Effects of contamination on properties of W–15Cu prepared from mechanically alloyed powders

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To eliminate the contamination of activator elements, such as Fe and Ni, W–15Cu compacts were prepared from mechanically alloyed powders using an attritor with a zirconia tank, balls and agitator arms. Coarse tungsten and copper powders, 9·9 μm and 13·3 μm, respectively, were milled to 1·26 μm composite powders after 145 h of milling. The milled powder contained little free copper and was highly combustible in air. After sintering, the 50 vol.-% dense green compacts attained a density of 15·8 g cm^{-3} or 96·2%. The microstructure consists of uniformly interdispersed tungsten and copper. When stainless steel grinding balls were used, the powder was heavily contaminated with Fe and Ni. The contamination improved the density slightly, but the grain size and the electrical resistivity increased significantly as well. The sintering behaviours of the two composite powders were similar. Most densification occurred during heating before reaching the melting point of copper. PM1044

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INTRODUCTION

With the increasing demand for thermal management devices for use in electronic packages, materials that have high thermal conductivity and a low thermal expansion coefficient have become desirable.[1–3] Among the various systems that can meet these requirements, W–Cu has become one of the key materials that are widely used. These W–Cu products are usually produced by either infiltrating presintered tungsten skeletons[4–6] or by sintering the tungsten and copper powder mixtures in the liquid phase.[7–13] The method of liquid phase sintering requires the use of mechanically alloyed W–Cu composite powder,[7–9] co-reduced oxides[10–12] or reduced copper tungstates.[13–15] The resulting properties are strongly affected by the size of the starting powder and the impurities, particularly the amounts of the transition metals. Several studies have used the attritor to reduce the particle size and to increase the internal energy of the powder so that the driving force for sintering was enhanced. The sintered density of the milled powder was thus improved compared with those in which the raw tungsten and copper powders were used. Most of these studies, however, used stainless steel balls and containers for milling.[5–9] Since there was a high possibility that the powder thus milled was contaminated by Fe, Ni and Cr, the actual factor causing the improved sintered density was not clear. Moreover, few comparative studies have reported on the effects of contamination on the electrical properties and the thermal properties. The objective of this work was thus to use grinding balls, agitating arms and a grinding tank, all made of zirconia, to produce W–Cu composite powders that are free of contamination of Fe, Ni and Cr. The resulting properties are compared with those of materials produced using stainless steel grinding balls.

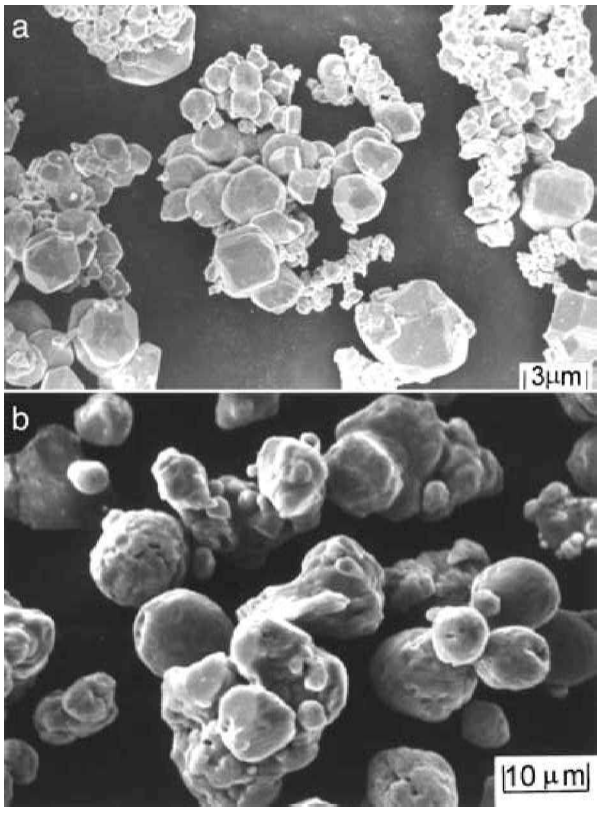
EXPERIMENTAL PROCEDURE

The morphology and the characteristics of the raw tungsten and copper powders are shown in Fig. 1 and Table 1, respectively. To increase the fineness of the starting powder, an attritor was used to further grind the powder. The chamber size of the attritor was 750 000 mm^3 and the grinding balls were 3 mm in diameter. The grinding barrel, grinding balls and the agitating arms were all made of zirconia. The grinding shaft was made of stainless steel but was coated with high polymers to prevent the powder from being contaminated by the transition metals, such as Fe, Ni and Cr. The grinding speed was 500 rev min^{-1}. Since tungsten and copper are easily oxidised, wet milling in heptane and alcohol was employed. The tank was also purged with nitrogen. After heavy milling, the powder slurry was vacuum dried and then kept in a nitrogen filled box. Otherwise, spontaneous ignition of the powder would have occurred at room temperatures due to the high stored energy and the high surface area of the milled powder. The particle size of the milled composite powder was measured by the laser scattering technique.

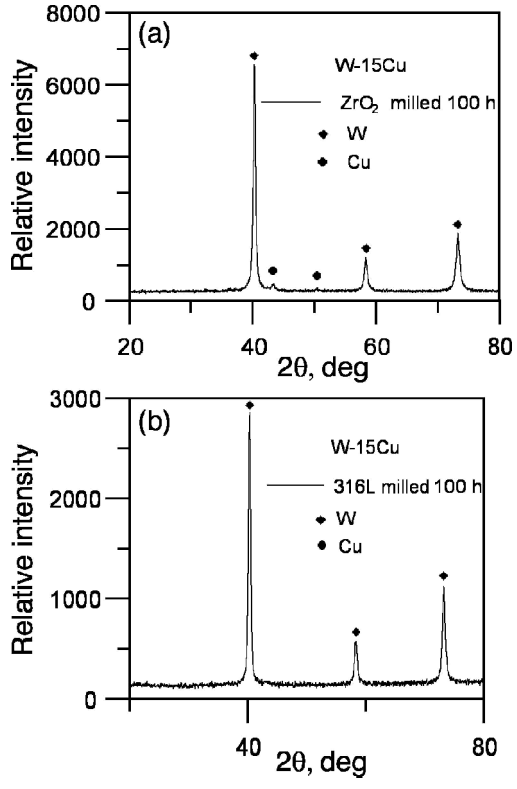
After drying, the powders were reduced under hydrogen at 200°C for 1 h and then heated at 5 K min^{-1} to 800°C and held at that temperature for a further 2 h. The chemistry of the milled powder was analysed by using the inductively coupled plasma (ICP) method. The reduced powder was compacted into discs, 12 mm in diameter and 5 mm in thickness, using the floating die method. The compacts were heated at 5 K min^{-1} to 950°C held for 1 h, and then heated at 2 K min^{-1} to 1230°C and sintered for a further 2 h. After sintering, the density was measured by the Archimedes method. The resistivity was determined by the four point probe method, which measured the voltage across a distance of 20 mm on the specimen at the fixed current of 100 mA.

Table 1 Characteristics of tungsten and copper powders used in study

Powder	Theoretical density, g cm^{-3}	Pycnometer density, g cm^{-3}	Average particle size (laser scattering), μm
W	19·26	19·053	9·88
Cu	8·96	8·407	13·3



1 Morphology of raw *a* tungsten and *b* copper powders used in present study



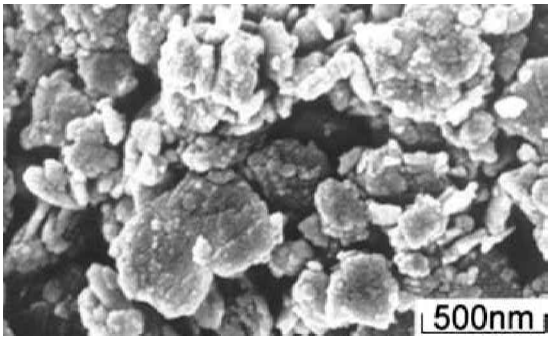
a with zirconia balls; *b* with stainless steel balls

3 X-ray diffraction patterns of milled W–Cu composite powder

RESULTS AND DISCUSSION

Several processing parameters, including the powder to ball ratio, grinding time, grinding liquid and the cover gas, were evaluated. The early runs for milling the tungsten powder employed a powder to ball ratio of 2·5 to 1. After 100 h of milling, the particle size was reduced from 9·88 μm to 3·55 μm, which was still quite large. When the powder to ball ratio was changed to 1:5, the particle sizes of the tungsten after 30, 50 and 100 h of milling were 5·72, 2·89 and 1·73 μm, respectively. To prepare the W–Cu composite powder, the raw tungsten powder was first milled for 100 h using the powder to ball ratio of 1:5. The raw copper powder was then added and milled for another 45 h. The resulting powder had a particle size of 1·26 μm. The morphology of the powder is shown in Fig. 2.

Other processing parameters were also found to influence the powder characteristics. When alcohol was used as the grinding liquid, the powder showed serious agglomeration and some of it stuck to the agitating arms. A switch to heptane eliminated this problem. Using nitrogen as the cover gas was also found helpful in preventing the oxidisation of the powder. It is believed that, without the cover gas, the air would have been trapped in the slurry and reacted with the powder, causing a high oxygen content. The best combination of these processing parameters was to use a powder to ball ratio of 1:5, 145 h of total grinding time, with non-polar heptane and with nitrogen as the cover gas.



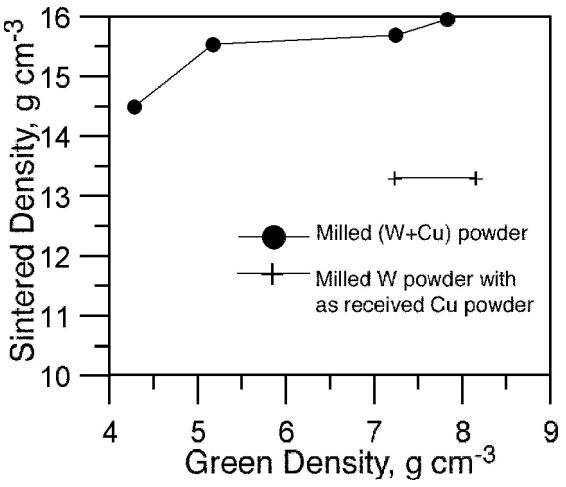
2 Morphology of W–Cu composite powder after 145 h of milling

To examine the degree of mechanical alloying, X-ray analysis was carried out. The results shown in Fig. 3*a* indicate that there was a small amount of free copper when zirconia balls were used. When replaced with stainless steel balls, all the copper was mechanically alloyed into the tungsten. No copper peaks were detected, as shown in Fig. 3*b*. This difference is believed to have been caused by the heavier milling of the stainless steel balls.

It was noticed during the powder drying that a slight heating of the powder to 40°C in air caused spontaneous combustion. This phenomenon even occurred sometimes during drying at room temperature. Thus, vacuum drying without any heating was employed. After drying, the chamber was backfilled with nitrogen to avoid oxidation.

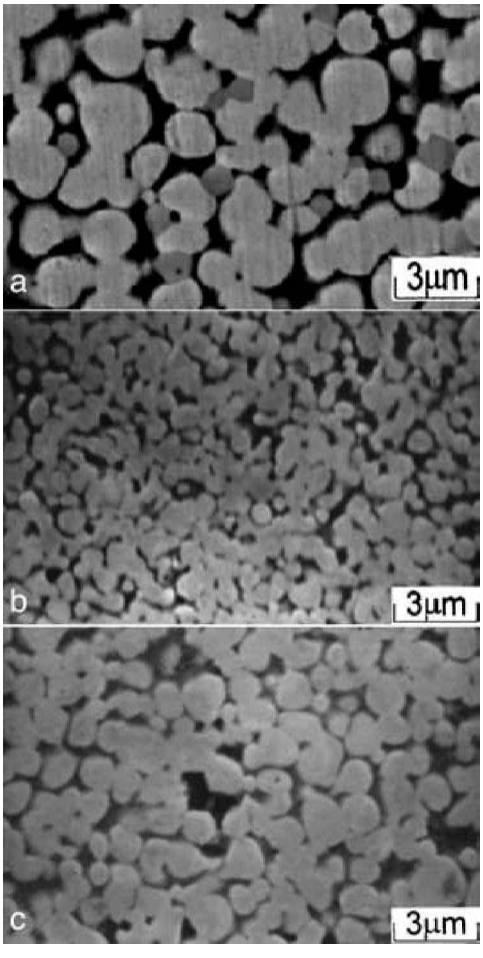
Figure 4 shows that the sintered density increased as the density of the green compact increased. To show the importance of the milling on copper powders, the milled tungsten powder was mixed with the as received 13·3 μm copper powder, pressed and then sintered. The sintered density was about 13·4 g cm^{-3}. Another trial using the 5 μm copper powder also attained a density of only 12·62 g cm^{-3}. The low sintered densities achieved when using unmilled copper powders indicate the importance of mechanical alloying.

The sintered densities of the compacts, which were made of the powders milled with zirconia and stainless steel balls, respectively, were compared. The powder milled with zirconia balls attained a density of 15·8 g cm^{-3}. With stainless steel balls, the density increased to 15·9 g cm^{-3}. The tungsten coated copper powder, which was prepared by the



4 Sintered density of composite powder compact increases as green density increases. With use of raw copper powders, sintered densities are lower

Osram Corp., was also compared.[13] It attained a density of 16·0 g cm^{-3}. Figure 5 compares the microstructures of these compacts. It was noticed that the grain size of the zirconia ball milled powder was the smallest, less than 1 μm. The Osram's powder attained a slightly larger grain size due to the larger raw powder used. The powder that was milled with the stainless steel balls had the largest grain size.



a milled with stainless steel balls; *b* milled with zirconia balls; *c* with Osram's tungsten coated copper powders

5 Microstructures of compacts processed with different powders

Table 2 Contents of Fe, Ni and Cr analysed by ICP method on composite powders

Grinding balls	Fe	Ni	Cr
Zirconia	<0·1%	<0·1%	<0·10%
Stainless steel	1·09%	0·31%	0·39%

Several studies on the sintering behaviour of W–Cu compacts have reported that shape accommodation and grain growth occurred during sintering.[5,9,12] Since the solubility of tungsten in copper is negligible, it should be difficult for these two mechanisms to occur. However, it is very likely that a small amount of Fe or Ni was present in the system, allowing shape accommodation and grain growth to occur. Figure 5 confirms that such grain growth was present only when the stainless steel grinding balls were used. The ICP analyses on the content of Fe, Ni and Cr for W–Cu composite powders that were processed with zirconia and stainless steel balls, respectively, are given in Table 2. It shows that the contamination was quite significant.

Although the small amount of Fe, Ni and Cr improved the sintered density slightly, the contamination seriously deteriorated the electrical properties of the W–Cu compacts. Table 3 compares the electrical conductivity of the W–Cu compacts using oxygen free copper as the standard. The results show that the compact processed with zirconia balls attained an electrical conductivity of 35·1% IACS, while the stainless steel balls attained only 16·1% IACS. This suggests that stainless steel balls should not be employed when electrical or thermal properties of the products are of major concern.

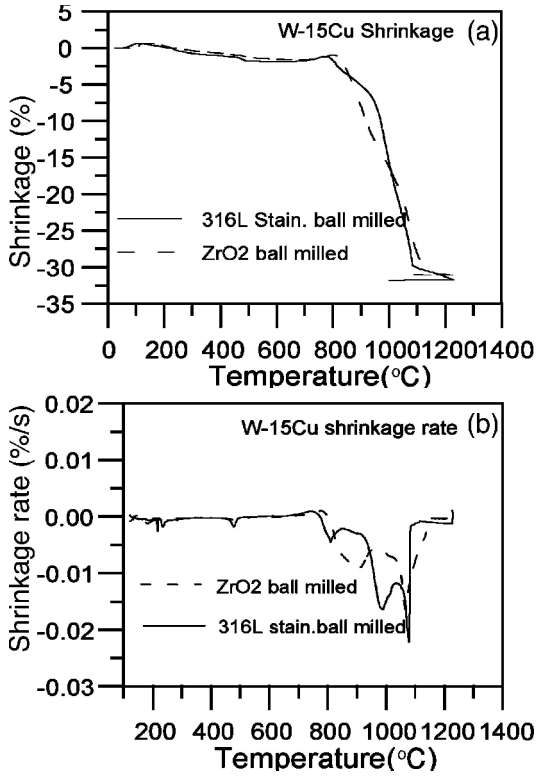
To examine whether these contaminations also influence the sintering behaviour of W–Cu compacts, the dimensional changes were monitored through a dilatometer. Figure 6 shows that no significant difference can be found between the compacts prepared with the zirconia and stainless steel balls. Both compacts started densification at about 810°C. Most densification was completed during heating in the solid state before reaching the melting point of copper. At 1083°C, copper melting was still noticeable, as is indicated by the maximum shrinkage rate, shown in Fig. 6*b*. When melting occurred, the densification rate decreased significantly. The contamination did not help densification during heating. However, at the later stage of sintering, these contaminations help improve the sintering slightly. This is believed to have been caused by the occurrence of the shape accommodation and the Oswald ripening effects, as was demonstrated by the difference in the microstructures, shown in Fig. 5.

CONCLUSIONS

After heavy milling of tungsten and copper powders with zirconia balls, fine 1·26 μm W–Cu composite powders were obtained. The Fe, Ni and Cr contents were all less than 0·1%. Without the activation effect from the Fe and Ni, a high sintered density of 15·8 g cm^{-3} was still attained due to

Table 3 Electrical conductivity and resistivity of W–Cu compacts, which were processed with zirconia and stainless steel balls during attritoring

Grinding balls	Resistivity, Ω cm^{-1}	Conductivity, % IACS
Zirconia	$4·91 \times 10^{-6}$	35·1
Stainless steel	$1·07 \times 10^{-5}$	16·1
Oxygen free copper	$1·74 \times 10^{-6}$	98·5



6 *a* dilatometer curves; *b* their derivatives of compacts prepared from powders using zirconia and stainless steel balls, respectively

the high stored energy in the powder and the fine particle size. When stainless steel balls were used, the density increased to 15·9 g cm^{-3}, but the electrical conductivity decreased from 35·1% IACS of the zirconia balls to 16·1% IACS. Grain growth and shape accommodation also occurred. These were all attributed to the contamination of the Fe, Ni and Cr from the grinding balls. The dilatometer curves show that the sintering behaviours of the two powders were similar. Most densification proceeds in the solid state.

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