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Microstructure and mechanical properties of spark plasma sintered tungsten heavy alloys

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ABSTRACT

The effect of cobalt (0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt%), as an alloying element, on the microstructure and mechanical properties of W-Ni-Fe tungsten heavy alloy (WNF) prepared through spark plasma sintering (SPS) process is investigated in this work. The sintering is performed at 1400 °C with a heating rate of 100 °C/min and holding time for a period of 2 min. The properties of the cobalt added heavy alloys (WNFC) are found to be superior to that of the tungsten heavy alloy without cobalt addition. The 1.0% cobalt alloy is observed to give higher yield and tensile strengths compared to other alloys. As the mechanical properties of the alloys depend on the microstructural features, a detailed study on the influence of the microstructural parameters such as average grain size, contiguity and matrix volume fraction on the properties of the alloys is carried out. The average tungsten grain size of WNF alloy is 12.3 μm and that of WNFC alloys is from 9.5μm to 11.5 μm. The control of grain size is significantly evident in the case of spark plasma sintered alloys. The yield strength is found to be influenced by the W-grain size of the microstructure. The contiguity of the WNFC alloys is observed to decrease with increase in percentage of cobalt addition. The fractograph analysis of the tensile tested specimen helps in understanding the tensile behaviour of the alloys. The WNFC alloys show predominantly W-grain cleavage fracture compared to the WNF alloy, possibly due to the good cohesive strength of the matrix phase and W/matrix interface, because of cobalt addition and also due to the high heating rate followed in the SPS process.

1. Introduction

The tungsten heavy alloys (WHA's) are used in applications where higher density, good mechanical properties and workability are required. A typical WHA consists of 88–98 wt% of tungsten, with low melting alloying elements of nickel, iron or copper constituting the remaining proportion [1]. The heavy alloys are fabricated as a bcc structured W phase dispersed in a fcc binder matrix phase of Ni-Fe-W or Ni-Cu-W. Due to its uniqueness of possessing high strength as well as ductility, the WHAs are used in variety of applications such as gyroscope rotors, counter balance weights, kinetic energy penetrators, radiation shields, vibration dampers, rocket nozzles, machining tools and electrical contacts [2]. To attain higher strength and hardness, these alloys are subjected to post sintering treatments such as swaging and aging [3–5]. There is a continuous research in improving the mechanical properties of the base alloys without any post sintering processes i.e. to obtain near net-shaped samples by including other alloying elements like cobalt, rhenium, and molybdenum in the binder matrix and by using novel sintering techniques and improving the processing conditions. Therefore, the understanding of the effects of alloying elements and the best process conditions are necessary to obtain a good performance alloy material.

The small additions of rhenium and molybdenum are found to control the tungsten grain growth and refine the grains during liquid phase sintering of the alloy, thereby, improving its strength and hardness [6–8]. The molybdenum addition decreases the melting point of the heavy alloy and produces fine W grains. Though the rhenium alloying gives a better performance than molybdenum, its use is limited due to the high cost involved in processing the element. The use of cobalt as alloying element increases strength and ductility of the alloy. The impact strength of the alloy is also increased [6,9]. The presence of cobalt offers solid solution strengthening of the binder matrix as well as strengthens the tungsten-matrix interface.

The WHAs are generally processed through powder metallurgy technique. The sintering through conventional technique requires high dwell time of several hours to obtain a dense alloy and also leads to a coarser microstructure and degradation of mechanical properties, if the process conditions are not ideally controlled. During the last two

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decades, different sintering techniques have evolved and used by researchers like microwave sintering [10–13], two stage sintering [14,15] and field assisted sintering technique (FAST) or spark plasma sintering (SPS) [16,17]. The objective of using these new techniques is to process the alloys at faster heating rate and thereby controlling the grain growth. The research focus is also on obtaining the required mechanical properties at a lower sintering temperature by using nano sized powder particles, high energy ball milling process [18–20] and solid state processing of the alloy, combining with novel sintering techniques.

Spark plasma sintering (SPS) is a novel technique used for the past few years in consolidating metal powders and their alloys [16]. A pulsed direct current is supplied to the metal powders that are kept inside a die with simultaneous application of uniaxial pressure (< 100 MPa). Prior compaction of the powders is not required. The sintering cycle is very short due to the high heating rate (up to 300 °C/min) which is possible in the SPS process. The overall process of densification is completed within few minutes. The grain growth during the sintering process is restricted due to the rapid rate of heating and thereby better mechanical properties are achieved. The SPS process is also used to consolidate tungsten heavy alloys [21,22]. The present work investigates the effect of different proportions of cobalt addition to W-Ni-Fe system processed through spark plasma sintering technique.

2. Experimental procedure

The as-received powders of tungsten, cobalt, nickel and iron are blended in the required proportions to design five grades of alloy, namely, WNF (92W-5.6Ni-2.4Fe), WNFC1 (91.5W-5.6Ni-2.4Fe-0.5Co), WNFC2 (91W-5.6Ni-2.4Fe-1.0Co), WNFC3 (90.5W-5.6Ni-2.4Fe-1.5Co) and WNFC4 (90W-5.6Ni-2.4Fe-2.0Co). The characteristics of the powders are presented in Table 1. The blending of powders is done in a V-Mixer for one hour. The compositions are sintered in a spark plasma sintering furnace (Dr. Sinter, Fuji Electronic Industrial Co. Ltd.), at a temperature of 1400 °C with heating rate of 100 °C/min. The blended powder is placed in a graphite die. The powders are separated from the punch and die by a thin graphite foil for easy removal of the sintered part. The sintering is carried out at the required temperature in vacuum with simultaneous application of 30 MPa pressure on the punch and die system. The samples of 30 mm diameter with average height of 7 mm are obtained. The sintered density is measured using Archimedes density measurement principle.

All the samples are initially ground using silicon carbide abrasive papers of 240, 320, 400, 600, 800, 1000 and 1200 grit. The grinding is followed by cloth polishing using a disc polisher (Make: Bainpol-VT, Chennai Metco Pvt Ltd.) with aluminium oxide powder abrasive suspended in water solution. The polished samples are etched using murakami agent (100 ml Distilled water, 10 g Potassium ferricyanide and 10 g Sodium hydroxide) to highlight the microstructural features. The photo micrographs of the sintered samples are obtained through an optical microscope (Zeiss-Axio, Chennai Metco Pvt Ltd.) with digital image acquisition capability. The micrographs with higher magnification are obtained through scanning electron microscope (SEM, ZEISS EVO 18) provided with an energy dispersive spectrometer (EDS) system. The chemical composition of the alloys are analysed using EDS.

The average grain size is measured using line-intercept method from SEM micrographs taken from the prepared surfaces of the samples [23]. The contiguity (C_{WW}) is calculated by measuring the number of tungsten-tungsten grain contacts (N_{WW}) and tungsten-matrix interfaces (N_{WM}) using the line-intercept method [24] and applying the same in the Eq. (1),

$$C_{WW} = \frac{2N_{WW}}{N_{WM} + 2N_{WW}} \quad (1)$$

The matrix volume fraction is measured using the SEM micrographs of the prepared samples by point counting method (ASTM E562-99e1). The microhardness of the samples is measured using digital Vicker's hardness tester (Econonet VH-1D, Chennai Metco Pvt Ltd.) by applying 50 g of load for 10 s. The indentations are created on ten random locations of the sample surface and the mean of the ten readings is taken as the test result. The tensile specimens are prepared from the sintered samples following ASTM E-8 standards and experimented in a universal tensile testing machine (Instron 8801). The fractured surfaces of the tensile tested samples are inspected using scanning electron microscope (SEM).

3. Results and discussions

The compositions of the alloys WNF, WNFC1, WNFC2, WNFC3 and WNFC4 are shown in Table 2. The alloys are sintered using spark plasma sintering technique at a temperature of 1400 °C with a heating rate of 100 °C/min.

3.1. Densification

The supply of high current and high heating rate, followed in the SPS process, results in good physical activation of the powder particles, thereby, cleaning the particle surfaces [25]. The sintering necks start to form between the particles and local diffusion takes place. At faster heating rates the powder particles are subjected to good activation and the sintering mechanism of neck formation and diffusion between the particles occur at a lower temperature [25–27]. An ideal heating rate of 100 °C/min is followed in this experiment, as the compact can be exposed to higher temperatures for a longer period of time, so that, the mass transfer is more efficient. The reduction of surface free energy of the particles is required for the solid-state sintering mechanism to progress. This is achieved through atomic diffusion and mass transfer between the particles [25]. The densification process continues with increase of temperature. A solid solution of mutually soluble elements is formed and they spread over the W particle surfaces through surface diffusion or viscous flow [28]. The pores in the structure get filled simultaneously, resulting in enhancement in values. The possible transfer mechanisms include coalescence of W-W particle contacts, dissolution and precipitation through the binder solution and surface diffusion at W-matrix boundary [29,30].

The Fig. 1 shows the variation of sintered relative density of the tungsten heavy alloys through the SPS process. The cobalt is added to the W-Ni-Fe system to enhance the sintering behaviour of the alloy [6,9]. The cobalt addition provides solid solution strengthening of the matrix phase and increases the tungsten dissolution in the phase [31].

Table 1
Powder characteristics.

Powder	W	Ni	Co	Fe
Particle size (μm)	10	3	4	5
Purity %	99.9	99.9	99.9	99.9
Supplier	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich
Density (g/cm^3)	19.3	8.908	8.9	7.87

Table 2
Composition of tungsten heavy alloys.

Alloy	Composition, wt%			
	W	Ni	Fe	Co
WNF	92	5.6	2.4	–
WNFC1	91.5	5.6	2.4	0.5
WNFC2	91	5.6	2.4	1.0
WNFC3	90.5	5.6	2.4	1.5
WNFC4	90	5.6	2.4	2.0