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Microwave and conventional sintering of 90W–7Ni–3Cu alloys with premixed and prealloyed binder phase

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ABSTRACT

The present study investigates the possibility of consolidating premixed 90W–7Ni–3Cu alloy – designated as 90W–PM (Ni–Cu) – through microwave sintering. An attempt has been made to compare the results between microwave and conventionally sintered samples. This study also compares the sintering behavior of 90W–7Ni–3Cu with prealloyed 90W–PA (Ni–Cu) in both conventional as well as microwave furnace at various temperatures. The comparative analysis is based on the sintered density, densification parameter, hardness and microstructures of the samples. The present investigation also includes the variation of matrix composition as a function of temperature by EPMA analysis. The results show that microwave sintering requires about 75% less processing time than required by conventional method and still provides better physical and mechanical properties.

1. Introduction

Tungsten heavy alloy (WHA) is a group of two-phase composites, based on W–Ni–Cu and W–Ni–Fe alloys. Tungsten–nickel–copper alloys are widely used for ordinance application, electrical contacts of switches, radiation shielding, mass balances, etc. In general the tungsten heavy alloys have been processed through powder metallurgy route since 1930s [1]. These heavy alloys contain mainly pure tungsten as principal phase in association with a binder phase containing transition metals (Ni, Fe, Cu, Co) [2]. In W–Ni–Cu alloys, normally the nickel-to-copper ratio ranges from 3:2 to 4:1. Price et al. [3] were the first to propose Ni–Cu as the binder for tungsten heavy alloys. Over the last several years, these alloys have been extensively investigated for densification mechanism, microstructural evolution and properties [4–7].

The effect of tungsten and copper powder size variation on the sintered properties of W–Ni–Cu heavy alloys was carried out by Srikanth and Upadhyaya [8,9]. The effect of composition and sintering temperature on the densification and microstructure of W–Ni–Cu heavy alloys was studied by Ramakrishnan and Upadhyaya [10]. Kuzmic [11] proposed that rapid cooling from the sintering temperature prevents the formation of brittle phase in order to obtain good mechanical properties. Ariel et al. [12] correlated the mechanical properties of W–Ni–Cu system with sintered microstructure. Their study showed that the mechanical properties are a function of mean free path between tungsten grains, volume fraction of tungsten grains and the contiguity of tungsten spheroids.

The solubility of tungsten in the liquid binder plays a dominant role in determining the mechanical properties of the sintered W–Ni–Cu alloys. The solubility of tungsten in copper is negligible. Even at temperatures as high as 1350 °C only 0.04 at.% of tungsten goes in solution with copper [13]. In contrast, tungsten exhibits appreciable solubility (up to 40 wt.%) in nickel. It is therefore possible to tailor the tungsten solubility, wetting and the dihedral angle and thereby, the accompanying sintering response and properties of the system by varying the Ni:Cu ratio [10,14]. Nowadays, W–Ni–Cu alloys are also being consolidated by employing prealloyed powders [15]. Use of prealloyed powder improves homogeneity. The homogenization process accelerates sintering and promotes densification. The alloy formation during sintering decreases the material viscosity and, hence, stimulates material flow under the action of capillary forces [16].

Despite widespread application, difficulties still exist in the manufacture of liquid phase sintered tungsten heavy alloys. In order to avoid thermal shock, processing of tungsten heavy alloys in conventional furnace involves heating at a slower rate (<10 °C/min) and with isothermal holds at intermittent temperatures. This not only increases the process time, but also results in significant microstructural coarsening during sintering, leading to the degradation of mechanical properties. This problem is further aggravated when the initial powder size is extremely fine. Hence, it is envis-

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Table 1
Powder characteristics of as-received elemental W, Ni, Cu and prealloyed Ni–Cu powder.

Property	W	Ni	Cu	69Ni–31Cu
Supplier	Widia	Inco	A Cu Powder International, LLC	Ametek
Processing technique	Chemical reduction	Carbonyl process	Gas atomization	Gas atomization
Powder shape	Irregular	Spiky	Spherical	Spherical
Powder size (μm)				
D_{10}	2.0	3.8	19.4	8.2
D_{50}	4.2	11.0	47.0	17.3
D_{90}	6.2	31.8	96.3	40.4

aged that a fast heating rate would mitigate this problem. One of the techniques to achieve fast and relatively uniform sintering is through microwaves [17]. The W–Ni–Cu alloys are usually prepared by mixing the constituent powders. One of the challenges in the processing of these alloys is to ensure homogenous melt distribution [15]. Nickel and copper are known to interdiffuse at temperatures higher than 900 °C. However, in case of rapid sintering in microwave this may not be readily feasible.

Microwave heating is much more uniform at a rapid rate resulting in reduction of processing time and energy consumption. Also rapid heating leads to finer microstructure enhancing the mechanical properties. Clark and Sutton [18] cited many other benefits of the process such as precise and controlled heating, environmentally friendly etc. Microwave heating is a very sensitive function of the material being processed and depends on several factors, such as sample size, as-pressed density, its mass and geometry [19,20]. Though there have been attempts to explain microwave heating of metal powders, still there is not yet any consensus on a comprehensive theory to explain the mechanism [21].

Applicability of microwave sintering to metals was ignored due to the fact that they reflect microwaves. Roy et al. [22] reported that particulate metals can be heated rapidly in microwaves. This has led to the use of microwaves to consolidate a range of particulate metals and alloys [23–25]. While researchers have reported microstructural refinement due to rapid heating in microwaves, the effect of microwave sintering on the microstructural homogeneity and mechanical properties seem to be system specific [23–25]. Researchers have also attempted to consolidate refractory materials such as pure W, W–Cu, W–Ni–Fe and W–Ni–Cu [26–33] using microwave energy and reported significant reduction in process time, elimination of brittle intermetallic formation and superior mechanical properties.

This paper reports the sintering behavior of premixed and prealloyed 90W–7Ni–3Cu powders in both, microwave as well as in a conventional (radiatively heated) furnace. The comparative analysis is based on the sintered density, densification parameter, hardness and microstructures of the samples.

2. Experimental procedure

The as-received powders were characterized for their size, size distribution and morphology. Table 1 summarizes the characteristics of the as-received elemental W, Ni, Cu and prealloyed Ni–Cu powder used for this study. For investigating the densification response and compaction studies of various compositions, cylindrical pellets (diameter: 16 mm and height 8 mm) were pressed at 200 MPa using a uniaxial semi-automatic hydraulic press (model: CTM 50, supplier: FIE, India) of 50 T capacity. To facilitate compaction and subsequent removal of compacted samples, zinc-stearate powder was applied as die-wall lubricant. The as-pressed green compact density varied from 56% to 58% of the theoretical density of the alloy, where the theoretical density was calculated using the inverse rule of mixtures.

To study the densification behavior; the green (as-pressed) compacts were sintered using conventional and microwave furnace. The experimental details have been mentioned elsewhere [32].

The sintered density was obtained by both dimensional measurements as well as Archimedes' density measurement technique. To compare the densification response of various compositions, the sintered densities were normalized with respect to the theoretical density. To take into account the influence of the initial as-pressed density, the compact sinterability was also expressed in terms of densification parameter which is calculated as follows:

$$\text{densification parameter} = \frac{\text{sintered density} - \text{green density}}{\text{theoretical density} - \text{green density}} \quad (1)$$

An Anter 1161 V vertical dilatometer was used for measuring axial shrinkage and shrinkage rate during sintering with constant heating rate of premixed and prealloyed 90W–7Ni–3Cu compacts. It measures dimensional changes over the entire sintering cycle with precision of 1 μm. The dilatometery studies were performed at constant heating and cooling rate of 10 °C/min. The sintered samples were wet polished in a manual polisher (model: Lunn Major, supplier: Struers, Denmark) using a series of 6 μm, 3 μm and 1 μm diamond paste, followed by cloth polishing using a 0.04 μm colloidal SiO_2 suspension. The scanning electron micrographs of as-polished samples were obtained by a scanning electron microscope (model: FEI quanta, Netherlands) in the secondary electron (SE) mode. A quantitative analysis was also carried out on selected specimens using EPMA equipment (model: JXA-8600 SX Super-Probe, supplier: JEOL, Japan). Phase determination and phase evolution, if any were studied for all the samples using an X-ray Diffractometer (model: Rich. Seifert & Co., GmbH & Co., KG, Germany).

Bulk hardness measurements were performed on polished surfaces of sintered cylindrical compacts at a load of 5 kg using Vickers hardness tester (model: V100-C1, supplier: Leco, Japan). The load was applied for 30 s. Micro hardness tester (model: 8299, supplier: Leitz, Germany) was used to evaluate the hardness of the matrix phase. The load applied on matrix phase during the micro hardness measurement was 15 g. The bulk hardness of the compact and the micro hardness of the matrix phase for each sample were an average of 5 readings taken at different locations on respective phases. Transverse rupture strength (TRS) measurements of premixed and prealloyed samples were performed following the procedure described in MPIF Standard 41 [34].

3. Results and discussion

3.1. Heating response and densification of W–Ni–Cu alloy

Fig. 1 compares the thermal profiles of 90W–7Ni–3Cu compacts (prepared using premixed and prealloyed Ni–Cu binder) in a conventional and microwave furnace. It is evident from the figure that W–Ni–Cu alloys couple with microwaves and undergo rapid heating. In case of conventional furnace, in order to ensure uniform heating, the compacts heating rate was restricted to 5 °C/min and isothermal holds were provided at intermittent temperatures. In