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

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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.

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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-
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–C, 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 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:

$$\text{densification parameter} = \frac{\text{sintered density} - \text{green density}}{\text{theoretical density} - \text{green density}}$$  \hspace{1cm} (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 dilatometry 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 SiO₂ 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: Leico, 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
Fig. 1. Thermal profiles of 90W–7Ni–3Cu alloys heated up to 1450 °C in conventional and microwave furnace. The heating profile of W–Ni–Fe alloys prepared using premixed and prealloyed Ni–Cu binder is shown separately in case of microwave processing.

In contrast, the overall heating rate achieved in the microwave furnace was 22 °C/min. Taking into consideration the slow heating rate and isothermal holds associated with conventional sintering, the compacts were consolidated through microwaves with significant (~75%) reduction in the processing time. Figs. 2 and 3 show the photograph of the 90W–7Ni–3Cu alloys sintered in the temperature range of 1200–1450 °C in conventional and microwave furnace, respectively. Note that irrespective of the heating mode and the binder chemistry, none of the 90W–7Ni–3Cu compacts distorted or developed any cracks during sintering even up to temperatures as high as 1450 °C. It is interesting to note that despite a fast heating rate, no macro cracking was observed in any of the microwave sintered samples. This is attributed to the volumetric heating of the compacts, a unique feature of microwave heating. From the microwave heating profile (Fig. 1), it is interesting to note that alloys with premixed Ni–Cu binder heat at slightly faster rate than those containing prealloyed matrix. Elsewhere, Sethi et al. [23] and Upadhyaya and Sethi [35] too have reported similar heating response of the premixed and prealloyed Cu–12Sn bronze in microwave furnace. It can therefore be inferred that the chemical state of the alloying constituents influences the microwave coupling and the resultant heating. It is well recognized that microwave heating is material dependent. Peelamedu et al. [36] and Roy et al. [37] demonstrated in multi-phase systems, the phases heat up at different rates and lead to local an isothermal heating effect. Through model experiments in systems, such as Y2O3–Fe3O4, BaCO3–Fe3O4, and NiO–Al2O3, Peelamedu et al. [36] demonstrated that the hotter

Fig. 2. Photograph of 90W–7Ni–3Cu compacts conventionally sintered at various temperatures ranging from 1200 °C to 1450 °C.

Fig. 3. Photograph of the 90W–7Ni–3Cu compacts prepared using (a) prealloyed and (b) premixed Ni–Cu binder and sintered in a microwave furnace at various temperatures.

Fig. 4. Effect of binder state (premixed vs. prealloyed), heating mode and sintering temperature on the (a) sintered density and (b) densification parameter of 90W–7Ni–3Cu alloys. For the sake of comparison, the density and densification parameter data points (denoted by symbol ♦) for the same composition (in premixed state) sintered at 1300 °C and 1400 °C are also superimposed.
Composition as a function of temperature and heating mode of the matrix phase of liquid phase sintered 90W–7Ni–3Cu alloys prepared by (a) premixed and (b) prealloyed powders.

Table 2
Composition as a function of temperature and heating mode of the matrix phase of liquid phase sintered 90W–7Ni–3Cu alloys prepared by (a) premixed and (b) prealloyed powders.

(a) Premixed powders

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heating mode</th>
<th>Elemental content (wt.%)</th>
<th>W</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>Conventional</td>
<td>19.13 ± 1.93</td>
<td>53.15 ± 2.71</td>
<td>25.69 ± 0.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>18.43 ± 0.37</td>
<td>55.03 ± 0.85</td>
<td>24.18 ± 0.61</td>
<td></td>
</tr>
<tr>
<td>1250</td>
<td>Conventional</td>
<td>20.41 ± 0.72</td>
<td>56.16 ± 0.89</td>
<td>20.77 ± 0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>Conventional</td>
<td>18.66 ± 0.42</td>
<td>56.04 ± 0.68</td>
<td>23.98 ± 0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>24.29 ± 4.65</td>
<td>54.01 ± 1.84</td>
<td>18.37 ± 5.72</td>
<td></td>
</tr>
<tr>
<td>1450</td>
<td>Conventional</td>
<td>22.06 ± 4.66</td>
<td>57.03 ± 1.02</td>
<td>20.27 ± 5.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>23.57 ± 3.37</td>
<td>59.36 ± 0.35</td>
<td>14.41 ± 3.09</td>
<td></td>
</tr>
</tbody>
</table>

(b) Prealloyed powders

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heating mode</th>
<th>Elemental content (wt.%)</th>
<th>W</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>Conventional</td>
<td>29.25 ± 0.73</td>
<td>53.62 ± 1.00</td>
<td>15.59 ± 0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>27.26 ± 0.96</td>
<td>54.42 ± 0.65</td>
<td>15.20 ± 0.40</td>
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</tr>
<tr>
<td>1250</td>
<td>Conventional</td>
<td>25.12 ± 0.57</td>
<td>55.68 ± 0.78</td>
<td>16.32 ± 0.55</td>
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</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>Conventional</td>
<td>26.37 ± 0.38</td>
<td>56.36 ± 0.39</td>
<td>15.36 ± 0.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>28.73 ± 4.80</td>
<td>50.34 ± 6.99</td>
<td>17.08 ± 10.63</td>
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</tr>
<tr>
<td>1450</td>
<td>Conventional</td>
<td>23.25 ± 7.56</td>
<td>56.96 ± 2.3</td>
<td>18.80 ± 5.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave</td>
<td>19.34 ± 3.09</td>
<td>57.97 ± 2.71</td>
<td>20.62 ± 5.80</td>
<td></td>
</tr>
</tbody>
</table>

species diffuse rapidly into the relatively colder ones and correlated it with the very rapid diffusion rates observed in microwave processed compacts. It is likely that a similar mechanism is also active in the W heavy alloys system as well. The presence of such effect will result in densification enhancement in the microwave sintered components.

To test the above hypothesis, the densification responses of the compacts consolidated at various temperatures was evaluated for both the heating modes and is summarized in Fig. 4a and b. From Fig. 4a, it is evident that the density of the compacts increases with increasing sintering temperature. Since the green density of all the compacts were the same, the densification parameter results (Fig. 4b) closely follow the same trend as sintered density. Note that with the exception of 1200 °C, for all other sintering temperatures, microwave sintering results in better densification.

3.2. Dilatometric evaluation of 90W–7Ni–3Cu alloy

For better understanding the phenomenology of the densification of the W–Ni–Cu compacts the dimensional changes were measured in situ during sintering using dilatometry. However, owing to the instrument’s limitations, dilatometric evaluation could be performed through conventional heating mode only. Fig. 5a and b plots the dilatometric data of shrinkage and shrinkage rate vs. temperature for the as-pressed 90W–7Ni–3Cu compacts prepared using premixed and prealloyed binder. From the figures, it is evident that both compacts undergo gradual densification during heating till 1280 °C. Subsequent heating beyond 1280 °C results in sudden increase in the axial shrinkage and shrinkage rate.
This spurt in the densification is attributed to the onset of binder melting which results in densification through capillary-induced rearrangement and solution-reprecipitation. The rapid shrinkage resulting from liquid phase sintering sustains until 1400 °C wherein nearly full densification (98%) was achieved. Elsewhere, Wu et al. [44] and Martin et al. [15] too have reported similar dilatometric curves for 80W–14Ni–6Cu alloys and prealloyed 90W–6.9Ni–3.1Fe, respectively. For the range of compositions used, both researchers [15,44] have demonstrated that the onset of melt formation in the W–Ni–Cu system with Ni and Cu in the ratio 7:3 occurs at 1282 °C. From the binary phase diagram [45] and the experiments [44] the solidus and the liquidus temperatures of the 70Ni–30Cu matrix was determined to be 1345 °C and 1380 °C, respectively. However, in case of ternary W–Ni–Cu system, due to substantial solubility of the tungsten in the matrix the solidus and liquidus temperatures are lowered [42].

From the dilatometric results (Fig. 5a and b), it can be discerned that the 90W–PA (Ni–Cu) alloy exhibits slightly higher densification particularly at lower temperatures as compared to the 90W–PM (Ni–Cu) compact. This trend is similar to that reported by Huang et al. [46] who investigated the influence of prealloyed Ni–Fe–Mo binder on the sintering behavior of tungsten heavy alloys. They [46] noted that prealloying results in a more homogenous microstructure and lowers the interfacial energy of the tungsten (solid)–matrix (liquid) phase providing a higher density compact. The analyses of matrix composition of the W–Ni–Cu compacts in the present study (Table 2a and b) – particularly, the ones sintered at 1200 °C – are in accordance with this hypothesis. At 1200 °C, the dissolved tungsten amount in 90W–PM (Ni–Cu) is lower than its prealloyed counterpart. Consequently, the latter exhibits higher densification (Fig. 4b). For compacts heated or sintered at higher temperatures, the densification in both the compacts is not too different and is attributed to homogenization of the premixed matrix through interdiffusion. It is well known that Cu and Ni have mutual intersolubility [45]. Using X-ray analysis, Heckel et al. [47] have experimentally shown that significant interdiffusion and homogenization through in situ alloying occurs in the Ni–52 at.% Cu compact after sintering at 950 °C for 1 h. Since the Cu:Ni ratio in the present system (90W–7Ni–3Cu) is much lower, hence, it is quite reasonable to assume that the premixed Ni–Cu powders will get completely homogenized during conventional sintering.

3.3. Microstructural evolution and properties

Fig. 6a and b compares the effect of heating mode and sintering temperature on the phase evolution in 90W–PM
(Ni–Cu) and 90W–PA (Ni–Cu) alloys, respectively. For all XRD experiments, the sample size and other test parameters were kept constant. It is therefore rather surprising to note that in case of microwave sintered compacts some of the peaks do not even register on the diffractogram. Similar observations have also been reported by Padmavathi [48] in case of microwave sintering of various aluminium alloys.

The reduction in the intensity indicates that the microwave sintered compacts have less perfect crystals and contain more defects as compared to their conventionally sintered counterparts. Recently, many researchers, [37,49–51] have reported that

Fig. 7. SEM micrographs of 90W–7Ni–3Cu alloys prepared using prealloyed Ni–Cu binder and consolidated in a microwave furnace at (a) 1200 °C, (b) 1250 °C, (c) 1300 °C and (d) 1450 °C, respectively.

Fig. 8. SEM micrographs of (a) premixed and (b) prealloyed 90W–7Ni–3Cu alloys sintered at 1300 °C in conventional (left) and microwave (right) furnace.
exposure to microwave heating leads to decrystallization and sometimes even amorphization in some of the ceramic and semiconducting systems. The defects within a crystalline structure are known to activate sintering [52]. Hence, it may be possible that in the present system too the defects generated on exposure to microwaves contribute to densification enhancement.

The phenomenology of microstructural evolution in conventionally sintered W–Ni–Cu alloys has been extensively investigated by several researchers [3,10,15,40]. In the present study, the attention was focused on the microstructural response of microwave sintered W–Ni–Cu system and its comparison with that obtained through conventional sintering. Fig. 7a–d shows the effect of sintering temperature on the representative microstructure of 90W–PA (Ni–Cu) alloy consolidated in a 2.45 GHz multimode microwave furnace. It is quite evident that higher temperature not only results in pore elimination but is also accompanied by redistribution of the matrix and coarsening of tungsten grains. It is worth noting that the microstructure of the compacts sintered in solid-state (1200°C and 1250°C) is drastically different from the liquid phase sintered counterparts (Fig. 7c and d). In case of compacts sintered at 1200°C, the binder phase is inhomogeneously distributed (Fig. 7a) and the tungsten grains are faceted. In contrast, at 1250°C (Fig. 7b), while the W-grains still remain faceted, the binder is more uniformly distributed. The well rounded and coarser grains associated with liquid phase sintering (Fig. 7c and d) are associated with higher solid-solubility (Table 2) and relatively faster solution-reprecipitation kinetics.

Fig. 8a and b compares the effect of heating mode on the microstructures of the 90W–PM (Ni–Cu) and 90W–PA (Ni–Cu) alloys, respectively, sintered at 1300°C. The corresponding microstructures of compacts liquid phase sintered at 1450°C are shown in Fig. 9a and b. From Figs. 8 and 9, it can be discerned that irrespective of the sintering temperature and the heating mode, the prealloyed sintered compacts have slightly higher coarsening than their premixed counterparts. This can be attributed to a more homogenous microstructure and better spreading of the melt due to the relatively lower tungsten (solid)–matrix (liquid) interfacial energy in case of alloys prepared using prealloyed binder [46]. More recently, Martin et al. [15] showed that the Ni–Cu additive phase in 90W–6.9Ni–3.1Cu alloy with prealloyed matrix is more effectively distributed within the tungsten grains during sintering and contributes not only to densification but also leads to enhanced tungsten grain coarsening as compared to premixed alloys.

One of the intriguing observations in the present study is the dramatic difference between the microstructure of W–Ni–Cu compacts sintered in conventional and microwave furnace (Fig. 8a and b). In case of conventionally sintered compacts, the microstructure at 1300°C is quite similar to that obtained through solid-state sintering. Some of the earlier researchers [10,53,54] too have reported similar findings at this temperature for premixed 90W–7Ni–3Cu compacts. The larger tungsten grain size in microwave sintered W–Ni–Cu compacts at 1300°C is contrary to the observations in various systems that a fast heating rate will result in lower grain size [30,55,56]. However, similar contrary results have recently been reported by Zaspalis et al. [57] in microwave sintered Mn–Zn ferrites and by Kim et al. [58] in spark plasma sintered alumina. The exact explanation of such observations is still lacking and further detailed experiments need to be carried out in future to elucidate this better. In contrast to 1300°C sintered compacts, both conventional as well as microwave sintered 90W–7Ni–3Cu alloys (at 1450°C) exhibit well-defined liquid phase sintered microstructure with rounded tungsten grains interspersed in the Ni–Cu matrix (Fig. 9a and b). Table 3 summarizes the effect of heating mode on the average tungsten grain size in premixed and prealloyed 90W–7Ni–3Cu alloys liquid phase sintered at 1450°C. From Fig. 9 and Table 3, it can be inferred that irrespective of the state of ini-
of 90W–7Ni–3Cu alloys prepared using premixed and prealloyed Ni–Cu binder and sintered at 1450 °C.

Table 3
Effect of heating mode on the average tungsten grain size in 90W–7Ni–3Cu alloys prepared using premixed and prealloyed Ni–Cu binder and sintered at 1450 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Heating mode</th>
<th>W grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90W–PM (Ni–Cu)</td>
<td>Conventional</td>
<td>23 ± 10</td>
</tr>
<tr>
<td>90W–PA (Ni–Cu)</td>
<td>Microwave</td>
<td>21 ± 7</td>
</tr>
</tbody>
</table>

Effect of heating mode on the bulk hardness (in kgf/mm²) of 90W–7Ni–3Cu alloys prepared using premixed and prealloyed binder.

Table 4

<table>
<thead>
<tr>
<th>Heating mode</th>
<th>90W–PM (7Ni–3Cu)</th>
<th>90W–PA (7Ni–3Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300 °C</td>
<td>276 ± 21</td>
<td>290 ± 19</td>
</tr>
<tr>
<td>1450 °C</td>
<td>301 ± 16</td>
<td>330 ± 13</td>
</tr>
</tbody>
</table>

As a note of comparison in one of the previous reports [10] the bulk hardness of the same composition has been listed as 175 VHN and 220 VHN for compacts sintered at 1300 °C and 1400 °C, respectively.

Fig. 10 shows the effect of heating mode and powder chemistry on the transverse rupture strength of the 90W–7Ni–3Cu alloy sintered at 1300 °C and 1450 °C. One of the very interesting observations is that microwave sintered compacts have higher transverse rupture strength as compared to those sintered conventionally. The enhancement of strength is as high as up to threefold (~211%) in case of alloys processed at 1300 °C. This can be correlated to a less contiguous microstructure consisting of rounded tungsten grains that result in alloys microwave sintered at 1300 °C (Fig. 8). Elsewhere, Chermant and Osterstock [60] have demonstrated similar influence of microstructure on the fracture toughness of WC–Co system. The transverse rupture strength of the conventionally sintered 90W–PM (Ni–Cu) system is similar to that reported earlier by Kalina et al. [61]. Another observation that can be inferred from Fig. 10 is that the transverse rupture strength of alloys prepared with prealloyed Ni–Cu is marginally higher than those prepared using premixed binder. This could be due to better homogeneity of the alloying additives in case of the prealloyed system.

4. Conclusions

90W–7Ni–3Cu alloys, compacts were prepared using both premixed and prealloyed Ni–Cu binder and were sintered at temperatures ranging between 1200 °C and 1450 °C. As compared to conventional sintering, both premixed and prealloyed 90W–7Ni–3Cu alloys were microwave sintered in significantly (~75%) less time. In spite of higher heating rate in microwave sintering, no micro- or macro-cracking was observed in all microwave sintered samples. Dilatometric analysis of the 90W–7Ni–3Cu alloy at slower heating rates (<10 °C/min) reveals that – unlike the W–Cu system – the W–Ni–Cu system exhibits significant solubility of tungsten in the matrix. Consequently, a major portion of the overall densification in this alloy occurs prior to melt formation. Due to the inter-diffusivity between nickel and copper, by the time the sintering temperature was attained, both Cu and Ni form a homogeneous solid solution. Hence, the sintering response of the 90W–7Ni–3Cu alloy was per se independent of the initial matrix type (premixed vs. prealloyed). An interesting finding in the present study was the observation of the heating mode effect on the microstructure of the compacts sintered at 1300 °C. While the conventionally processed alloy had a typical solid-state sintered structure, the microwave processed samples had a well-developed microstructure, typically associated with liquid phase sintering. Consequently, as compared
to conventional sintering, microwave sintering resulted in about 9% improvement in hardness (to ~350 VHN) and about threefold (~211%) enhancement in flexural strength to around 1625 MPa.

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