Original Article

Fabrication of tungsten heavy alloy long rods by warm powder extrusion and vacuum sintering

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\section{ABSTRACT}

The long rods of tungsten heavy alloy (WHA) which contain W–5Ni–1.5Fe (wt.%) were fabricated by using warm powder extrusion. The elemental powders were first mixed, and then the mixture was prepared for warm back extrusion by adding a proper binder at 5–10 wt.% concentrations. The extrusion temperature was finely adjusted to facilitate the powder extrusion and eliminate cracks based on an extensive pre-study. Thermal debinding was also utilized prior to vacuum sintering. The results showed that the extruded rods with high length-to-diameter ratios could be obtained at the proposed binder content and extrusion temperature. The metallurgical and the mechanical characteristics of the extruded rods were evaluated and discussed with respect to the preparation route.

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\section{1. Introduction}

Tungsten heavy alloys have premium physical and mechanical properties. The current uses of WHAs are covering a huge scope of applications like aerospace counter weights, radioisotope storage/transport containers, collimators for radiation therapy, well logging tools, kinetic energy penetrators, etc. With the quick material improvement, tanks and heavily clad vehicles advancement, higher length-to-width proportion of tungsten alloys long rod penetrators are required [1,2].

Many reports have discussed the fabrication of WHA by traditional methods of powder metallurgy where mechanical alloying of elemental powders of W, Ni and Fe was used to produce tungsten heavy alloys by high energy ball milling in argon atmosphere [3,4]. Comparison in hardness, density, microstructure and mechanical properties between two different alloys of tungsten; W–Ni–Cu and W–Ni–Fe has also been made [5,6]. Moreover, the microstructures, physical and mechanical properties of WHAs sintered at various temperatures were investigated [7–9]. Also, the microstructures and mechanical properties of oxides dispersion WHAs were studied and were shown as a potential improvement [10,11].

Manufacturing of long rods has been the aim for many applications of WHAs (and other alloys), where such products geometries are difficult to be obtained by using conventional
PM compaction and sintering processes. Several technologies have been adjusted to form these types of products like cold isostatic pressing and hot extrusion. Hot extrusion has been previously used for processing light weight alloys. Examples include studies of the properties of rectangular bars produced by hot extrusion of magnesium alloy where compression samples were investigated and the texture evolution during the extrusion process was discussed [12,13]. Silver alloy and wood powders are also among materials manufactured by hot extrusion [14,15]. Cold extrusion and powder rolling were also used to manufacture long products by powder metallurgy [16].

Precipitation of extruded 95W–5(Ni/Fe/Co) alloy at 300–600 °C and its effect on high temperature plasticity were previously investigated [17]. The fabrication of the tungsten heavy alloys by hot-hydrostatic extrusion of a liquid-phase sintered 93W–4.9Ni–2.1Fe alloy was performed at 1200 °C with various extrusion ratios. Comparison between the sintered alloy and the extruded alloy presented a much higher mechanical strength, tensile strength of the extruded alloy [18]. Hydrostatic hot extrusion of tungsten heavy alloy has also been extensively investigated in numerous other research papers, and has proven to be one of the best candidates to manufacture WHAs with good physical and mechanical properties [19–24]. Conventional hot extrusion has also helped the realization of long rods of WHAs [25–27]. Besides, severe plastic deformation was a good solution to further improve the properties of WHAs [28,29]. Many papers also reported about powder injection molding to produce long rod with good properties, and developed wax-based binder for powder injection molding of WHAs, where the mechanical properties were shown to be better than or equivalent to those of the same alloy made by the conventional compaction and sintering [30–32].

Most of the previously discussed methods for producing long rods have shown promising results for long rods, but they all use quite expensive machinery. Powder warm extrusion is one more simple way which has also been previously utilized to manufacture alloys with high length-to-diameter ratios. Powders are usually prepared for extrusion by adding an appropriate amount of binder to convert the mixing powder to paste-like easily extrudable substance in warm temperature, and then are forced through the die. The warm extrusion process includes basically four steps: mixing, extrusion, debinding and sintering. Successful production of parts by extrusion is closely related to the binder system utilized and how successful the process of getting rid of it is. However, little information has been reported concerning the binder, especially for tungsten heavy alloy extrusion. The binder should have low viscosity at high temperature to mix with powder, and good low-temperature fluidity during extrusion. Debinding is usually achieved by slowly heating the green extrusions, causing the binder to decompose and vaporize, which is the thermal debinding. During debinding, the extruded rod should hold its shape, and the binder is totally removed without any deformation or crack. The debinding process is difficult because green extrusions have relatively large amount of mainly organic binder in the solid state, below its melting point [33].

The aim of the current work is the fabrication and characterization of tungsten heavy alloy long rods via warm extrusion and vacuum sintering at low cost with good properties. Due to the limitation in the number of research papers discussing warm powder extrusion, some process parameters of other methods were used as guide values. An example of that is the use of a binder the originally designed for injection molding.

2. Experimental procedures

Powders used in this study were brought from various companies with purity 99.9% so that their characteristics match. Tungsten powder with the average particle size of 2 μm was brought from Buffalo Tungsten INC, while both nickel and iron powders of 1 μm average particle size were brought from Jin Sheng International Industries LTD. Powder mixtures with the composition of 93.5W–5Ni–1.5Fe (wt.%) were mixed in a cylindrical container horizontal ball mill for 8 h to get homogeneous particle size distribution and particle size reduction to improve the material flow during extrusion. The container for mixing is made of H13-hardened tool steel, while the balls are made of stainless steel having 6 mm diameter. The ball to powder mass ratio was 10:1 and milling speed was 80 rpm. Then, the mixture was prepared for extrusion by adding an appropriate amount of binder. The binder used in this study consisted of 65% paraffin wax (PW), 15% vegetable oil, 15% low density polyethylene and 5% stearic acid. Addition of binder to powder with proportions 5, 7.5 and 10 wt.% was done at warm temperature of about 80 °C while continuously stirring [32]. These values of binder percentages were selected to minimize the voids while providing the fluidity and strength needed for the extruded rods. After that, the powder mixture with binder was warm-extruded, at about by indirect die extrusion at 70 °C to allow wax melting and ensure uniform distribution of binder. The use of binders with percentages below 5 wt.% lead to cracks in the extruded rods. The rods were extruded by using the die shown in Fig. 1. The die consists of four parts designed to perform indirect extrusion process so that the internal diameter of the cylindrical container is 18 mm, and the diameter of the extruded rod is 6 mm (i.e. using the extrusion ratio of 9:1).

The extruded rods are shown in Fig. 2. The main factor in extruding a long rod is maintaining the degree of cohesion of the powder mixture and binder. By increasing the extrusion
Metallurgical investigation was then performed on the sintered specimens by examining the polished surfaces of specimens after grinding (with emery papers till 4000 grit) and polishing using 0.25 micron diamond paste. The microstructure of the extruded rods of WHAs was observed by scanning electron microscopy (model JEOL-JSN-5410). The phase identification of the investigated WHAs was performed using XRD (model X, Pert PRO analytical with Cu ka2α radiation, λ = 0.15406). The volume fractions of voids in sintered samples have been estimated using image analysis Zeiss Axio Vision SE 64 software release 4.9 (11-2012). The density of the sintered materials was measured by Archimedes principle using water as the floating liquid. The sintered rods were then machined to get cylindrical test specimens with 5 mm diameter and 10 mm length to be tested for compressive strength by Uniaxial compression tester using the cross head speed of 5 mm/min. The macro hardness of extruded rods of WHAs was evaluated as the average of five readings along the cross-section surface of the specimens using Vickers hardness tester (model Indentec 5030 SKG) at a load of 30 kg for 15 s.

3. Results and discussions

The warm powder extrusion process of tungsten alloys containing 5, 7.5, and 10 wt.% binder resulted in the microstructures shown in the SEM images in Fig. 4a–c, respectively. All images in the figure show the homogenous distribution of grain size all over the specimen surface. It can also be shown that the percentage of the voids and their size has been increased as the binder content increased. The lack of clustered voids has proven the success of the powder mixing, binder addition, powder extrusion and debinding operations to homogenize the material. The above findings conform well to the results of the estimated volume fractions of voids in Fig. 5. The void volume fraction increases consistently with increasing the binder content. Converting the original binder weight fractions of 5, 7.5 and 10 wt.% into volume fractions using both the alloy and binder densities gives the values of 48.7, 59.3, and 66.7 vol.%, respectively. These high values represent the density of the as-extruded alloy rods, which during sintering undergo shrinkage (due to particle re-orientation and bonding) which reduces the eventual void fraction to those shown in Fig. 5 which are comparable to values of the original binder contents.

The optical microstructure of the sintered extruded rods of the tungsten alloy of 5, 7.5, and 10 wt.% binder content samples are shown in Fig. 6a–c, respectively. All samples have shown the homogenous distribution of the matrix phase (white areas) consisting of iron and nickel within a network of the W phase (light gray areas), while black areas denote the voids. The matrix phase consists mainly of iron and nickel. It is worth mentioning that the size of the voids can be clearly observed increasing with the higher binder content, a similar observation to that of Fig. 4, while the size of the matrix phase has almost remained unchanged. All samples have been analyzed by using EDS analysis, and Fig. 7 shows an example of that of 5 wt.% binder specimen. The W-rich phase has shown the average of 97, 98, and 98 wt.% of tungsten for 5, 7.5, and 10 wt.% binder specimens, respectively. On the other hand, the
Fig. 4 – SEM micrograph of W–5Ni–1.5Fe (wt.% alloy at binder contents (a) 5 wt.%, (b) 7.5 wt.%, and (c) 10 wt.%.

Fig. 5 – The void volume fraction at various binder contents.

Fig. 6 – Optical microscope of W–5Ni–1.5Fe (wt.%) alloy at binder contents (a) 5 wt.%, (b) 7.5 wt.%, and (c) 10 wt.%

Fig. 7 – EDS analysis results of 5 wt.% binder content specimen.

matrix phase has shown less amount of nickel and iron than the original compositions due to the diffusion of W and also because a considerable amount of the iron and nickel additions has been consumed in the formation of the inter-metallic compound.

XRD pattern has revealed the presence of elemental tungsten as well as the formation of some inter-metallic compounds for Fe–W, Fe–Ni, and Ni–W combinations, as shown in Fig. 8. Those inter-metallic compounds has been formed at the sintering stage due to the diffusion that usually occurs
between neighboring powder particles, which improves the sinterability and the final sample integrity. The diffusion is also evident from the EDS analysis results shown in Fig. 7 where the Fe–Ni matrix phase shows some W content and the W phase shows some Fe and Ni content.

Sintered densities were measured by Archimedes method, and the results have shown that the specimen with the least binder content has the highest relative density of 94.2%, as shown in Fig. 9. Moreover, the specimens with binder content 7.5 and 10 have shown relative densities of 91%, and 74%, respectively. Those values show that the debinding process has enabled the specimen to get rid of the binder prior to sintering. They also show that the sintering process could integrate powder particles successfully, as the values of the relative density are comparable to those previously reported using traditional techniques [3–5].

The Vickers hardness values of the sintered specimens are shown in Fig. 10. The hardness values of samples given in the figure are the average of five readings. It can be seen that the hardness of 5% binder has the highest value among the three specimens, about 315 HV. Increasing the binder content to 7.5 and 10 wt.% has resulted in the decrease in hardness value, as a direct result of the higher void content.

The compressive strength was determined using cylindrical samples with a diameter 5 mm and length 10 mm and the results for the extruded rods of WHAs are shown in Fig. 11. The compressive strength of 5% sample has the highest value. By increasing the binder content, the compressive strength has fallen to lower levels while the fracture strain has slightly increased. The increase in fracture strain was also accompanied by a decrease in the elastic modulus. This conforms well to the results of hardness, relative density and the microstructure, where the main reason for decreasing all the results is the percentage of voids at higher binder level which degrades the material. The above results of hardness and compressive strength show that the proposed process of warm extrusion and vacuum sintering can give comparable results as previously reported [3–5,11].

The observation of the fracture surfaces of compression test specimens have shown the clear effects of voids on the fracture of the test specimens, as shown in Fig. 12. The size of voids has tremendously increased by increasing the binder content from 5 to 10 wt.%, which eventually resulted in the formation of micro-cracks which have connected the voids together into a macro-cracks constituting the final fracture surface. On the other hand, there are no signs of primary powder particle separation which shows that processing the alloy (specially in the case of 5 wt. % binder) could lead to successful manufacturing of the alloy.
4. Conclusions

The powder extrusion process has been applied to the tungsten heavy alloy W–5%Ni–1.5%Fe to manufacture long rods which are extremely difficult by other techniques, except with expensive machineries. By warm extrusion, the powder could be formed into long rods with diameter of 6 mm and the length could reach 150 mm. The removal of the 5, 7.5, and 10 wt.% binder contents have been the important task, which could be performed using thermal debinding on a sand bed to enhance the binder removal by the capillary action. The process lasted for a long time (about 336 h) till all the binder is removed without distortion. The microstructure, density, and mechanical properties of the sintered extruded rods suggest that the powder warm extrusion process can be a very successful candidate to manufacture long rods of tungsten heavy alloys. Although this task could be previously done by other techniques, the proposed warm powder extrusion process provides simpler way for realizing long rods of WHA. Moreover, the binder contents used in this study are much lower than those previously used for the other techniques, which also adds another merit of using the proposed technique. The lower the binder content, the better the density and consequently the better the mechanical properties will be.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


