

Tungsten–copper composite production by activated sintering and infiltration

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ABSTRACT

Activated sintering of tungsten has been used to have infiltrable skeletons. For this purpose the effects of sintering temperature and activator amount were studied and appropriate production parameters were obtained. The results showed that by activated sintering, moderate sintering temperature such as 1400 °C can be used instead of conventional temperatures i.e. >2000 °C. Activated sintering has the ability to produce fully open and interconnected porosities with desirable density that is ideal for infiltration. This method of production for infiltrated W–Cu composites has not been reported elsewhere.

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1. Introduction

W–Cu composites combine high electrical and thermal conductivity of copper with refractoriness and high erosion resistance of tungsten. They have extensive electrical and thermal application such as ultrahigh-voltage electric contacts [1–3]. W–Cu composites with high tungsten content i.e. >60 wt.% are producible only by infiltration technique. This includes two steps; first preparation of tungsten porous skeleton by pressing and sintering of W powder; second infiltration of molten copper into skeleton [4]. A green compact of tungsten powder with average particle size of 6 μm needs a sintering temperature as high as 2150 °C to have sintering densification form 60% of theoretical density to 78% of that [5].

Small amounts of transition metals such as nickel can lower the activation energy of sintering, allowing a lower sintering temperature [6]. This process is called solid state activated sintering and accelerates tungsten diffusion through transformed disordered grain boundaries [7,8].

At high densities, Ni containing tungsten compacts undergo severe grain growth with a decrease in strength [6]. Because of low strength at high temperatures and brittleness, activated sintering is not usually used for pure tungsten bulk products [9].

In W–Cu composites, nickel addition improves the wetting and adhesion of copper and tungsten and facilitates nonporous composite production [10,11]. The effect of activated sintering on production of W–Cu composites and their properties has not investigated well. In this research, W–Cu composites were produced via activated sintering and different aspects of its effect were studied.

2. Experimental procedure

Tungsten powder with fisher subsieve size of 6 μm was used. Fig. 1 shows the polygonal primary tungsten particles. Nickel was added to W in amounts of 0.05, 0.25 and 0.5 wt.% as sintering activator. For this purpose, equivalent amount of nickel chloride (NiCl₂·6H₂O) was dissolved in methanol and was mixed with tungsten powders. The mixture was dried at 80 °C while mixing with a spoon continuously. The dried powder was heated at 650 °C for 30 min at hydrogen atmosphere for removing of Cl and H₂O through calcination and reduction of nickel oxide to metallic nickel. The obtained powders were compressed at 200 MPa via cold isostatic press. The green specimens were sintered at a temperature range from 1250 to 1550 °C for 4 h in high purity hydrogen atmosphere. Sintered skeletons with desirable density i.e. 78 ± 2% were infiltrated by molten electrical copper. Infiltration was carried out at 1300 °C in hydrogen atmosphere for 1 h.

Apparent densities of sintered specimens were measured by Archimedes water immersion method according to ASTM B328 standard. SEM and XRD were used for in detail studying of microstructure.

3. Results and discussion

Nickel particles in a green specimen are shown in Fig. 2. Since nickel as activator was added by soluble salt, its particles mostly have small size and uniform distribution. However, because of manual process, inhomogeneities are unavoidable. Fig. 2a illustrates submicron well distributed Ni particles but Fig. 2b shows a relatively big cluster of nickel particles.

Throughout heating up, nickel segregates to grain boundaries and surfaces [7,12,13]. Nickel leads to tungsten surface transformation from faceted to round morphology. That takes place above 1100 °C and as it is shown in Fig. 3, it is not associated with considerable densification.

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Fig. 1. SE-SEM micrograph of primary tungsten powder.

Extra activator that had not been spent for high diffusivity layer formation appeared as nickel-rich phases. As it is shown in Fig. 4, below eutectic temperature, these phases were isolated particles but at melt formation temperatures, nickel-rich phase has wetted all triple grain boundaries and also accelerated sintering densification.

Relative density of sintered W specimens vs. activator amount and temperature are illustrated in Figs. 5 and 6 respectively. Apart from 1550 °C, all sintering temperatures are below eutectic temperature (1495 °C [14]). Therefore at temperatures of 1250–1450 °C solid state activated sintering takes place but at 1550 °C Ni-rich liquid phase can appear.

Little amounts of nickel such as 0.01 wt.% cannot enhance densification and is not enough to provide interconnected high diffusivity path but it seems that 0.05 wt.% Ni can supply enough activator. As it is shown in Fig. 5, the best densifications for solid state activated sintering were obtained at 0.25 wt. % Ni. Further nickel addition has minor negative effect. During the heating up, each Ni particle diffuses into grain boundaries and on surfaces. Therefore

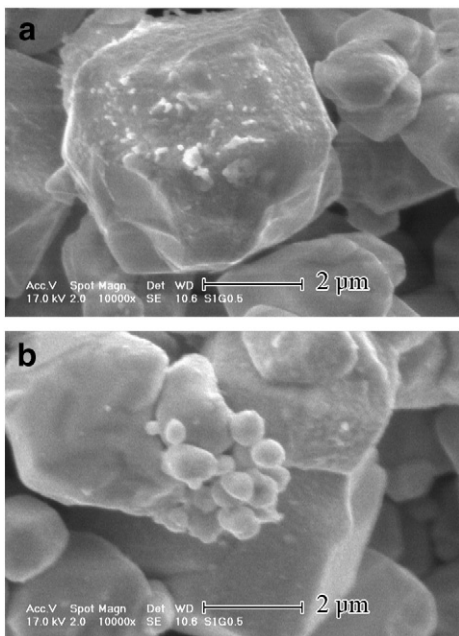


Fig. 2. Ni particles on a W particle after calcination and reduction of soluble salt; a) submicron Ni particles, b) a Ni cluster.

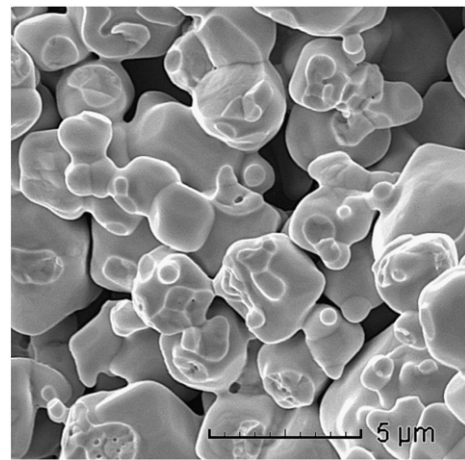


Fig. 3. SE-SEM micrograph of fracture surface of Ni-doped W after sintering at 1150 °C for 1 h shows surface roughening.

adjacent W particles lose one neighbor and a relatively big pore appears. During the sintering big pores enlarge and small pores shrink due to coarsening and densification respectively [6]. Coarsening processes also consume the surface energy that is responsible for densification, but do not reduce pore space [6]. As nickel exceeds over optimum amount, concentration of Ni-induced pores increases and reduced the densification capacity. To have same final density, specimens with 0.5 wt.% Ni must be sintered at a higher temperature. Enlarged pores come out as tungsten-free copper pools in infiltrated

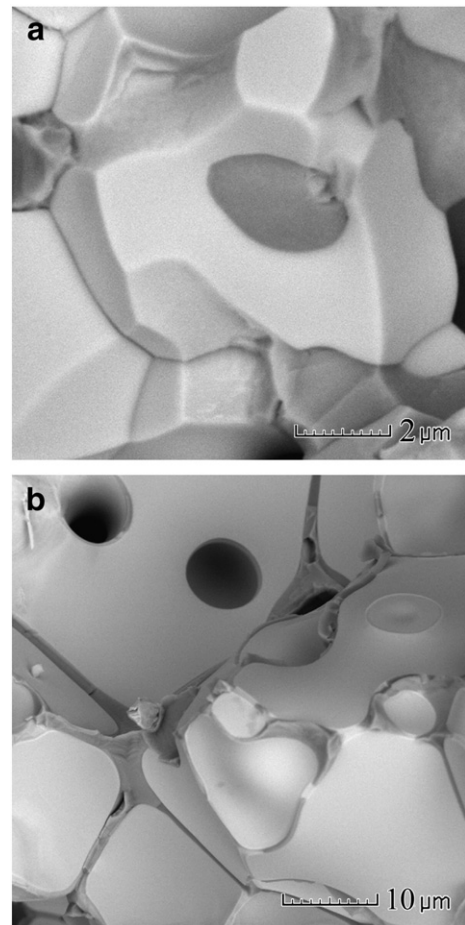


Fig. 4. Nickel-rich phase as gray phase in sintered tungsten with 0.5 wt.% Ni, sintering temperature of: a) 1450 °C and b) 1550 °C.

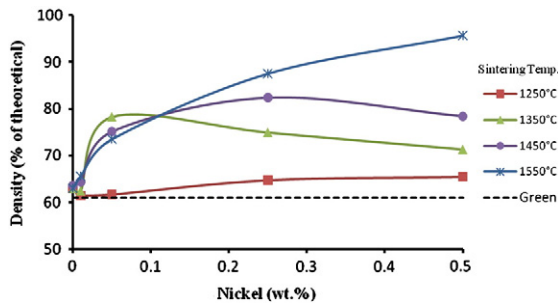


Fig. 5. Density of tungsten specimens after activated sintering vs. nickel amount.

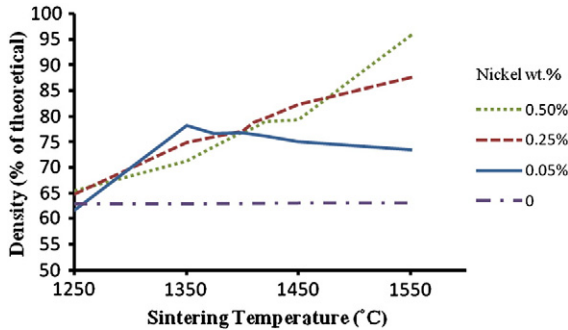


Fig. 6. Density of tungsten specimens after activated sintering vs. sintering temperature.

microstructure. As it is shown in Fig. 7, these pools were more frequent and larger in 0.5 wt.% Ni specimen. They have bimodal porosities. Small pores had to have more shrinkage to compensate the negative effect of big pores.

Although several aforementioned parameters affected densification, at any sintering temperature, specimens had less and more same densities. Suitable sintering temperatures having the same densification for different Ni contents are illustrated in Table 1.

In contrast with the expected trend of increasing densification with the sintering temperature, for the samples having 0.05 wt.% Ni, increase of sintering temperature more than 1350 °C caused less densification (Fig. 5). Nickel vapor pressure vs. temperature is according to the following formula [15]. It shows more the 200 times increase in nickel vapor pressure at the range of 1250–1550 °C.

$$\log P_v = -\frac{22500}{T} + 13.6 - 0.96 \log T \quad (\text{Torr})$$

At higher temperatures, nickel has higher evaporation rate. It evacuates nickel content. Probably in 0.05 wt.% Ni specimens, nickel amount has reduced below sufficient amount and activated sintering has been disrupted. Microstructures of Ni-doped tungsten skeleton with density of about 78% after infiltration are shown in Fig. 7.

The density of infiltrated composites vs. skeleton is illustrated in Fig. 8. Higher nickel contents had less infiltration efficiency. As nickel content increased, bi-modal microstructure has developed and porosities have become smaller in dense parts. This increased probability of close pore formation as well as impervious narrow channels.

4. Conclusions

1. Nickel addition by soluble salt route cannot guarantee uniform distribution of the activator.
2. Perfect W–Cu composites are producible by activated sintering of tungsten at about 1400 °C and infiltration.

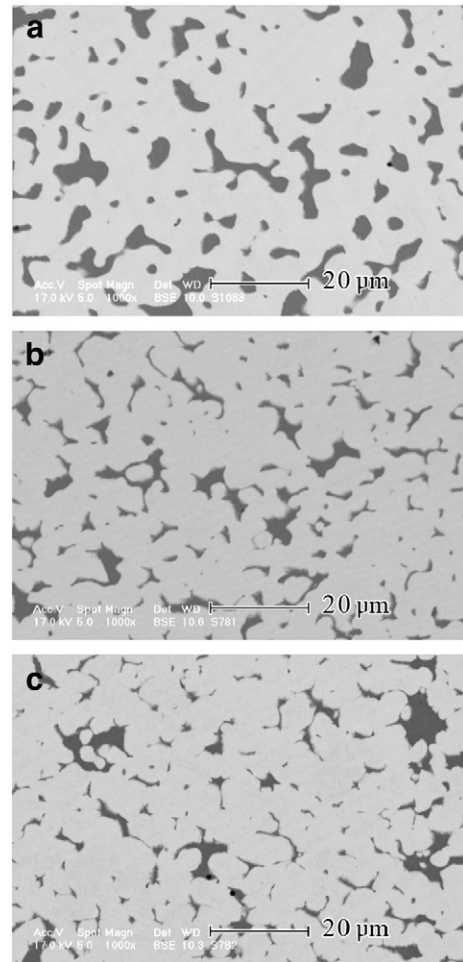


Fig. 7. BS-SEM micrographs from cross section of Ni-containing W skeleton with 78 ± 2% of theoretical density after infiltration; (a) 0.05 wt.%, (b) 0.25 wt.% and (c) 0.5 wt.% Ni in skeletons.

3. Activated sintering begins at a small amount of nickel i.e. 0.05 wt.% and more nickel damages the microstructure uniformity and infiltration efficiency.

Table 1

Proper sintering temperature to achieve 78 ± 2% of theoretical density for different nickel amount.

Nickel content (wt.%)	0.05	0.25	0.5
Sintering temperature (°C)	1350	1400	1420

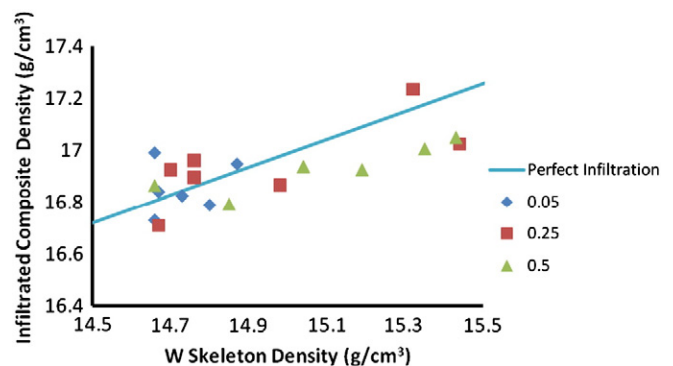


Fig. 8. Density of infiltrated composites vs. density of skeletons shows infiltration efficiency.

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