Activated Sintering of Tungsten Heavy Alloy

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Abstract:
In the present work, characterization of sintering behavior of Tungsten heavy alloy has been done through powder metallurgy route using Spark plasma sintering (SPS). Fine powder of Tungsten (<30 µm) was separately mixed with Ni, Co, Fe, Mo and Cu each with 1 weight%. Spark Plasma Sintering (SPS) technique (1200°C, 20 MPa pressure with 1 min holding time) was used to sinter the mixed powders. The maximum density was observed in W-Ni followed by Co, Fe, Cu, Mo and with least in pure tungsten sample. Optical microscopy as well SEM was done to determine the microstructure and grain coarsening. Due to the short heating time very less grain coarsening was observed. Vickers hardness test was conducted which resulted in maximum hardness in case if W-1Fe SPS sample.

Keywords: Powder metallurgy; Tungsten heavy alloy; Spark plasma sintering; Holding time.

1. Introduction

Tungsten in its pure form looks like steel-grey or like a whitish metal and belongs to group VI-D of the periodic table. It is one of the metal with high melting point temperature (3422°C) with good mechanical and thermal properties like high density (19.3 g cm⁻³), strength, ductility, low thermal expansion coefficient and high thermal conductivity [1-2]. Tungsten is also considered as an inert material, which is resistant to many compounds and elements. It is compatible with most glasses and ceramics up to high temperatures and shows good resistance to many molten metals. With these properties, tungsten finds its application in military, aerospace industry, automobile industry, electronic devices, weights and counter weights [3]. In the military, tungsten heavy alloys (WHS) are used for bullets, shells, bullet proof vehicles and kinetic energy penetrators applications because of its higher dynamic strength [4-5]. In the automobile industry, tungsten due to its higher density is used in racing cars as “vehicle weight”, which helps to balance the car during the race. In case of I.C. engines, counter weights made up of tungsten are used to balance the primary unbalance forces. Due to its high melting point, superior wear resistance and low vapour point, tungsten alloys are used to manufacture ignition tubes of rocket engines [6]. Other application of tungsten includes light bulb filaments and heating elements. In SPS, the bonding is achieved by the viscous melt flow of binder on the particle surface. Initially, due to the presence of porosity in the compact, the heat is generated within the sample due to Joule’s heating [7-8]. The gas present between the powder particles gets ionized and transforms into plasma. SPS also provides self-purification at the particle surface, interfaces, and grain boundary. Formation of the small electric field between the small gaps of particles, make the electrons, anions, and cations

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which strikes the surface of the opposite particle and purifies its surface and provides favorable diffusion bonding between the particles thus results in densification of the compacts. Although in previous studies, many authors claim high pulsed current generates spark and plasma between the particles, experimental evidence is still lacking [9].

In the current study, the effect of Ni, Co, Fe, Mo and Cu alloying in tungsten has been investigated by using spark plasma sintering technique.

2. Experimental Procedure

2.1 Powder Preparations

Commercially available W, Ni, Co, Fe, Mo, and Cu were selected for this study (Supplier: Sigma-Aldrich, India). All the powders were weighed accurately and five different compositions with 99 wt% W and 1 wt% of Ni, Co, Fe, Mo and Cu, each, were prepared in addition to one sample of pure tungsten (100 wt%). Before mixing the powders, the morphology of the powders was examined with a Scanning electron microscope (Zeiss EVO180-Research).

![SEM micrographs of the as-received powders](image)

**Fig. 1.** SEM micrographs of the as-received (a) Tungsten, (b) Nickel, (c) Cobalt, (d) Iron, (e) Molybdenum and (f) Copper powders.
Fig. 1a to Fig. 1f shows SEM morphology of the six as-received powders. SEM analysis reveals a polyhedral and irregular shape of tungsten particles (Fig. 1a), while the cobalt powder (Fig. 1c) is agglomerated. Nickel, iron, molybdenum, and powders were found non-porous and round in shape (Fig. 1b, Fig. 1d, and Fig. 1e respectively). All the powders were manually mixed as per the pre-mentioned composition using a ceramic mortar for about 30 minutes each.

2.2 Sintering

The powders after mixing were sintered by SPS in a 30mm inner diameter die. Graphite foils of thickness 0.3 mm were placed between the punch-powder and die-powder interface to reduce die wall friction and allow easy removal of the sintered sample from dying after sintering. Sintering was done in a vacuum chamber and a constant pressure of 20 MPa was applied on the punches throughout the process. For all the composition, sintering was done at 1200°C [10]. The heat rate was controlled by an automatic heat controller with a set value of 1200°C/min. The sintering cycle was completed within 1 min. The temperature was measured using a thermocouple. After the required temperature reached, heating was stopped and the pressure from punches was released. The sample was then allowed to cool in the die itself. Similarly, six different samples (each 30 mm diameter and 7 mm height) with W-1Ni, W-1Co, W-1Fe, W-1Mo, W-Cu and pure tungsten were sintered with the same process parameters.

2.3 Relative density measurements

Initially, all the specimens were cleaned to ensure the proper removal of graphite contaminants from all the surfaces. The density of the sintered samples was calculated by using mass-volume relation. Fig. 2a shows the sintered density achieved by different compositions. Based upon the weight fraction of alloying element in tungsten, theoretical density of all the composition was calculated. To compare the densities of all sample percentage sintered density was calculated using equation (1).

\[
\text{Percentage sintered density} = \left( \frac{\text{Sintered Density}}{\text{Theoretical Density}} \right) \times 100
\]  

(a)  

(b)  

Fig. 2. Effect of Ni, Co, Fe, Mo, Cu on (a) sinter density and (b) Percentage Sintered density.
2.4 Microstructural Characterisation

To obtain the microstructure, metallographic preparation was done for all the sintered specimens for which the samples were first polished with SiC sheet of grit size (µm): 200, 400, 600, 800, 1000, 1200, 1500 and 2000 µm, followed by disc polishing using Alumina solution and Water, separately. As per ASTM standards (ASTM E407), the prepared samples were then chemically etched by dipping the samples in a solution of 10g Potassium ferricyanide (K₃[Fe(CN)₆]) and 10g Sodium hydroxide (NaOH) in 100 ml of water for the 20s to observe the microstructure and grain size. For higher magnification microstructural analysis, SEM (Model: Zeiss EVO180 - Research) was also done. Grain size measurement was also done using the Intercept method.

2.5 Mechanical Property Characterisation

For mechanical property characterization, Vickers microhardness test was performed at room temperature with indenter load of 500g and dwell time 10s on all the prepared sample by a Vickers Hardness Tester (Model). Ten readings from each sample were taken and arithmetic mean with standard deviation was calculated.

3. Results and discussion

3.1 Effect on densification

Comparison of sintered density and Percentage sintered density for all the sintered sample (W- 1Ni, W- 1Co, W- 1Fe, W- 1Mo, W- 1Cu and Pure Tungsten) is shown in Fig. 2a and 2b respectively. A maximum of 91.46% density has been achieved in case of W- 1Ni followed by W- 1Co and W- 1Fe. J. Kurtz et.al. [10] in his own study also reported more shrinkage in case of W-Ni heavy alloy. Since tungsten has less self-diffusion, the presence of Ni in the W leads to the phenomenon called Oswald ripening which results in the high density of the W- Ni system. At higher temperature, the large spherical balls of tungsten start growing into a matrix of fine grains, which gives the space to the Ni particles to settle at the grain boundary. J. Kurtz et.al. [11] also concludes that presence of Ni at W grain boundaries raise the grain boundary self-diffusion coefficient, which validates the above-mentioned reason. The least density was observed in the pure tungsten SPS sample which lies close to 70%. This may be due to the absence of any activator in the tungsten matrix. The less self-diffusion is also one of the main reason of less densification of the tungsten sample [12]. It can be seen from Fig. 2b that Ni, Co, and Fe are the best sintering activators to produce tungsten heavy alloy compacts using SPS.

3.2 Microstructural Characterisation

To investigate the microstructural behavior and homogeneity the sintered samples were metallographically prepared. Fig. 3 and 4 shows the optical and SEM micrographs of W-1Ni, W-1Co, W-1Fe, W-1Mo, W-1Cu and Pure Tungsten SPS samples respectively. In case of W-1Ni (Fig. 3a, Fig. 4a) optical and SEM micrographs clearly reveals that the Tungsten particles did not have significant growth but Ni was able to penetrate and fill almost all pores and voids available in between the W-Ni particles. Ni particles settled at the grain boundary has resulted in good densification of the W-Ni SPS system. The formation of sintering neck between the tungsten nickel grain boundaries has also promoted the diffusion and has contributed to the densification of tungsten nickel heavy alloy [11, 13]. The presence of Ni enhances mass diffusion, big grain size has been observed in Fig. 1. Tungsten doped
with Ni shows globular grains and well developed sintered necks as clear evidence of fast surface diffusion.

**Tab. I** Average grain diameter of W- 1Ni, W- 1Co, W- 1Fe, W- 1Mo, W- 1Cu and Pure W sintered samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>W- 1 Ni</th>
<th>W- 1 Co</th>
<th>W- 1 Fe</th>
<th>W- 1 Mo</th>
<th>W- 1 Cu</th>
<th>Pure Tungsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Grain Diameter (µm)</td>
<td>35.40</td>
<td>29.34</td>
<td>18.69</td>
<td>23.82</td>
<td>16.65</td>
<td>27.52</td>
</tr>
</tbody>
</table>

Table I shows, the average grain diameter of W- 1Ni, W- 1Co, W- 1Fe, W- 1Mo, W- 1 Cu and Pure W SPS Samples. Neck formation has been observed between the grains of W- 1Co samples as shown in Fig. 3b and Fig. 4b. This has resulted in good densification of the sample after sintering. In W- 1Fe probably less melting of Fe took place and resulted in Solid phase sintering and consequently its microstructure distributes in homogeneously and hence resulted in less density and smaller grain size than W-1Ni and W-1Co. One more possible reason can be the less sintering time (1 min), due to which the particle didn’t get the sufficient time to diffusion with the particle in the vicinity. Fig. 3e and Fig. 4e shows the microstructure of W-1Cu, a large number of micropores has been observed. According to Wang et al. [14], in vacuum sintering, temperature enables easy volatilization of the binding phase, due to which very less density has been achieved in case of W-1Cu SPS sample. Fig. 3d, 3f and Fig. 4d, Fig. 4f compares the microstructure of rest of sintered sample i.e. W- 1Mo and pure tungsten respectively. Since the melting temperature of both Mo and W is very high (~2600°C and ~3422°C respectively), very less diffusion has been observed which has resulted in less densification in the both the sintered sample.
Fig. 3. Optical microscope images of the (a) W-1Ni, (b) W-1Co, (c) W-1Fe, (d) W-1Mo, (e) W-1Cu and (f) Pure Tungsten sintered samples.

Fig 4. SEM micrographs showing microstructure of (a) W-1Ni, (b) W-1Co, (c) W-1Fe, (d) W-1Mo, (e) W-1Cu and (f) Pure Tungsten.
3.3 Mechanical Properties

Fig. 5 shows the microhardness of the W-1Ni, W-1Co, W-1Fe, W-1Mo, W-1Cu and Pure W Sintered samples. Maximum hardness has been achieved in the W-1Fe SPS sample followed by W-1Co, W-1Ni and least in W-1Cu. Good densification in W-1Ni, W-1Co and W-1Fe may be the possible reason for higher hardness. In W-1Ni the hardness was found to be 302 HV which is slightly less than W-1Fe SPS sample (334 HV). In W-1Cu SPS sample, minimum hardness (171 HV) has been observed which may be due to the soft ductile phase of copper in the W-Cu solid solution. Presence of excessive porosity in the sample is also a reason for the less hardness value of W-1Mo, W-1Cu and Pure tungsten.

![Image of hardness graph]

**Fig. 5.** Hardness of W-1Ni, W-1Co, W-1Fe, W-1Mo, W-1Cu and Pure Tungsten.

4. Conclusion

In this work, characterisation of five different tungsten SPS samples doped with 1 wt% of Ni, Co, Fe, Mo and Cu with one pure tungsten sample was presented. Spark plasma sintering has showed a good technique for consolidating high temperature refractory metals in a short period of time. Doping of the different elements i.e. Ni, Co, Fe, Mo and Cu in tungsten with SPS has revealed that:

1. Maximum density has been achieved in tungsten with 1 wt%Ni, which also concludes that the Ni act as the best activator for Spark plasma sintering of tungsten.
2. Due to less sintering time (1 min), very less grain growth and coarsening have been observed. In case of W-1Ni and W-1Co sintering neck formation have been observed. The fine powder of Ni is located between the tungsten particles, which shows the sign of mass diffusion.
3. Due to densification maximum hardness has been observed in case of W-1Fe followed by W-1Ni and W-1Co. Since there was no activator present in the pure tungsten sample, very less hardness has been recorded due to porosity and less density.

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Садржај: У овом раду, окаквомисано је понашање тешких легура волфрама током синтеровања, коришћењем металургије праха кроз синтеровање плазме у варици. Фини прах волфрама (<30 µm) је одвојено мешан са Ni, Co, Fe, Mo и Сi, свакиса 1 wt.%. Техника синтеровања плазме у варици (SPS) (1200°C, 20 МPa притиска са 1 мин временом задржавања) је коришћена за синтеровање смесе прахова. Максимална густина је добијена у систему W-Ni, а потом у Co, Fe, Сi, Mo, са најмањом густињом добијеном у чистом волфраму. Оптичком микроскопом и CEM-ом је одређена микроструктура и раст кристалних зрна. Раст кристалних зрна је минималан због врло кратког времена загревања. Викерсовим тестом тврдоће је утврђено да синтетварани узорак W-Fe има највећу тврдоћу.
Кључне речи: тешке легуре волфрама, синтетовање плазме у варници, механичка својства, микроструктура.

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