Microstructure and Mechanical Properties of Tungsten Heavy Alloy Prepared Using Tungsten Metal Powder Produced from Heavy Alloy Scrap

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ABSTRACT

Tungsten metal powder, using a hydrometallurgical route, was extracted from tungsten heavy alloy scrap that was generated during machining of penetrator cores for the manufacture of Fin Stabilised Armour Piercing Discarding Sabot (FSAPDS). The powder was subjected to extensive characterisation that included physical property evaluation and analysis of the alloy chemistry in order to assess its suitability for the preparation of tungsten heavy alloys with enhanced mechanical properties. Subsequently, a tungsten heavy alloy based on W-Ni-Co was consolidated using this powder through liquid phase sintering followed by heat treatment and swaging operations to realize long rods (~500 mm). This was followed by a detailed characterisation that included microstructure and mechanical properties, which in turn underscores the potential of these recycled powders in the production of premium quality heavy alloy long rods for stringent applications such as kinetic energy penetrators.

Keywords: Tungsten metal powder; Scrap recycling; Sintering; Mechanical properties; Tensile strength; Impact toughness

1. INTRODUCTION

Tungsten metal is designated as 'critical raw material'/'strategic material' in many countries such as the US and the European Union. The metal is available in the earth's crust in the form of oxide minerals viz. wolframite (Fe,MnWO₄) and scheelite (CaWO₄). There are, however, different types of tungsten commodities that are marketed in the global market which include Ammonium Paratungstate (APT), tungsten mineral concentrate (65%WO₂), tungstic acid, high purity tungsten oxide (WO₂), tungsten carbide (WC) etc. and ferro-tungsten that is widely used in steel additions. Nearly 60% of the world total reserves are located in China¹ and about 90% of global tungsten supplies are controlled by China; the other players are Vietnam, USA, Russia, Canada and a few European countries. World consumption of tungsten and tungsten commodities which is generally expressed in terms of total tungsten oxide content, is around 1,00,000 MT (metric tonne) per annum². Resources of tungsten metal are primarily naturally occurring minerals. However, over the years, secondary resources such as hard metal scraps, ore fines, process rejects that are known as tailings material in the gold ore processing, are gaining importance as natural mineral reserves get exhausted.

Currently, about 40 % of the global tungsten supplies are sourced through recycling of various types of W-based metal

scraps. Hard metal scraps are generally marketed and many companies in the world are engaged in the recycling of scraps with home grown technologies.

In India, tungsten metal requirement is mainly in the defence sector. High Energy Projectile Factory (HEPF), Tiruchirapally, Tamil Nadu which was established in mid 1980s with the technology developed by DRDO, manufactures different types of W based heavy alloy ammunition products including anti-tank penetrators (FSAPDS). Currently the requirement of HEPF is placed at about 100-130 MT/year. Future estimates are however, expected to be around 500 MT/ year. Majority of tungsten metal powder required by HEPF has been sourced through imports.

Indian reserves of tungsten are limited to a few occurrences in the states of Rajasthan, Maharashtra, AP, Karnataka, Bengal and Jharkhand. Realizing the importance of developing an indigenous tungsten supply chain, the premier research organizations in the country viz. BARC, IBM, NMDC, NML, RRL (Bhuvaneshwar), TRDDC, MECL etc. carried out extensive studies pertaining to tungsten mineral characterization, mineral separation, beneficiation for enrichment of WO₃ content and preparation of mineral concentrates, preparation of APT and high purity WO₃³⁻⁸. Under a DRDO sponsored program (the early '90s), NML developed process flow sheets for preparation of mineral concentrate (40%WO₃) from tungsten ores mined in the Degana regions of Rajasthan⁴. DMRL operated a tungsten pilot plant involving

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pilot scale testing of processes for tungsten metal extraction from mineral concentrate ($65\%WO_3$) through APT³. However, the process was rendered unviable due to dumping of tungsten commodities including the metal powder at far cheaper prices into the international market, which effectively stifled the indigenous efforts on tungsten extraction as a whole for about two decades.

However, in recent times, the efforts on tungsten extraction have been revived in view of uncertain supplies of tungsten in the international market partly because of dwindling resources and partly because of the anticipated monopoly of limited suppliers. In order to establish indigenous tungsten production facility to meet the requirement for strategic needs, DMRL has taken up the task of development of process technologies for tungsten metal extraction in collaboration with CSIR-NML and CSIR-IMMT. Since there is no active tungsten mine in the country, the developmental efforts have been taken up using heavy alloy scrap, APT and tailings as raw materials. The purity, size and other physical characteristics of the metal powder for targeted applications of ammunition systems are of utmost importance; therefore, the program includes complete characterization of metal powder that is generated in the developmental efforts jointly carried out by CSIR laboratories along with DMRL.

The process technologies development undertaken by the CSIR labs include experimentation on laboratory scale and bench scale to develop process flow sheets for tungsten metal extraction with an objective of achieving desired powder specification, maximum materials utilization, energy effectiveness and minimum environmental pollution keeping in mind large scale production plants. Large number of samples of tungsten metal powders that are obtained in the various stages of process technologies development have been taken up for characterization and testing at DMRL through tungsten heavy alloy preparation for penetrator applications.

An alloy based on W-Ni-Co (92%W-Ni-Co, Ni/Co ratio kept at 7/3) has been increasingly used for penetrator applications because of their enhanced mechanical properties⁹⁻¹¹. The alloy shows superior combination of tensile and impact properties. The investigation describes the details of characterization and property evaluation of the heavy alloy cores based on afore mentioned composition and prepared using tungsten metal powder extracted by an indigenously developed heavy alloy scrap recycling process technology.

2. EXPERIMENTAL WORK

2.1 Processing of Tungsten Powders from Scrap

The scrap that is generated in an industry is typically in the form of machine turnings swarf and fragmented pieces etc. (Fig. 1). The heavy alloy with nominal composition of W (90 wt. %), Ni (6 wt. %), Fe (2 wt. %), Co and Mo (2wt. %) was taken as a starting scrap material. The process flow sheet for heavy alloy scrap recycling is shown in Fig. 2. Initially the scrap was sorted out and subjected to cleaning with water and surfactant to remove oils and grease. The scrap was then taken up for high temperature oxidation roasting (700-800 °C) in an electrical rotary furnace of 120 kg capacity. All the metallic species including tungsten were converted to metal oxides.



Figure 1. Scrap generated during manufacturing of tungsten heavy alloy penetrators.



Figure 2. Flow sheet for preparation of tungsten metal powder from tungsten alloy scrap.

Catalyzed chlorine leaching followed by a series of hot water washing of the oxidized material generated a solution in which oxides of Fe, Ni, Co and Mo were dissolved and solid residue was separated. The solid residue constituted yellow tungsten oxide which was subjected to high temperature reduction by hydrogen in a moving belt pusher type custom built specific electrical furnace, to produce high purity tungsten metal powder. During the standardization of process and pilot scale testing, a number of metal powder samples were collected and taken up for microstructural characterization and properties.

2.2 Analysis of W powder: Particle Size Distribution and Chemistry

As received tungsten powder, obtained from recycling of tungsten heavy alloy scrap, was characterized for its particle size distribution that was carried out using Laser particle size analyzer (Beckman Coulter, Model: LS13320, India). To carry out chemical analysis of W powder, 1 gm of the powder sample was weighed on a Sartorious analytical balance and transferred into a clean 150 ml teflon beaker with a tight lid. The sample was dissolved by adding a triacid mixture (9 ml HCl + 3 ml HNO, + 2 ml HF) to the sample followed by heating the content on a hot plate at 100±5 °C. After digestion, the vessel was allowed to cool and samples were transferred to a 100 ml plastic volumetric flask (with 1 ppm of Y as an internal standard). The final volume was made up to 100 ml with MilliQ Water. A reagent blank was also prepared in a similar manner. The samples were dissolved in triplicate to check repeatability of the values. A Horiba-JY ICPOES (inductively coupled plasma optical emission spectrometer) Model: ULTIMA Expert was used for carrying out the analysis in a sequential manner. The



Figure 3. Process flow sheet for preparation of tungsten heavy alloy blanks.

above made up to 10000 ppm solution was aspirated into the plasma of ICPOES through a peristaltic pump and analysis was carried out at their respective wavelengths of the corresponding elements.

To carry out the analysis of gaseous impurities in the powder samples (O, N and H), 0.2 g of the sample was weighed and packed into a tin capsule before transferring it into a sample holding chamber. For carbon and sulphur analysis, 0.2 g of the powder sample was weighed and transferred into a ceramic crucible. Leco TC-600 oxygen and nitrogen determinator, Leco CS-444 carbon and sulphur analyzer and Leco RH-404 hydrogen analyzer were used to analyze the afore mentioned elements.

2.3 Processing of Heavy Alloy and Characterisation

Tungsten heavy alloy of composition of 92W-5Ni-3Co (Wt. %) was made using these powders. Mixing was carried out in a ball mill for 24 hours using stainless steel balls with ball to powder ratio (BPR) of 1:1. The mixed powders were reduced at 700°C for 2 hrs in hydrogen atmosphere in order to remove oxide or oxygen enriched layer. The powders were then cold iso-statically pressed (Make: National Forge, Belgium) at a pressure of 200 MPa. Fig. 3 shows the processing steps for tungsten heavy alloys. Green compacts were pre-sintered at 1250-1300 °C for 120 minutes. Sintering was performed in a pusher type furnace (FHD Furnaces Ltd, England) in a hydrogen atmosphere (-35°C dew point) at 1450-1490°C for 70 min. The blanks were subjected to chemical analysis for the determination of impurity content. Subsequently, the sintered blanks were subjected to vacuum heat treatment that comprised heating the sample up to 750-900 °C and holding for 3 hrs, followed by heating to 1100-1150 °C for 1.5 hrs. The cycle was repeated 4 times followed by furnace cooling. The samples were again heat treated at a temperature of 1150 °C with 4h soaking time followed by water (brine) quenching. Two stage swaging operation with an intermediate heat treatment (1150°C/water quench) was carried out followed by detailed characterisation.

Metallographic samples of as heat treated samples were prepared following standard metallographic techniques and examined using optical and scanning electron microscopes (Leica, Germany, model: L V 500, FEI Quanta 400 ESEM). Microstructural parameters such as average grain size and volume fraction of matrix were determined using Image J software. Contiguity of W-particles was measured manually¹².

Compositional analysis was also carried out on sintered plus heat treated samples using Electron Probe Micro Analyser (SX-100, Cameca, France). Tensile tests of the samples were performed using a Universal tensile testing machine (Model: Instron 5500R); UTS, 0.2% YS and % elongation to failure values were determined from the stress-strain curves. Charpy impact testing was carried out using un-notched specimen of dimensions 10 mm x 10 mm x 55 mm (Fuel Instruments –India, Model: IT 30 ASTM, 0 to 300 Joules). Fracture surface of the tensile and impact tested specimens were examined using scanning electron microscopy (FEI Quanta 400 ESEM). Grid method of analysis was used to carry out quantitative fractography.

Table 1.	Impurity	analysis o	of tungsten	powders.	()) indicates	standard	deviatio	n in	the	value	S
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Element	Pre defined specification	Tungsten from scrap	Element	Pre defined specification	Tungsten from scrap
0	750	1300 (100)	Na	100	<10
С	40	26 (3)	As	10	<10
S	10	40 (5)	Si	40	<10
Н	10	24 (3)	Cr	30	<10
Co	20	<10	Bi	10	<10
Mn	15	<10	Cu	20	<10
Ca	40	<10	Al	20	<10
Р	10	<10	Sn	20	<10

Table 2. Characteristics of tungsten powders

Characteristics of powders/values	Pre-defined specification	Imported W powder (Source: Metal Tech, Israel)	Indigenous W powder (Tungsten from scrap)
		$D10 = 4.10 \ \mu$ $D50 = 29.3 \ \mu$ $D90 = 67.8 \ \mu$	$D10 = 3.7 \mu$ $D50 = 12.5 \mu$ $D90 = 37.7 \mu$
Particle size (µ)	3-5µ (FSSS) (Avg.)		
Apparent Density (g/cc)	3.9 - 4.3	4.0	4.1
Tap density (g/cc)	-	5.8	5.8



Figure 4. Indigenous tungsten metal powder obtained from tungsten alloy scrap.

3. RESULTS AND DISCUSSION

3.1 Powder Characterization

The recovery of tungsten achieved in this process is about 93-95%. Recovery exceeding 90% has been reported earlier in the extraction of tungsten from tungsten carbide scrap generated from tools and inserts¹³. A predefined specification (Table 1 and Table 2) has been arrived at based on the experience gained during the processing of heavy alloys and information available in literature¹⁴⁻²⁰. The major impurities in the tungsten



Figure 5. Secondary electron images (scanning electron microscopy) of indigenous tungsten powders at different magnifications.

powders are listed in Table 1. It can be seen that the powders meet the purity levels as per the predefined specification except for hydrogen, oxygen and sulphur.

A picture of tungsten powders (greyish in colour) extracted from tungsten heavy alloy scrap is shown in Fig. 4. The secondary electron image of the powder showing the morphology is shown in Fig. 5. The powders are faceted and cuboidal in shape with an average particle size of $3-5 \mu m$, which is in the range of the specifications as listed in Table 2 which also compares the characteristics of the powders obtained from an imported source (Source: Metal Tech, Israel) with the present study. The D₁₀, D₅₀ and D₉₀ of the indigenous tungsten

 Table 3. Impurity levels in the alloy processed using recycle

 W powder

O	N	H	C	S
(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
170 ± 10	50± 3	14± 5	170±30	35 ± 7



(c) Figure 6. (a) Green tungsten heavy alloy compact, (b) sintered rod and (c) swaged rod.

powders are 3.7 μ m, 12.5 μ m and 37.7 μ m respectively while those of the imported W are 4.1 μ m, 29.3 μ m and 67.8 μ m. This clearly indicates the powder obtained via scrap recycling is finer. During the extraction, the yellow oxide residue is left as fine particles, which may lead to finer tungsten powders during reduction. Another variable could be the temperature of reduction that has not been studied in detail. The apparent densities of the powders are within the range of specification. Post sintering the blanks were also analysed for impurities and the results are shown in Table 3.

3.2 Microstructure

Figure 6 shows green compacts, as sintered and as swaged blanks during different stages of processing of W-Ni-Co alloy. As can be seen, the material is free from defects during different steps of processing.

The optical micrographs of the alloy (sintered plus cyclic heat treated) at different magnifications is shown in Fig. 7. The microstructure is characterized by nearly spherical tungsten particles with a particle size of $20\pm9 \,\mu\text{m}$ suggesting significant coarsening of particles during liquid phase sintering from the starting size of $3-5 \,\mu\text{m}$. This is a result of liquid phase sintering that involves Ostwald ripening²¹, the W-liquid interface energy



Figure 7. Optical micrographs of tungsten heavy alloy in sintered and heat treated condition at different magnifications. Fine W particles seen in matrix at higher magnification.

being the driving force. The particle size distribution is shown in Fig. 8. Majority of grains are in the 10-20 μ m range.

The finer details of microstructure especially the matrix in back scattered electron mode are shown in Fig. 9. As can



Figure 8. Particle size distribution in the sintered microstructure.

be seen from Fig. 9d that the cyclic heat treatment in the alloy results in precipitation of fine tungsten particles in the matrix. It has been reported that by increasing the number of cycles, the fraction of tungsten precipitates in the matrix can be increased9. In addition undulations in the tungsten grains at tungsten matrix interface are also observed in the high magnification image (Fig. 9d). This is a result of the sequence of phase transformation that leads to the precipitation of W. Initially, an intermetallic is formed at the W matrix interface at 850 °C (the lower temperature of cyclic treatment) that subsequently dissolves at higher temperature of cyclic treatment leaving behind W precipitates. The undulations may be attributed to prior W-intermetallic interface following the precipitation of intermetallic that may prefer to grow in certain crystallographic direction in W-particles. Similar observation of undulations, although due to different reasons, along the tungsten-matrix interfaces has been reported by Song et al.²². This undulation has a favourable effect on the ballistic performance of these alloys. It promotes adiabatic shear bands during the process of penetration that results in the removal of material from the penetrator tip thereby aiding the penetrator core maintain



Figure 9. Back scattered electron images of the microstructure in as heat treated condition. Fine tungsten particles and undulation at W-matrix interface shown by arrows in (d).

		1		
Alloy	Present study	Literature 23., W-Ni-Co	Literature 24., W-Ni-Co	Literature 29., W-Ni-Fe
Contiguity	0.25-0.27	0.23	0.23-0.24	0.2-0.4
Matrix volume fraction (%)	24 ± 2	20.4 ± 2	23	17-25
Avg. Grain size (µm)	20±9	22.8±9.8	22.7	30-35
Dissolved tungsten (wt. %)	39±1	44.5±1	44.4	17-32

Table 4. Microstructural parameters



Figure 10. Elemental mapping of W, Ni, Co, C, O and S on as heat treated condition using electron microprobe.



Figure 11. Line scan analysis of C, S, O in the microstructure.

a sharp tip. The reason for this is not clear but it is felt that these undulations may act as nucleation sites of adiabatic shear bands which is not a homogenous process. The comparison of microstructural parameters of the present study and a published study on the same alloy is shown is shown in Table 4.

It is observed that the particle size of the present alloy is similar to that of the alloys shown in the literature²³⁻²⁴. The EPMA analysis shows 40 wt.% Ni, 21 wt.% Co and 39 wt.% W is dissolved in the matrix of the alloy. Cobalt containing heavy alloys have higher solubility of tungsten in the matrix as compared to W-Ni-Fe or W-Ni-Fe-Co alloy systems. This is consistent the results of with Cury et al.25 who investigated W-Ni-Co alloys. Also the alloys exhibit significantly lower contiguity with respect to alloys based on W-Ni-Fe alloys (Table 4). This is consistent with the result of a study carried out by Dincer et al.²⁶, attributed to the effect of Co in reducing the W-matrix interface energy. Slight difference in grain size, matrix volume fraction and contiguity compared to those in W-Ni-Co alloys (reported in literature) may be attributed to difference in the processing technique employed. The W content is discernibly lower compared to those reported in literature²³⁻²⁴ for the same alloy. This may be due to difference in the technique employed for the determination of composition.

Figure 10 shows the elemental mapping of the alloy for C, O and S. While O appears to partition to W particles, S goes



Figure 12. True Stress-true strain curves of the alloy in sinter plus heat treated and final swaged condition (strain rate=10⁻³ s⁻¹).

to the matrix phase. Occasionally, segregation of C is seen on the W-matrix interface. The line scan analysis reveals the distribution of C, O and S present in the alloy (Fig. 11). While O appears to partition to coarse W particles, S partitions to the matrix phase. No clear preference is observed for C.

3.3 Tensile and Impact Properties

True stress-true strain curves for both cyclic heat treated and swaged samples are shown in Fig. 12. Corresponding tensile properties of the alloy after heat treatment is shown in Table 5. The alloy from the indigenously processed tungsten powders attains strength in the range of 1025-1090 MPa with elongation values of 20-28 % in heat treated condition. Stuitje *et al.*⁹ reported, in their patent, a tensile strength of 1100 MPa with 40 % elongation. Thus, there appears to be a possibility of further enhancement in properties by fine tuning sintering and heat treatment parameters. Future work involves enhancement of properties using following approaches:

- Using purer raw materials that include Ni and Co in addition to W
- Optimisation of sintering time and temperature
- Improvement in the quenching facility
- Standardisation of swaging in terms of deformation and temperature of swaging

Tensile properties evaluated after two-stage swaging are listed in Table 6. Significant improvement in tensile strength is observed after swaging compared to those after the heat treatment (Table 5). However, this is the expense of the elongation values. Ravi Kiran *et al.*²⁷ have clearly shown the effect of swaging on tensile properties of a tungsten heavy alloy. While the strength increases, the ductility goes down. This has also been reported by Nicolas *et al.*²⁸ on W-Ni-Fe alloy containing 93 % W.

Table 5 and Table 6 show the tensile data of W-Ni-Fe alloys based on 92 % W with Ni and Fe. The strength values of W-Ni-Co are clearly higher. This may be attributed to factors: (1) the presence of fine W particles in the matrix phase of W-Ni-Co alloy that is absent in W-Ni-Fe alloys. This imparts two phase strengthening in the matrix phase by providing obstacle to slip

 Table 5.
 Tensile properties of the alloy after sintering and cyclic heat treatment. CHT: Cyclic heat treatment; HT: Heat treatment;

 WQ: Water quench

		Tensile properties			
Alloy	Condition/ Property Ten		Elongation (%)		
Present study (Lot-I)	Sinter + CHT + HT (WQ)	1090±1 1025±2	28±1 20±1		
Literature 23.	Sinter + CHT + HT (WQ)	1061±6	23±5		
Literature 24.	Sinter+CHT+HT (OQ) (W-Ni-Co)	1047 1010 1015 1067	14 10 7 13		
Literature 29.	Sinter+ HT (OQ) (W-Ni-Fe)	901 ± 5 917 ± 1 924 ± 1 938 ± 2	21±1 28±1 34±2 32±1		

lable 6.	lensile properties of the alloy after cyclic heat treatment plus swaging operations.	CH1:	Cyclic he	at treatment;	HI:	Heat
	treatment; WQ: Water quench; SW: Swaging; OQ: Oil quench					

		Tensile p	operties	_ Impact toughness (J/cm²)	
Alloy	Condition/ Property	Tensile strength (MPa)	Elongation (%)		
Present study (Lot-1)	Sinter + CHT + HT (WQ) + SW1 + HT (WQ) + SW2	$\begin{array}{c} 1488 {\pm} \hspace{0.1 cm} 4 \\ 1537 {\pm} \hspace{0.1 cm} 2 \end{array}$	$\begin{array}{c} 8.5{\pm}\ 1\\ 10{\pm}\ 2 \end{array}$	100 124	
Present study (Lot-2)	Sinter + CHT + HT (WQ) + SW1 + HT (WQ) + SW2	$\begin{array}{c} 1433 {\pm}\ 2\\ 1409 {\pm}\ 2 \end{array}$	13.8 ± 1 10.2 ± 1	127 112 162	
Literature 25.	Heat treated plus swaged	1540	10.5	160	
Literature 29.	Sinter+HT (OQ)+swaged	1244±4 1279±10 1311±4 1345±5	6 ± 2 9 ± 1 10 ± 1 12 ± 1	58 119 119 123	



Figure 13. Log-log plots of true stress vs. true plastic strain of heat treated and heat treated plus swaged samples.

deformation, which has been confirmed by Prabhu *et al.*²³. in a detailed slip line study after deformation, (2) higher W (39%) in the matrix phase as opposed to 30 % in W-Ni-Fe alloys that provides solid solution strengthening. The same trend is also seen in the swaged alloys. The improvement in strength following double swaging in W-Ni-Co alloys is substantial with good elongation (>8%). Again enhanced properties are attributed to the presence of fine W precipitates in the matrix phase and enhanced W solubility in the matrix phase.

Log-log plots of true stress vs. true plastic strain of heat treated and heat treated plus swaged samples are shown in Fig. 13. A two slope behaviour is seen in the heat treated condition. This has been explained in the work carried out by Panchal *et al.*³⁰.While the lower slope corresponds to the deformation of the matrix phase, the higher slope is attributed to the possible deformation of the two phase aggregate. This distinction is not seen in the swaged samples where both matrix and W has been hardened by swaging deformation and they seem to deform together right since the onset of macroscopic plastic deformation.



Figure 14. Strength-elongation plots for W-Ni-Fe and W-Ni-Co tungsten heavy alloys.



Figure 15. Strength-impact toughness plots for W-Ni-Fe and W-Ni-Co tungsten heavy alloys.

The impact toughness values for the alloy processed in two different lots are shown in Table 6. It shows the impact values exceeding 100 J in all the samples. Higher impact toughness has been reported in literature^{9,25}. The inferior impact toughness reported in the present work may be due to higher impurity content (O, H and S) (Table 1). This may be also due to purity of Ni and Co powder used in the study. Thus, care while processing heavy alloys needs to be taken to ensure purity of not only W but other alloying elements also. Overall balance of strength and impact toughness appears to be satisfactory for stringent applications.

Figure 14 and Fig. 15 shows strength-elongation and strength-impact plots of W-Ni-Co and W-Ni-Fe alloys. Superior balance of properties is clearly seen in W-Ni-Co alloys as opposed to W-Ni-Fe alloys, especially impact toughness. Thus, it is strongly felt that the microstructural modification of the matrix phase (especially the presence of fine W precipitates) and enhanced solubility of W in the matrix phase results in substantial improvement in mechanical properties in W-Ni-Co alloys.

Fractograph of the failed impact specimen is shown in Fig. 16. A typical fracture surface of tungsten alloys comprises features such as W-W decohesion, cleavage of W particles, W-matrix failure and matrix failure. It is reported that matrix failure being ductile (micro-void coalescence), is expected to be an energy consuming process and it leads to improvement in impact toughness³¹. The intergranular failure that may be due to the presence of impurities at grain boundaries need to be controlled so as to realise enhanced properties. Further studies need to be taken up in this area by undertaking quantitative fractography.



Figure 16. Fractograph of impact tested sample.

4. CONCLUSIONS

Indigenously developed tungsten powders using heavy alloy scraps were characterized for purity, size and particle size distribution. Using this powder, tungsten heavy alloy rods were prepared by liquid phase sintering and thermomechanical treatment followed by characterization of microstructure and mechanical properties. Key observations are as follows:

- The purity of powders meets the specifications used for processing of heavy alloys except hydrogen, sulphur and oxygen
- Defect free tungsten heavy alloy rods have been prepared using these powders
- Microstructural features such as grain size, contiguity and

matrix volume fraction are comparable to those of W-Ni-Co alloys reported in literature

- Tensile strength of 1400 MPa with impact toughness of >100 J/cm² has been achieved in different lots of penetrator blanks, which suggest that these powders may be used for penetrator applications
- Choice of appropriate raw materials (powders) and fine tuning of processing parameters is needed to realize superior mechanical properties of heavy alloys.

REFERENCES

- 1. U.S. Geological survey, Mineral Commodity summaries, Janurary 2021.
- 2. https://wresources.com/projects/tungsten-overview. (Accessed on 17/03/2023).
- Acharyulu, S.L.N. & Rama Rao, P. An integrated approach to the optimum utilization of national resources: Technology gaps. *Bull. Mater. Sci.*, 1996, **19**, 179-199.
- 4. Krishna Rao, N. Beneficiation of tungsten ores in India: A review, *Bull. Mater. Sci.*, 1996, **19**, 201-265.
- 5. Pradip, Recent advances in the recovery of tungsten values in the fine and ultrafine size range. *Bull. Mater. Sci.*, 1996, **19**, 267-293.
- 6. Premchand, Processing of low grade tungsten ore concentrates by hydrometallurgical route with particular reference to India. *Bull. Mater. Sci.*, 1996, **19**, 295-312.
- Jakhu, M.R. & Ray, S. Degana tungsten project present plant practice and future scenario. *Bull. Mater. Sci.*, 1996, 19, 313-329.
- Srivastava, S.C.; Bhaisare, S.R.; Wagh, D.N. & Iyer, C.P.S. Analysis of tungsten in low grade ores and geological samples. *Bull. Mater. Sci.*, 1996, 19, 331-343.
- Stuitje, P.; Harkema, R. & Taal C.: Heavy metal alloy and method for its production. United State Patent, No. 5462576A, 1995.
- Skozylas, P.; Gulbinowicz, Z.; Goroch, O.; Barcz, K.& Mieczyslaw, K. Research into the production of tungsten heavy alloys with specific mechanical properties. *Problem Mechatron. Armament Aviat. Safety Eng.*, 2019, 10(4), 23-36.
- Bless, S.J.; Tarcza, K.; Chau, R.; Taleff, E. & Persad, C. Dynamic fracture of tungsten heavy alloy. *Int. J. Imp. Eng.*, 2006, **33**, 100-108.
- 12. German, R.M. Powder Metallurgy and particulate materials processing. Metal Powder Industries Federation, Princeton, 2005.
- 13. Bhosale, S.N.; Mookherjee, S. & Pardeshi, R.M. Current Practices in tungsten extraction and recovery. *High Temp. Mater. and Proc.*, 1990, **9**(2-4),147-162.
- 14. https://unitedwolfram.com. (Accessed on 17/03/2023).
- Edmonds, D.V. & Jones, P.N. Interfacial embrittlement in liquid-phase sintered tungsten heavy alloys. *Metall. Trans. A*,1979, **10A**, 289-295. doi: 10.1007/BF02658336.
- 16. Churn, K.S. & German, R.M. Fracture behavior of W-Ni-Fe heavy alloys. *Metall. Trans. A*, 1984, **15A**, 331-338.
- 17. Fernandez, G.A. & Ostlund, L. Experimental and theoretical study of the phase equilibria in the Fe-Ni-W system. *Metall. Trans. A*, 1986, **17A**, 1809-1823.

doi: 10.1007/BF02817278.

- Bose, A.; Sims, D. & German, R.M. Test temperature and strain rate effects on the properties of a tungsten heavy alloy. *Metall. Trans. A*, 1988, **19A**, 487-494. doi: 10.1007/BF02649263.
- Rabin, B.H. & German, R.M. Microstructure effects on tensile properties of tungsten-nickel-iron composites. *Metall. Trans. A*, 1988, **19A**, 1523-1532. doi:10.1007/BF02674026.
- Ekbom, L.B. The distribution and influence of impurities in tungsten heavy metals. *Int. J. Ref. Met. Hard Mater.*, 1991, 10, 155-159. doi:10.1016/0263-4368(91)90020.
- Ardell, A.J. The effect of volume fraction on particle coarsening: Theoretical considerations. *Acta Metall.*, 1972, 20, 61-71.
- Song, H.S.; Noh, J.W.; Beak, W.H.; Kang, S.J.L. & Chun, B.S. Undulation of W/matrix interface by resintering of cyclically heat-treated W-Ni-Fe heavy alloys. *Metall. and Mat. Trans. A*, 1997, **28**, 485-489.
- Prabhu, G.; Arockia Kumar, R. & Nandy, T.K. Effect of cyclic heat treatment on the microstructure and mechanical properties of W-Ni-Co alloys. *Int. J. Ref. Met. Hard Mater.*, 2019, 82, 31–42. doi:10.1016/j.ijrmhm.2019.03.024.
- 24. Venkateswara Rao, Y.; Prabhu, G.; Sankaranarayana, M. and Nandy, T.K. Development of W-Ni-Co alloy with two phase matrix and preliminary property evaluation-Part I. Technical report, DRDO-DMRL-PMG-108-2015.
- 25. Cury, R.; Joubert, J.M. & Couque, H. Evolution of Cofree tungsten heavy alloys for kinetic energy penetrator, *Powder Metallurgy*, 2013, **56**, 347–350.
- 26. Dincer, O.; Pehlivanolu, M.K.; Çalikan, N.K.; Karakaya and Kalkanli, A. Processing and microstructural characterization of liquid phase sintered tungsten–nickel– cobalt heavy alloys. *Int. J. Refractory Metals and Hard Mater.*, 2015, **50**, 106-112.
- Ravi Kiran, U.; Sambasiva Rao, A.; Sankaranaryana, M. & Nandy, T.K. Swaging and heat treatment studies on liquid phase sintered 90W-6Ni-2Fe-2Co heavy alloy. *Int. J. Ref. Met. Hard Mater.*, 2012, **33**, 113–121. doi: 10.1016/j.ijrmhm.2012.03.003.
- 28. Nicolas, G. Heavy tungsten-nickel-iron alloys with very high mechanical characteristics and process for the production of said alloys, United State Patent, No. 4938799A, 1990.
- Panchal, A.; Venugopal Reddy, K.; Azeem P.A; Nandy, T.K. &Singh, A.K.Effect of Ni/Fe ratio on microstructure, tensile flow and work hardening behavior of WHAs in heat treated and swaged conditions.*Philosophical Magazine*, 2021, **101**(2), 211-241.

doi: 10.1080/14786435.2020.1831704.

- Panchal, A.; Venugopal Reddy, K.; Azeem P.A; Nandy, T.K. & Singh, A.K.On the flow and work hardening behaviour of tungsten heavy alloy 92W-5.5Ni-2.5Fe. *Int. J. Ref. Met. Hard Mater.*, 2020, 88, 105203. doi: 10.1016/j.ijrmhm.2020.105203.
- 31. Panchal, A. & Nandy, T.K. Effect of composition, heat treatment and deformation on mechanical properties of

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