36	64
4	7/3	625	978	24	64
4	8/2	598	947	31	64
8	7/3	715	1030	20	66
8	8/2	688	1048	24	66
12	7/3	835	1103	10	68
12	8/2	773	1119	14	67
16	7/3	892	1145	07	69
16	8/2	843	1150	10	68

TUNGSTEN HEAVY ALLOYS WITH Y_2O_3

Because of special attributes of Tungsten, it is a standout amongst the metals used in fusion reactors for plasma facing [32–35]. The high ductile brittle transition temperature (DBTT) of Tungsten is a noteworthy concern and restricts its utilization in reactor applications. Ultrafine grains or nanostructured Tungsten materials have shown enhanced properties with diminished fragility and upgraded toughness [36, 37]. Nanostructured Tungsten materials have additionally been proposed to display an improved radiation resistance because of enormous volume part of grain boundaries [38–42]. The impediment of nanostructured materials is the poor thermal stability of the microstructure when presented to higher temperatures. At the point when exposed to higher temperature for longer lengths, nanoparticles of nanophase materials generally have a tendency to diffuse rapidly along these lines diminishing the high surface vitality which brings about recrystallization and grain development. The coarse grains diminishes the mechanical properties losing the advantages of nanostructured or ultrafine powders. The above issue can be taken care of by balancing out the microstructure through the dispersion of hard refractory materials like TiC, La_2O_3 and Y_2O_3. The oxide particles scattered captures the development of grains as well as settles microstructure when exposed to high temperatures. The principle favorable position of the finely scattered particles is it can deal with the incited defects of radiation [38].

Properties of Tungsten Heavy Alloys with Y_2O_3

Aguirre [39] explored two tungsten alloy combinations with compositions 2Ti–$0.47Y_2O_3$ and 4Ti–$0.5Y_2O_3$. These powders were formed by hot isostatic weight of ball processing. The powders of Tungsten (99.9 % purity) with a normal grain size of 14 μm, Titanium (99.8 % immaculateness) with a normal particle size of 20 μm and Y_2O_3 (99.5 % virtue) with nanoparticles in the scope of 10–50 nm. The examples arranged with the above powders were sintered under hot isostatic weight in two stages, at (1277 °C, 195 N/mm^2) and other at (1700 °C, 195 N/mm^2). Pure Tungsten and two tungsten composites with 4 % Ti and 0.5 % Y_2O_3 were utilized as reference materials in the past reviews [39].

The Young's modulus at room temperature, E_0, is like that of materials utilized as reference materials specified. The estimation of Young's modulus is somewhat lower for W–2Ti–$0.47Y_2O_3$ combination. The exploratory examinations have demonstrated that W–4Ti–$0.5Y_2O_3$ composition behaves like that of W–$0.5Y_2O_3$ [40] affirming that the yttrium oxide introduce in the compounds enhanced the oxidation resistance and appropriately enhance the mechanical properties at high temperature. The Fig. 6 demonstrates the yield qualities of the composites with plastic distortion and flexural quality with brittleness. The twisting quality of W–2Ti–$0.47Y_2O_3$ is discovered practically steady with change in temperature. The analysis likewise uncovered that W–4Ti–$0.5Y_2O_3$ begins from a lower value at room temperature yet noticed the resistance increased like that of W–4Ti and achieves a high value at a temperature of 800 °C because of the Y_2O_3. The yield quality or twisting quality of the composites are shown in chart with temperature up to 1200 °C which demonstrates that the quality of W–4Ti–$0.5Y_2O_3$ is considerably higher when contrasted with different combinations even at a lifted temperature of 800 °C. The oxide dispersion of Y_2O_3 assumes a vital part to enhance the quality of WHAs when the temperatures of the alloys are high. In this manner from the reviews and research did in the territory of WHAs with combinations with Y_2O_3 have made them applicable in fusion reactors to withstand the higher temperatures with enough quality [40].

The estimations of load and distortion recorded to evaluate fracture toughness on tests of SENB depends firmly on the dimensional qualities. In this way, it suggests that the outcomes from these tests must be considered as reference qualities. Some reference materials show an increased plainly visible plastic deformity with rise in temperature. The qualities computed are considered as obvious fracture toughness qualities and they frame the reason for its development with temperature [39]. Figure 7 shows the advancement with temperature which is similar to the curve of flexural strength shown earlier.

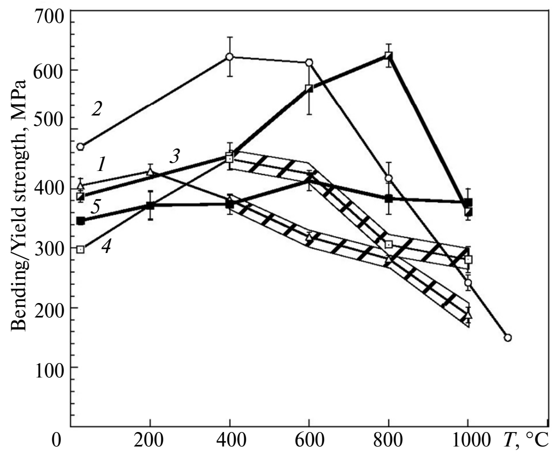


Fig 6. Temperature vs yield strength and flexural strength [39]: *1* – W; *2* – W–4Ti; *3* – W–4Ti–$0.5Y_2O_3$; *4* – W–$0.5Y_2O_3$; *5* – W–2Ti–$0.47Y_2O_3$.

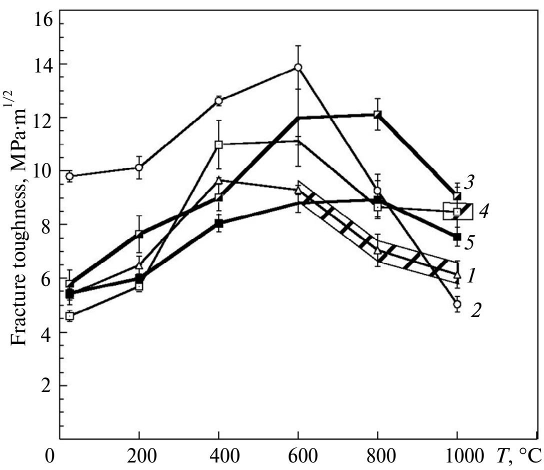


Fig. 7. Temperature vs fracture toughness (shaded portion indicates plastic deformation) [39]: *1* – W; *2* – W–4Ti; *3* – W–4Ti–$0.5Y_2O_3$; *4* – W–$0.5Y_2O_3$; *5* – W–2Ti–$0.47Y_2O_3$.

The values of fracture toughness are inferior as the tests were done in an oxidizing environment. It can be seen from the graphs that the values don't descend as quick as that of W–4Ti alloys and the values got at 1000 °C are practically equivalent to W–$0.5Y_2O_3$. It is additionally apparent that the Y_2O_3 introduced in the alloys enhance the oxidation conduct at higher temperature and thus enhanced mechanical properties are acquired. The lower estimations of strength at room temperature demonstrate that the Titanium introduced can't upgrade this property. The existence of Y_2O_3 in tungsten an alloy builds the oxidation resistance [41] and furthermore enhances the mechanical properties at high temperature (Fig. 8).

Consolidation of WHAs with Y_2O_3

The mechanical properties of oxide-dispersed WHAs are explored by Ryu and Hong [43] with natural powders of W, Ni, Fe (93W–5.6Ni–1.4Fe). The powders are mechanically alloyed with Y_2O_3 powders utilizing tumbler ball plants for more than 72 hours. The alloyed powders compacted were sintered in strong state at a temperature of 1300 °C for 1 hour and afterward took after by liquid stage sintering at 1470 °C for a period extending from 4 to 90 mins [43].

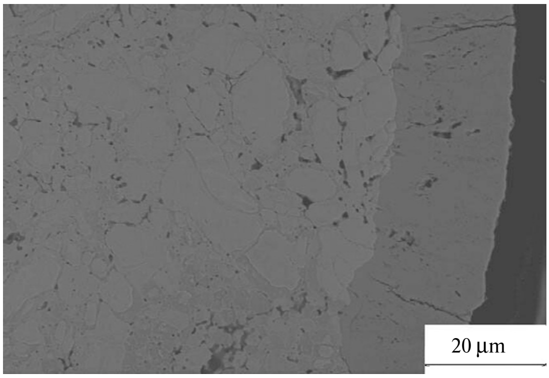


Fig. 8. W–2Ti–0.5Y_2O_3 tested at 1000 °C displaying the thick oxide layer [41].

Figure 9 shows a scanning electron micrograph (SEM) of a mechanically alloyed 93W–5.6Ni–1.4Fe WHAs with 1 % of Y_2O_3 weight included and sintered for 1 h at 1485 °C [41]. Sintered thickness was found as 19.76 g/cc and relative density was noted as 98.9 %. The impact of Y_2O_3 on microstructure of the oxide scattered WHAs (93W–5.6Ni–1.4Fe) with its range from 0.1 to 5 % on weight premise is shown in Fig. 10. The oxide dispersed WHAs were sintered in two phases to research the grain structure modifying conduct during the auxiliary liquid phase sintering at 1470 °C which is done after the solid state sintering at 1300 °C [44].

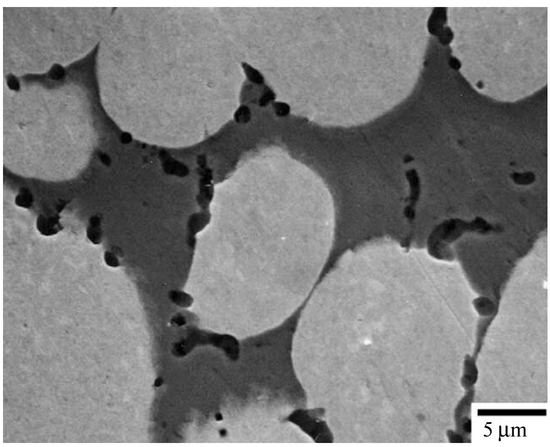


Fig. 9. SEM of oxide-dispersed WHA with 1 wt % Y_2O_3 with liquid-phase sintering at 1485 °C for 1 h [43].

The WHAs with 0.1 % Y_2O_3 are tested for quality, % elongation with change in sintering temperature and are organized in Table 5. Strength and lengthening of Y_2O_3 dispersed WHAs and without oxide dispersion are investigated [41]. WHAs with 0.1 % Y_2O_3 with density 17.04 g/cc, sintered at 1485 °C for 1 hour showed a tensile strength of 828 MPa and extension of 14.6 %. WHAs without Y_2O_3 having density 17.72 g/cc display a tensile strength of 940 MPa. The reduction in tensile strength of the oxide dispersed WHAs can be credited to low density of alloys. When the WHAs are sintered for 2 h that acquired a relative density of 99.1 versus 98.5 and showed tensile strength of 883 MPa. This demonstrates the sintering time fundamentally impacts the quality of the oxide dispersed WHAs.

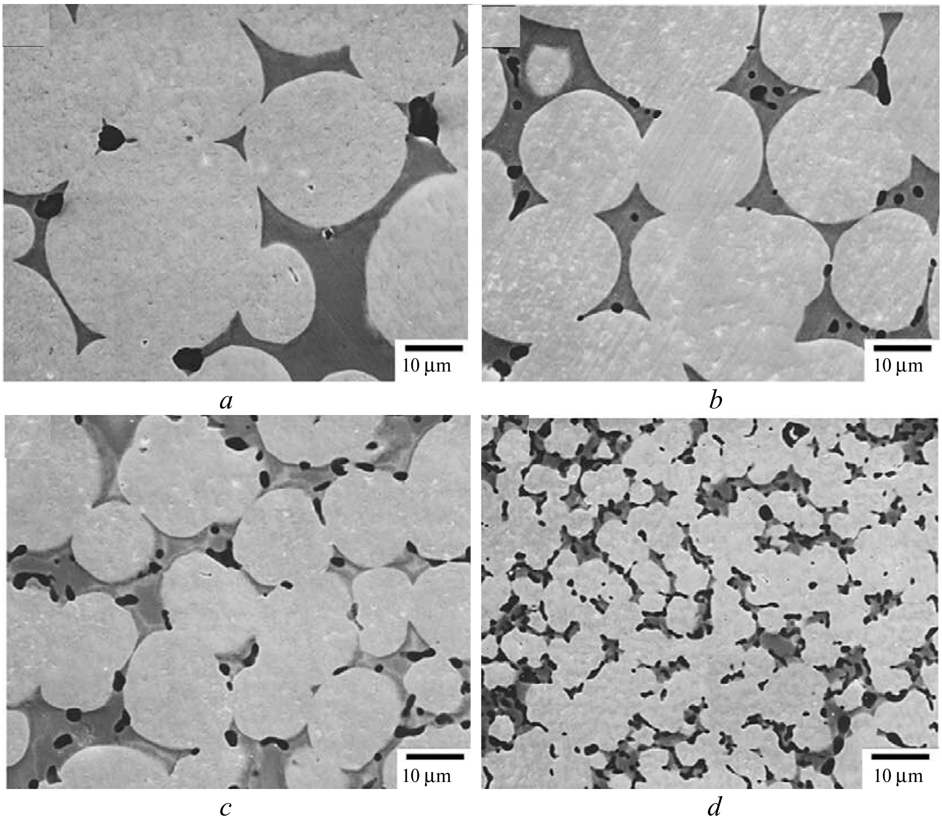


Fig. 10. SEM of oxide dispersed WHAs post liquid-phase sintering at 1485 °C for 1 h [43]: 0,1 (*a*, *c*) and 0.5 (*b*, *d*) wt % Y_2O_3.

Table 5. Properties of WHAs with and without Y_2O_3 [43]

wt % of Y_2O_3	0	0.1	0.1
Sintering time, h, at 1485 °C	1	1	2
Density, g/cm^3	17.72	17.04	17.15
Theoretical density, g/cm^3	17.74	17.30	17.30
Relative density, %	99.9	98.5	99.1
Tensile strength, MPa	940	828	883
Elongation, %	30	14.6	18.4

Ryu and Soon [41] conducted a compression test at lifted temperature of 800 °C, which was completed with a hot working test system (Thermecmaster-Z) with a strain rate of 10 s^{-1}. The essential goal behind this pressure test was to explore the disfigurement and the conduct of oxide scattered WHAs at high temperature. The amount of Y_2O_3 present in the WHAs influence the compressive as well as tensile strength of the alloys at higher temperatures. It is evident from the experiments that the strength is improved with the presence of Y_2O_3 and the same can be understood from Fig. 11. It shows that the oxide dispersion in the WHAs helps in strengthening the alloys at high temperatures and effectively enhances the compressive strength.

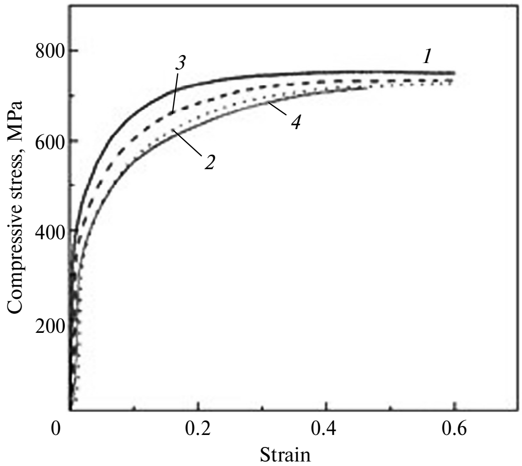


Fig. 11. Stress–strain curve of WHAs with oxide dispersion [43]: without oxide (*1*); 0.1 (*2*), 0.5 (*3*), 1.0 (*4*) % oxide; 800 °C, 10 s^{-1}.

TUNGSTEN HEAVY ALLOYS WITH LANTHANUM

Many of the previous studies [45–48] revealed that the interfacial segregation of some impurity elements may decrease the bonding force between W grains and matrix phase and also forms the bulky inclusion which destroys the continuity of the matrix leading to the fracture of alloy. Hence to control the impurity concentration and to improve their existence state and their distribution in the alloy, rare earth elements (Re) were added.

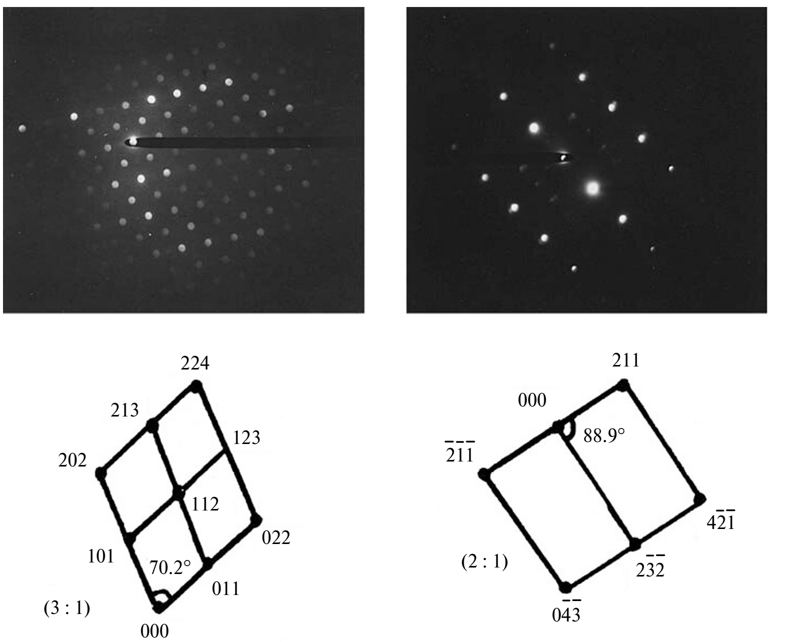
Many recent studies had proved that the application of rare earth elements (Re) to heavy alloys can improve the mechanical properties because of their extraordinary chemical and physical properties. Wu G. C. et al. [50] worked experimentally on improving the mechanical properties of WHAs by adding proper amount of La. In their experimental study, W–Mo–Ni–Fe alloy was used in which Mo has 17 % weight which is used in industries from few years. This alloy has very low elongation and also causes brittle cracks because of the presence of high content of Mo. To investigate on this, Wu G. C. used four samples of heavy alloys (W–Mo–Ni–Fe) by varying the La percentage [50].

By adding lanthanum to the alloy a new microphase is formed which is different from the conventional heavy alloys and possessing different colour from W grains and matrix phase. Adding small quantities of lanthanum oxide (La_2O_3, 1.0–2.0 %) to tungsten will improve its creep resistance and the recrystallization temperature. The machining performance for Lanthanum oxide-doped tungsten (Tungsten Lanthanum Alloy, W–La alloy) is better than pure tungsten. Adding Lanthanum to W–Fe–Ni alloys significantly enhances the toughness to manufacture warheads for breaking armour plates [60]. The new phase is identified by XRD analysis and the indexing of two new phases is done by diffraction pattern as shown below. Lanthanum oxide doped tungsten (Tungsten Lanthanum Alloy, W–La alloy) an ideal material for ion sources, welding electrodes and contact electrodes.

Properties of Tungsten Heavy Alloys with Lanthanum

Tungsten based heavy alloys are generally applied in different specialized fields, to deliver weights of spinners, adjusted backings of flying machine, compartments for radioactive materials, vibration attenuators, warheads for breaking protective layer plates, and so on. As far as the mechanical properties are concerned, such WHAs demand excellent strength and toughness along with elongation. Be that as it may, strength of tungsten based alloys may change extraordinarily, contingent on the alloying process and the purity of powder. Customary WHAs which have 93 wt % W–4.9 wt % Ni–2.1 wt % Fe based organization in which a piece of tungsten is substituted by lanthanum of around 0.1 to 0.3 wt % and 0.01 to 0.05 wt % for enhanced strength.

After addition of lanthanum to the alloy, La combines with oxygen forming $LaMnO_3$ and small amount of Mn_3O_4 which alter the existence and distribution of impurity element oxygen and also decrease the segregation of oxygen to interfaces (as shown in Fig. 12) which improves the tensile strength and elongation. The results had shown that the increase in tensile strength from 291 to 903, increase of elongation to 4.7 % and decrease of hardness (HRC from 37 to 30).



a *b*

Fig. 12. Indexing of two new phases by diffraction pattern [50]: $LaMnO_3$ (*a*), Mn_3O_4 (*b*).

By the fractographic observation, it is observed that the addition of 0.4 % lanthanum to the alloy improves the ductility by reducing the concentration of oxygen segregation by forming $LaMnO_3$ and Mn_3O_4. The fractured surfaces of two specimens one without La and another with 0.4 % La is shown in Fig. 13.

Consolidation of WHAs with Lanthanum

Hong et al. [51] worked experimentally on the effect of embrittlement of heavy alloys on addition of lanthanum to the alloy. In this experimental study, W alloy has 19 ppm of P concentration, 1 ppm of S concentration, 600 ppm of O concentration and 25 ppm of C concentration. For each experimental study four specimens were tested by varying the lanthanum percentage of weight by 0.03 to 0.3 %. It is observed that there is no change in sintering behavior of alloy on addition of P and La by an optical microscope.

Several experimental studies were conducted by varying P and La contents in the alloy. When 150 ppm of P and fairly doped La specimens showed no improvement in tensile strengths and elongation and also showed the decrease in impact energy when compared to undoped specimens which is shown in Fig. 14.

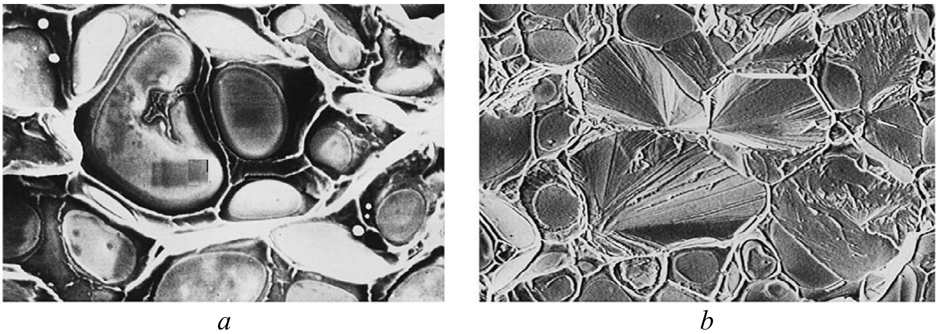


Fig. 13. Scanning electron micrographs: alloy without La (*a*), alloy with 0.4 % La (*b*) [50].

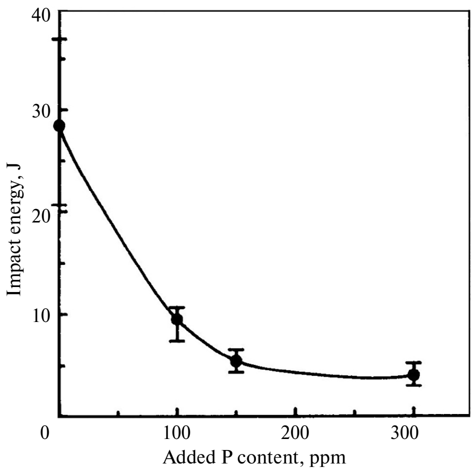


Fig. 14. Variation between impact energy and P content added to alloy.

When a percentage of 0.1 and 0.3 % of lanthanum is added to the alloy, it also shows no improvement in UTS and elongation also slightly decreases by 17 % and microhardness has not affected with lanthanum addition but the impact energy was increased on addition of 0.3 % of lanthanum when compared with P doping specimen which is shown in Fig. 15.

The fractured surface of the 0.03 % La doped alloy shows slight dimple appearance, but surface is very similar to undoped specimen. The fractured surface of 0.1 % lanthanum was similar to fractured surface of 0.3 % lanthanum. The 0.3 % La doped alloy showed the improvement as a typical ductile failure surface with a dimple structure when compared to undoped specimen having brittle failure as shown in Fig. 16.

The experimental study concluded that the embrittlement due to concentration of P can be completely eliminated by addition of lanthanum and also concluded that the impact property can also be improved by adding lanthanum and can control the segregation of P.

Hong et al. worked on improving toughness of heavy alloys by adding lanthanum and calcium to the tungsten alloy. Many recent studies had shown that due to boundary segregation of impurities mechanical properties are getting destructed. There are so many methods are there to avoid this boundary segregation, adding rare earth elements is also a method to avoid this boundary segregation. This study concludes, by addition of 0.01 to 1 % of lanthanum to the alloy increases the toughness of tungsten alloy and also by adding 0.01 to 0.3 % of calcium also increase the toughness of tungsten alloy.

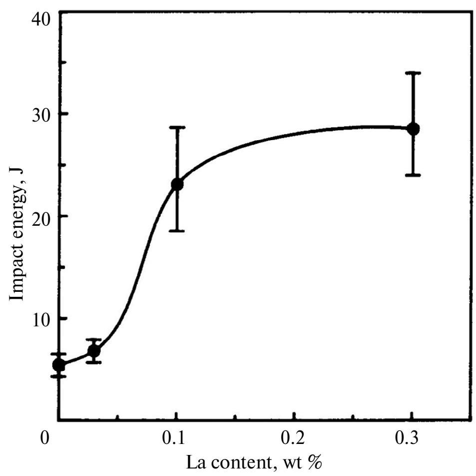
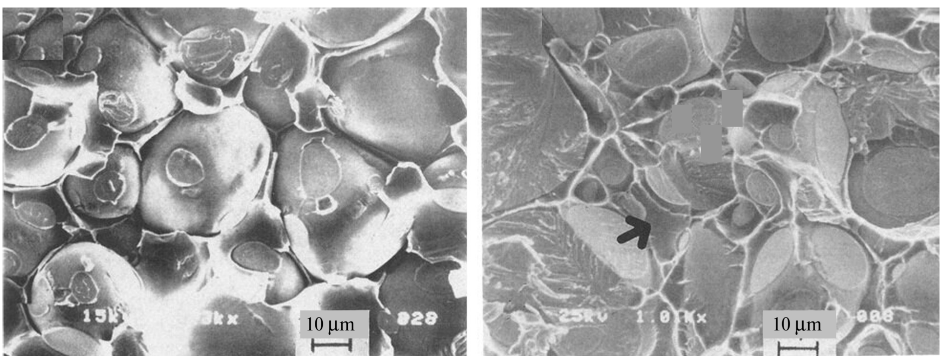


Fig. 15. Variation between impact energy and La content added to alloy.



a *b*

Fig. 16. Fractured surface of undoped specimen (*a*) and fractured surface of 0.3 % La doped specimen (*b*).

CONCLUSIONS

WHAs are used in defence, military and nuclear applications owing to its high density, high melting temperature and high strength. Though tungsten heavy alloys have high strength, elements like Re, Mo, Y_2O_3, lanthanum etc. play an important role to extend the applications of WHAs for nuclear and defense applications where high toughness and strength along with other mechanical properties are demanded at higher temperatures. A small addition of Mo reduces the W composition in metal matrix and improves the tensile strength and Yield strength significantly of WHAs with reduction in elongation percentage making them useful in heated dies. However excess of Mo make the WHAs more brittle making them not suitable for the desired applications. The high ductile-brittle transition temperature (DBTT) of Tungsten heavy alloys is a major concern to use them in fusion reactors, this problem can be overcome by adding Y_2O_3 in required small amounts. The Y_2O_3 added to WHAs improves the bending strength, fracture toughness and compressive strength by oxide dispersion in the matrix making them useful in fusion reactors. Research reveals that the lanthanum added to WHAs improves the tensile strength, percentage elongation and toughness and majorly used in manufacturing warheads to rupture armour plates. All these elements Mo, La and Y_2O_3 when added independently to traditional WHAs, alter the mechanical properties and make suitable for military and nuclear applications.

Представлено консолідовані результати досліджень легування вольфраму різними металами і сполуками (Ni, Fe, Cu, Mo, Y_2O_3, La_2O_3), показано переваги легування з урахуванням його умов, техніки мікрохвильового і плазмового спікання. Виявлено, що механічні властивості вольфраму значно покращилися при додаванні вищевказаних елементів. Отримані важкі слави вольфраму можуть бути використані для захисту від ядерного випромінювання.

***Ключові слова**: вольфрам, спікання, мікроструктура, мікротвердість, межа міцності на розрив, межа плинності, подовження, в'язкість, молібден, оксид лантану, оксид ітрію.*

Представлены консолидированые результаты исследований легирования вольфрама различными металлами и соединениями (Ni, Fe, Cu, Mo, Y_2O_3, La_2O_3), показаны преимущества легирования с учетом его условий, техники микроволнового и плазменного спекания. Обнаружено, что механические свойства вольфрама значительно улучшились при добавлении вышеуказанных элементов. Полученные тяжелые славы вольфрама могут быть использованы для защиты от ядерного излучения.

***Ключевые слова**: вольфрам, спекание, микроструктура, микротвердость, предел прочности на разрыв, предел текучести, удлинение, вязкость, молибден, оксид лантана, оксид итрия.*

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Received 19.01.18
Revised 25.01.18
Accepted 25.01.18