Effect of Processing on the Densification and Properties of Thermal Management Materials

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ABSTRACT:

Tungsten-copper alloys exhibit vastly different densification behavior with the processing conditions. In this study, the effect of milling media on densification, oxygen content and the thermal properties of W-15Cu are evaluated. Experiments were conducted with W and copper oxide powder milled using carbide milling media and tungsten milling media and sintered to different temperatures. Results indicate that oxygen content below 0.04 wt.% is not detrimental to the thermal properties. Instead, transition metal impurities have a strong impact on the density and the ensuing thermal properties.

INTRODUCTION:

W-Cu alloys can be tailored for their thermal expansion and conductivities by varying the particle characteristics and amount of copper content, making them a material of choice for thermal managements applications. Infiltration, milling and subsequent co-sintering, sintering of co-reduced tungsten and copper oxides, and mechanical alloying are among the processing routes that are investigated and practiced with a wide variation in the sintered properties for a given composition.

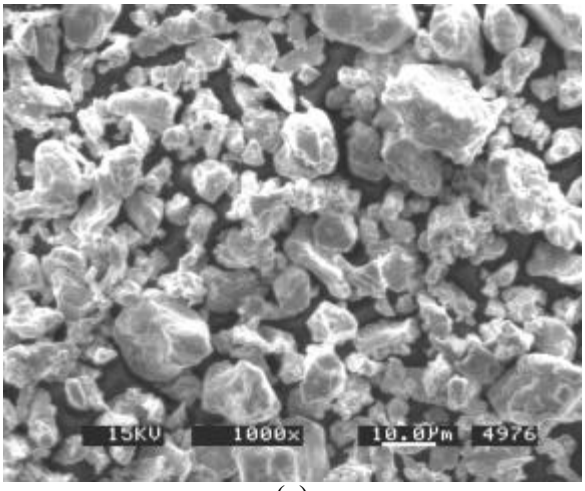
Previous research shows that full densification of W-Cu alloys is possible via solid-state sintering by suitably modifying the particle size of tungsten and copper [1,2]. In the absence of fine particles that promote solid-state sintering, the majority of densification occurs due to particle rearrangement after the liquid formation [3,4]. It is largely recognized that transition metal impurities introduced during the milling or mechanical alloying of W-Cu enhance the densification by promoting tungsten solubility in copper but are detrimental to the thermal properties [4-6]. On the other hand, there are few studies that examine the influence of oxygen content either on the densification or the ensuing thermal properties. The presence of oxygen increases the wetting angle in the W-Cu system from approximately 40° at 1100°C for spectroscopically pure copper to 110° for copper with 250 ppm of oxygen [7,8]. Hence, it can be expected that the presence of oxygen either as an oxide of tungsten, oxide of copper or simply dissolved in copper reduces the thermal conductivity of the sintered samples and may influence the densification. This research aims at identifying the effect of oxygen content and milling media on the densification and thermal properties of the alloy.

EXPERIMENTAL PROCEDURE:

Tungsten, copper and cuprous oxide powders were used for investigation. The particle characteristics are given in Table 1 and the powder morphology examined by scanning electron microscopy is given in Figures 1(a)-(c).

Table 1: Particle characteristics of the powders used.

Powder Type	Particle Size (μm)			Density (g/cm³)		
	D_{10}	D_{50}	D_{90}	Apparent	Tap	Pycnometer
Cu FP1700 Source: American Chemet Corp, MO	5.91	10.83	17.09	2.78	3.61	8.62
Cuprous Oxide, Grade AA Source: OMG Americas, NC	3.55	9.72	17.09	2.23	3.11	6.11
W (C3) lot 37274 Source: Alledyne Powder Tech., AL	1.68	5.46	17.98	2.61	4.80	19.15



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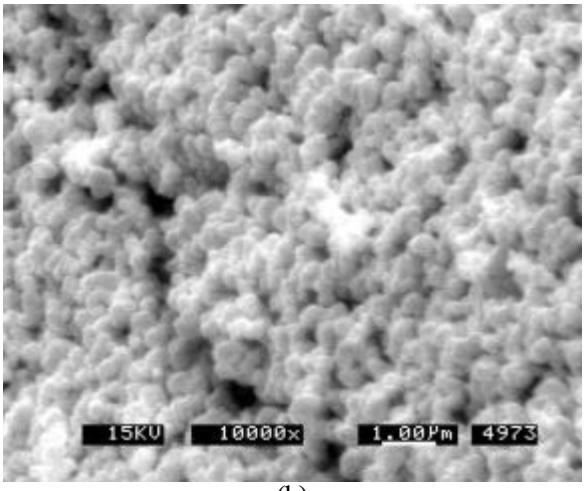

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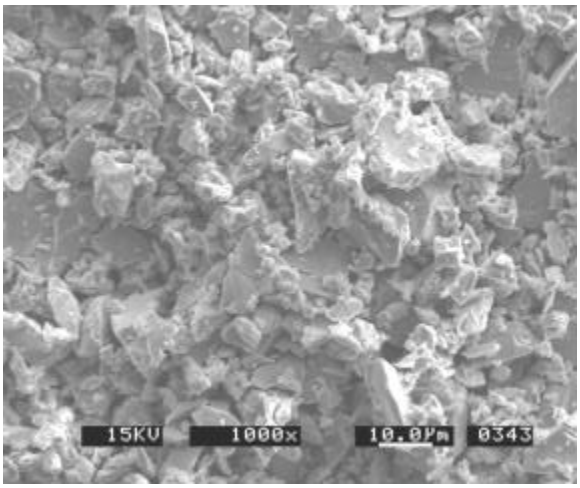


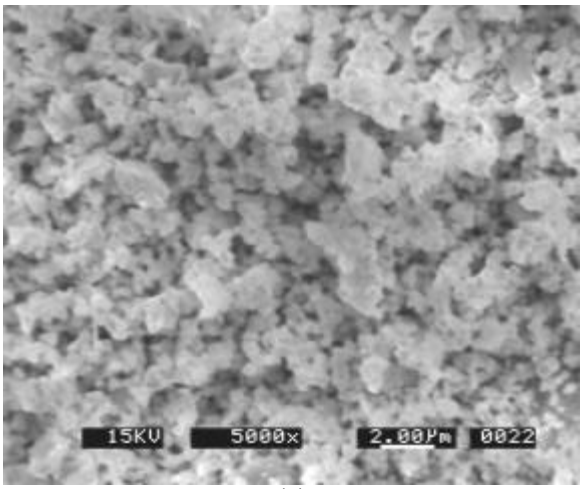
(c)

Figure 1(a) – (c): Scanning electron micrograph revealing the morphology of (a) Cu FP1700, (b) W (C3), and (c) Cu_2O powder.

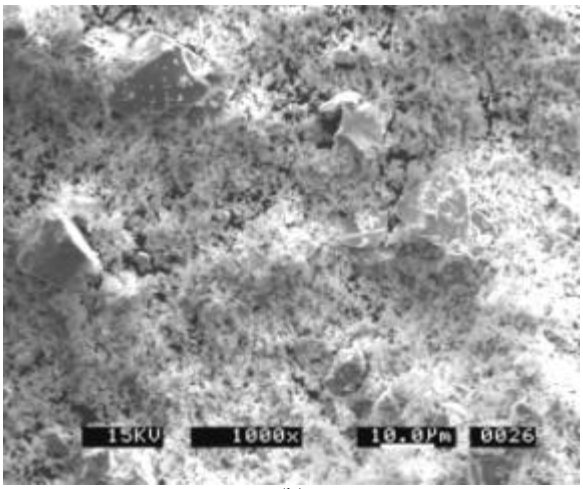
W powder was admixed with 17.12 wt.% Cu_2O powder, charged with 7.5 mm diameter WC-Co milling media with a powder to milling media ratio of 1:10. The powders and milling media were submerged in heptane, back filled with argon to reduce oxygen contamination during milling and milled at a rotational speed of 300 RPM for 24 hours in 2L Nalgene® jar. Admixed W- 17.12Cu_2O and W-15Cu powders were rod milled using 10mm diameter and 180 mm long tungsten rods in the weight ratio of 1:10. The powders and the rods were charged in a 2L Nalgene®, back filled with argon and milled at a rotational speed of 300 RPM for one hour. The morphology of the milled powders is given in Figures 2(a)-(c) and their particle sizes given in Table 2. The milled powders were mixed with 2 wt.% paraffin wax, heated to 70°C in an air oven for 15 minutes and manually blended using wooden spatulas. The blended powders were cooled to room temperature and compacted at 140 MPa using a 60 Ton Uniaxial Gasbarre press into cylinders with a diameter of 12.74 mm and a height of 3 to 5mm. The green density of the compacts was 60 to 65% of the theoretical density.

Table 2: Particle characteristics of the powders used.

Powder Type	Particle Size (μm)		
	D_{10}	D_{50}	D_{90}
W (C3), Ball Milled in heptane for 24 h	0.53	1.04	1.88
W (C3), Rod Milled in argon for 1 h	0.46	0.83	1.44
W (C3) – 17.12 wt.%Cu_2O, Ball Milled in heptane for 24 h	0.42	0.8	1.53
W (C3) – 17.12 wt.%Cu_2O, Rod Milled in argon for 1 h	0.56	1.4	10.14
W (C3)-Cu (635) Rod Milled	0.93	8.03	25.23



(a)



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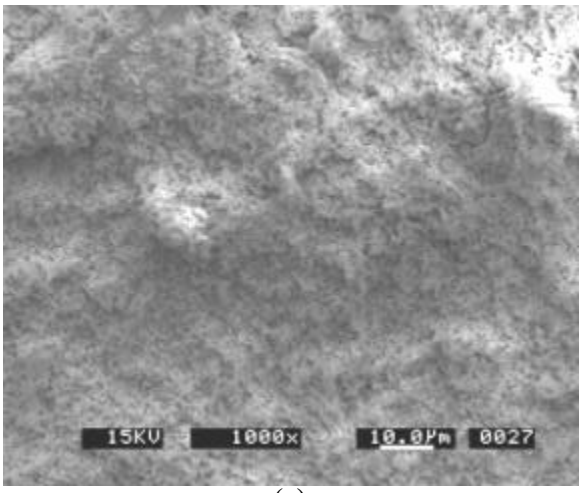

(c)

Figure 2: Scanning electron micrograph revealing the morphology of (a) W- Cu_2O -ball milled, (b) W- Cu_2O -rod milled, and (c) W-Cu-rod milled with tungsten particles impinged on copper platelets. The rod milled W- Cu_2O contains some coarse particles, indicating that the powder is contaminated during milling.

The W-Cu_2O compacts were sintered at 950°C, 1100°C, 1200°C, and 1300°C in H_2 using the following thermal profile.

i. 2°C/min to 500°C, 2°C/min to 950°C for 2 h and then cooled to room temperature at 10°C/min
ii. 2°C/min to 500°C, 2°C/min to 950°C for 2 h, 2°C/min to 1100°C for 2 h and then cooled to room temperature at 10°C/min
iii. 2°C/min to 500°C, 2°C/min to 950°C for 2 h, 2°C/min to 1200°C for 2 h and then cooled to room temperature at 10°C/min
iv. 2°C/min to 500°C, 2°C/min to 950°C for 2 h, 2°C/min to 1300°C for 2 h and then cooled to room temperature at 10°C/min

The W-Cu samples were sintered only at 1300°C. The sintered compacts were characterized for dimensional change and sintered density via Archimedes water immersion technique. Thermal diffusivity (α) was measured using the Anter Flashline 5000 thermal diffusivity laser flash analysis system [9]. The equipment was calibrated using Pyroceram and graphite. Oxygen content was measured using the Horiba EMGA-650 Oxygen/Nitrogen Analyzer based on infrared absorbance technique. Calibration and sample preparation were according to ASTM E 1019-00 standards [10] and the procedure and furnace setting were according to the equipment supplier's recommendations. Appropriate amount of the sample (0.01g to 0.2g) was either filed using a diamond file or cut using SiC blade with water as a coolant. The samples cut using SiC were cleaned with acetone and dried in an oven prior to analysis. The samples were loaded on to tin capsules and measured for oxygen content. The use of accelerants (Sn) is not required to measure the oxygen content in copper. However, it was found that tin capsules significantly reduced copper evaporation and subsequent condensation in the oxygen analyzer. The results remained unchanged with and without the use of tin capsules.

RESULTS:

Figure 3 shows the differential thermal analysis data for W- Cu_2O. Figure 4 shows the thermogravimetric analysis for Cu_2O and W- Cu_2O. A combination of DTA and TGA data indicates that reduction begins at temperatures as low as 66°C in nitrogen. Further, reduction of Cu_2O to Cu is essentially complete below

300°C. Consequently, no phase change is detected at the eutectic temperature of Cu and O (1066°C). It can be inferred from Figure 3 that Cu_2O reduces to Cu and Cu melts at 1091°C.

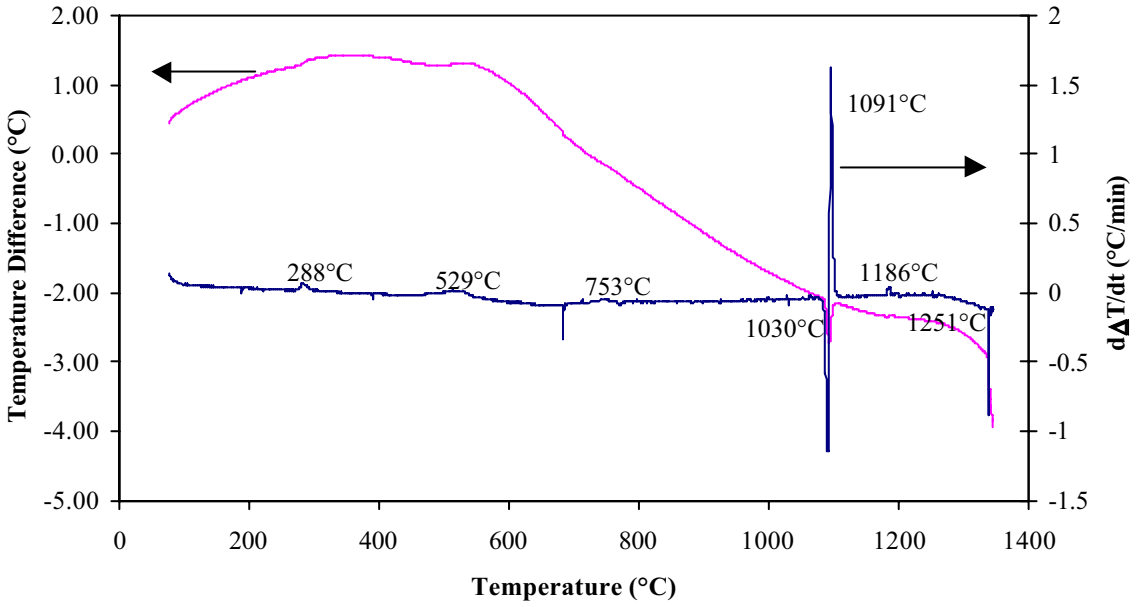

Figure 3: Differential thermal analysis of W-Cu_2O heated to 1300°C at 10°C/min in nitrogen.

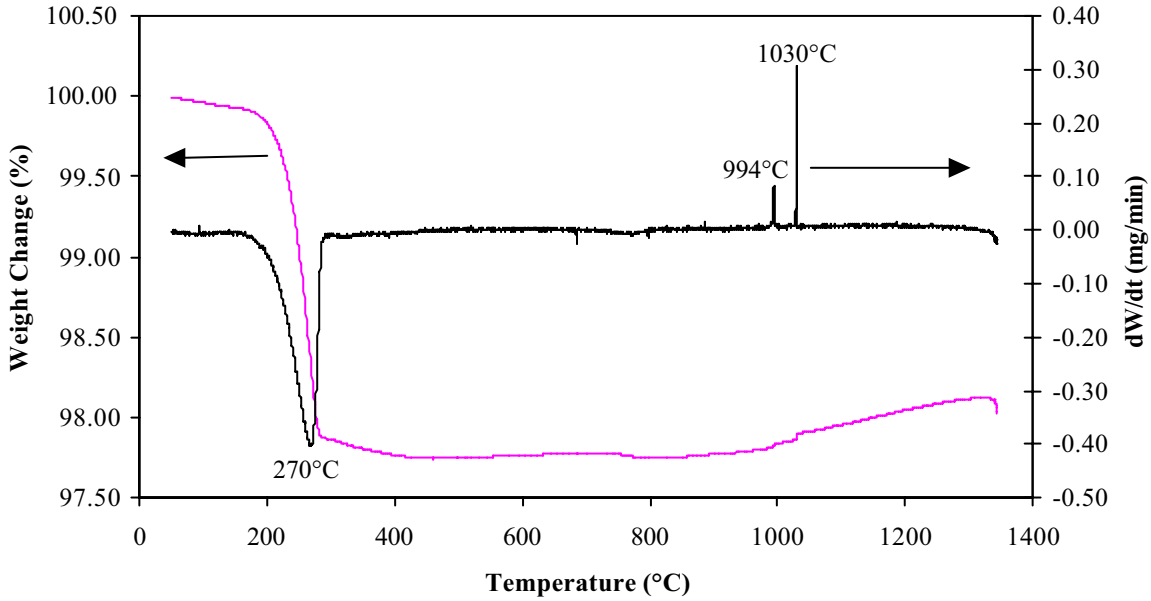

Figure 4: Thermogravimetric analysis of W-Cu_2O heated to 1300°C at 10°C/min in nitrogen.

Figure 5 shows the variation in the density of ball milled and rod milled W- Cu_2O with temperature. The density increases with an increase in temperature. Ball milled powders exhibited higher density. Chemical analysis on the sintered samples identified transition metal contamination (0.06 wt.% Co, 0.03 wt.% Fe, and 0.03 wt.% Ni) due to the milling media. While the extent of contamination is not significant enough to induce full densification, the transition metal impurities resulted in a slightly higher density (93.2% theoretical, compared to 89.5% for rod milled powders at 1300°C).

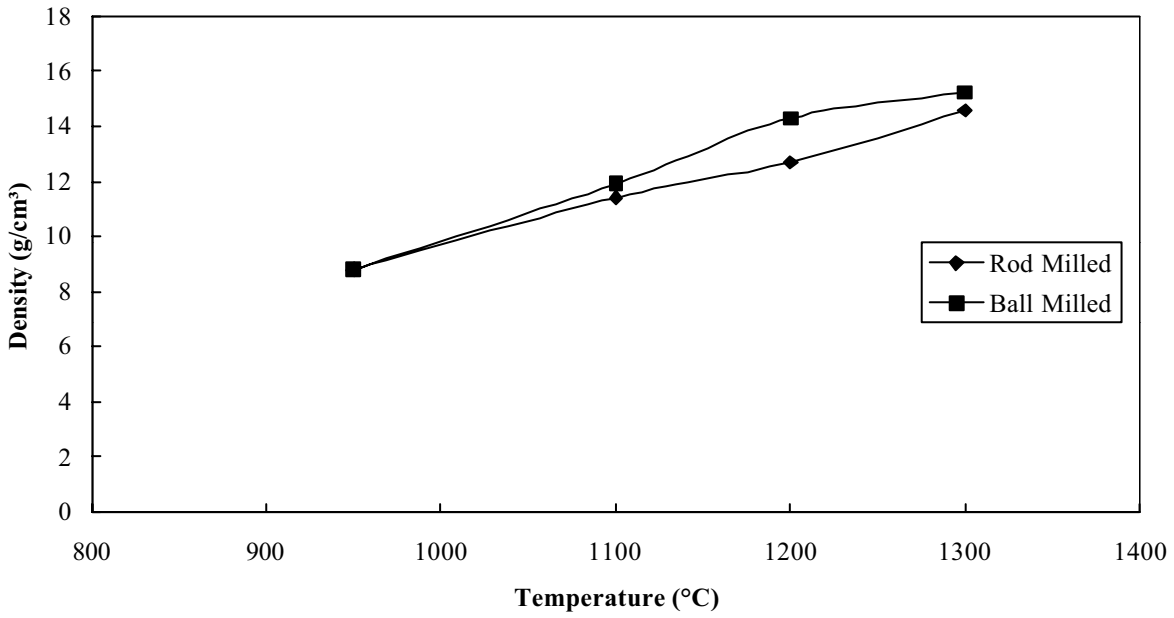

Figure 5: Variation in the density of ball milled and rod milled W- Cu_2O compacts with temperature. Ball milled powders exhibit higher density than the rod milled powders due to transition metal impurities introduced during milling.

An increase in temperature results in the reduction of the oxides and is given in Figure 6. It can be seen that oxygen content in the sintered samples decreases linearly with temperature. Further, there is no significant difference in the oxygen contents at different temperatures due to milling.

The variation in the thermal diffusivity of the compacts sintered to different temperatures is given in Figure 7. An increase in density and decrease in the oxygen content increase the thermal diffusivity. The influence of processing conditions is apparent from this figure. An increase in the sintered density from 14.3 g/cm³ at 1200°C to 15.25 g/cm³ at 1300°C and a corresponding decrease in the oxygen content from 0.13 to 0.017 wt.% contributed to a marginal increase in the thermal diffusivity from 0.381 cm²/s to 0.384 cm²/s for the ball milled powders. On the other hand, the sintered density of the rod milled W-Cu_2O increased from 12.7 g/cm³ to 14.6 g/cm³, oxygen content decreased from 0.12 to 0.005 wt.% and the thermal diffusivity increased from 0.46 cm²/s to 0.612 cm²/s.

In combination with specific heat (C_p = 173 J/kg· K for W-15Cu) and density data (ρ_s), thermal conductivity (κ) of a material may be calculated according to the relationship

$$\kappa = \rho_s C_p \alpha \qquad (1)$$

Figure 8 shows the variation in the thermal conductivity of the W- Cu_2O specimens sintered at different temperatures. As expected, the conductivity increases with an increase in density and diffusivity. Further, the effect of milling media is also evident – the thermal conductivity decreases from 153 W/mK to 100 W/mK due to transition metal impurities.

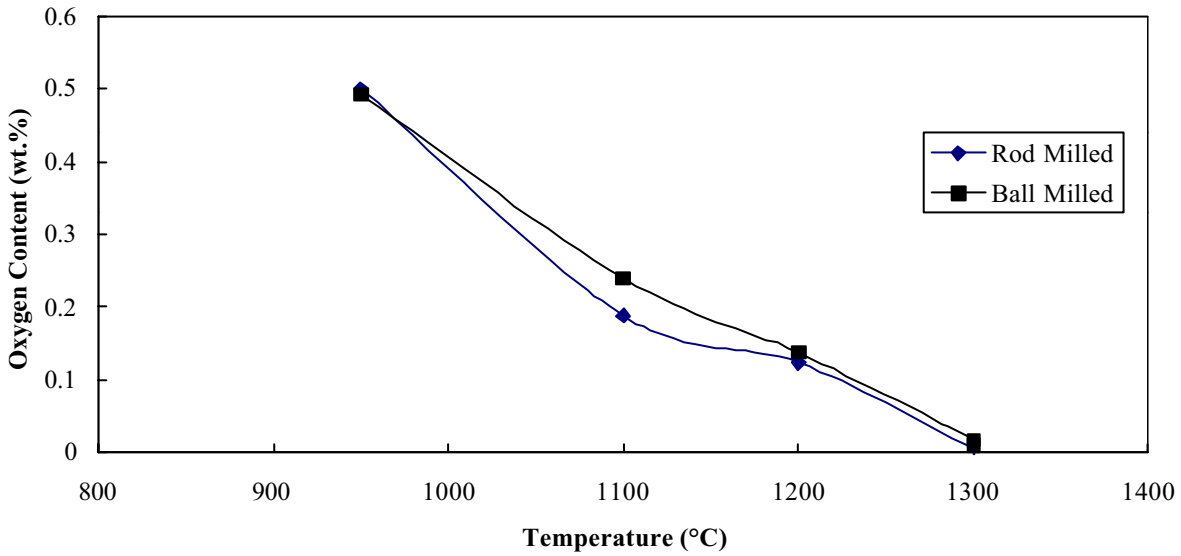

Figure 6: Variation in the oxygen content of the W- Cu_2O sintered at different temperatures for 2h in hydrogen.

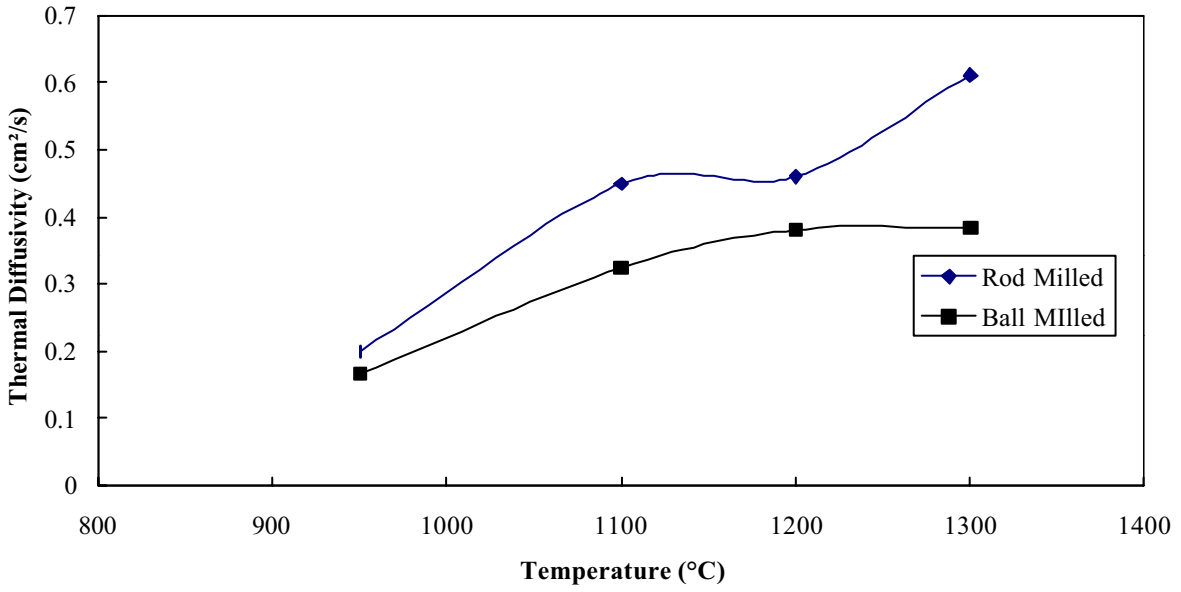

Figure 7: Variation in the thermal diffusivity of W- Cu_2O sintered at different temperature. Thermal diffusivity of the rod milled powders is higher by a factor or 1.6 at 1300°C compared to the ball milled powders

Sintering at 1300°C was also conducted in wet hydrogen (dew point = 15°C). Table 3 lists the effect of dew point on the density, thermal properties and the oxygen content. It can be seen that the oxygen content increases due to processing in the wet hydrogen, but it does not adversely affect the thermal properties.

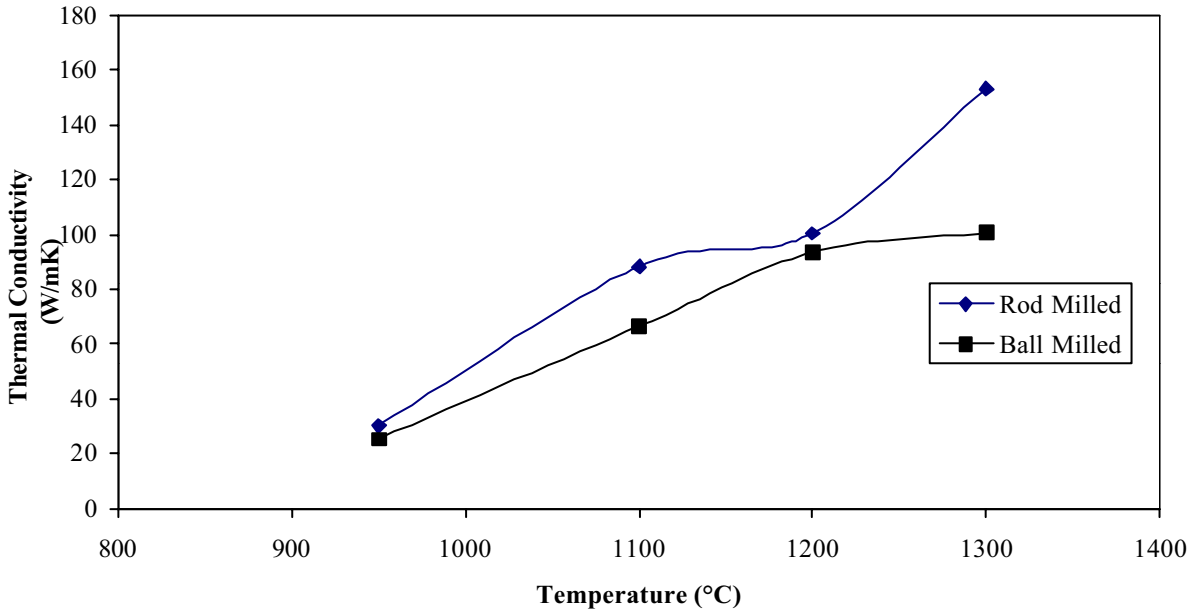

Figure 8: Variation in the thermal diffusivity of the W- Cu_2O sintered at different temperature.

Table 3: Thermal properties, sintered density and oxygen content of the rod milled and ball milled W- Cu_2O sintered at 1300°C for 2 h in hydrogen with a dew point of 15°C and rod milled W-Cu sintered at 1300°C for 2 h in wet and dry hydrogen.

Powder Type	Density (g/cm^3)	Thermal Diffusivity (cm^2/s)	Thermal Conductivity (W/mK)	Oxygen Content (wt.%)
W- Cu_2O, Rod Milled	13.37	0.528	127.5	0.038
W- Cu_2O, Ball Milled	15.37	0.371	98.0	0.009
W-Cu, Rod Milled	13.74	0.535	126.5	0.012
W-Cu, Rod Milled, sintered in dry hydrogen	14.35	0.54	133.3	0.006

DISCUSSION:

It can be seen from the initial powder characteristics, that the as-received tungsten powder is agglomerated. Milling aids deagglomeration and reduces the particle size of the powders. However, the rod milled powders contained very coarse particles (10 μm in diameter). Rod milling for longer periods of time reduced the size of the coarse particles and eventually resulted in a unimodal particle size distribution. Since tungsten powder was found to deagglomerate after one hour of rod milling, it is concluded that the coarse particles are that of Cu_2O. It can be seen from Figures 1 and 2 that milling

results in the deagglomeration of tungsten powder, reduces the size of the copper oxide powder to a certain extent while the copper powder deformed into platelets with tungsten particles impinged on the copper platelets.

Transition metal impurity due to milling media was evaluated via inductively coupled plasma mass spectrometry (ICPMS). The ball milled powder was determined to contain 0.06 wt.% Co, 0.03 wt.% Fe, and 0.03 wt.% Ni while the transition metal impurities in the rod milled powder were below the detection levels. The transition metal impurities due to ball milling are not significant enough to promote activated sintering of the W-Cu alloys [11], hence the densities of the compacts made with the ball milled powder is slightly higher (by 4.3%) than the rod milled powder sintered under similar conditions, but not significantly different. The maximum density of the ball milled powder, sintered at 1300°C for 2 h in dry hydrogen is 15.24 g/cm³ and 14.57 g/cm³ for the rod milled powders.

The effect of transition metal impurities is most significant on the thermal properties. Despite the higher density of the W-Cu samples obtained from ball milled W- Cu_2O, its thermal conductivity is significantly lower. Assuming that the variation of thermal conductivity with porosity follows as [12]:

$$\hat{e} = \hat{e}_0 \frac{1-\grave{e}}{1+11\grave{e}^2} \qquad (2)$$

where, κ_0 is the thermal conductivity of the pore-free material and θ is the porosity, the thermal conductivity of the fully dense W-Cu alloys produced via rod milling can be estimated at 197 W/mK and at 114 W/mK for the ball milled powder. Hence, transition metal contamination, even at the amounts insufficient for activated sintering, impedes the thermal properties of the sintered alloys.

Data from Figure 5 and Table 3 reveal the effect of oxygen content on the density and thermal conductivity. The rod milled powder has higher oxygen content when sintered at 1300°C for 2 hours in wet hydrogen (0.039 wt.% compared to 0.006 wt.% in dry hydrogen) where as ball milled powder has higher oxygen content, 0.017 wt.% when sintered in dry hydrogen, compared to 0.009 wt.% in wet hydrogen at 1300°C for 2 hours. Investigation into the reduction mechanism of W and Cu_2O [2,13] and tungsten oxide in presence of nickel [14] and cobalt [15] indicate that Cu_2O reduces to Cu and WO_3 forms at the interface of W and Cu_2O. Presence of nickel and cobalt accelerates the reduction of WO_3 by forming WO_2. However, current experimental results are not in agreement and must be investigated further.

Despite the differences in the oxygen content due to milling and hydrogen dew point, it is clear that the sintered density of the compacts increased with decreasing oxygen content as shown in Figure 9. This is expected, as an increase in the oxygen content is known to increase the wetting angle in the W-Cu system [7,8]. However, the effect of oxygen content on the thermal conductivity is negligible. Using Equation (2), it can be calculated that the relative change in the thermal conductivity of fully dense W-Cu compacts varies by less than 3%. Hence it can be concluded that below an oxygen content of 0.038 wt.%, oxygen content in W-Cu has no effect on the thermal properties of the alloy. It remains to be investigated if the oxygen is present in the form of oxide or as a solid solution and if the presence of oxygen can lead to full densification.

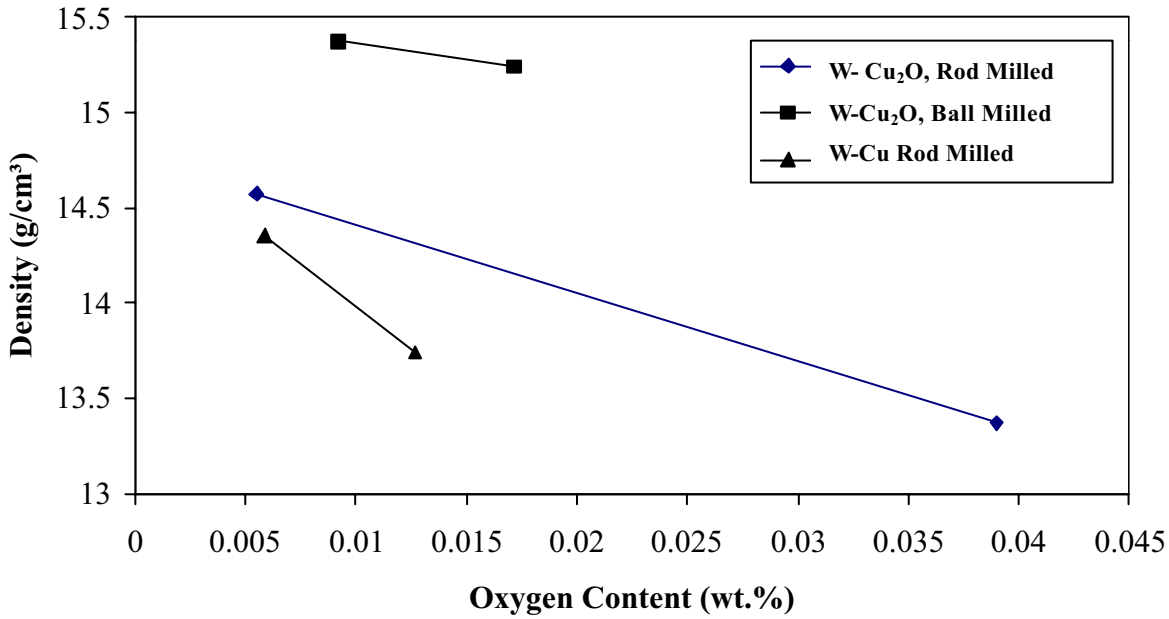

Figure 9: Variation in the sintered density of W-Cu alloys with oxygen content. Different oxygen contents were realized by processing in wet (dew point = 15°C) and dry (dew point = -55°C) hydrogen at 1300°C for 2 hours.

CONCLUSION:

Experiments were conducted to identify the effect of impurities and oxygen content due to processing conditions on the thermal properties of sintered W-15Cu alloy. While full densification was not realized for the sintered samples, it can be concluded that:

1. Transition metal impurities, as low as 0.12 wt.%, significantly lowers the thermal conductivity of the sintered W-Cu alloys.
2. An increase in oxygen content decreases the sintered density. It is predicted that for a full dense W-Cu alloy, oxygen content below 0.04 wt.% does not have an effect on the thermal properties. It remains to be examined if full densities can be achieved with varying oxygen levels in the sintered samples.

Reference:

1. J. L. Johnson and R. M. German, Metall. Mater. Trans. B, Vol. 27, 1996, p. 901.
2. L. P. Dorfman, D. L. Houck, M. J. Scheithauer, T. A. Frisk, J. Mater. Res., Vol. 17, No. 4, 2002, pp. 821-830.
3. W. D. Kingery, J. Appl. Phys., Vol. 30, 1951, p. 301.
4. A. Upadhayaya and R. M. German, Intl. J. Powder Met., Vol. 34, 1998, p. 43.
5. I. J. Moon, J. S. Lee, Powder Met., Vol. 22, 1979, p. 5.
6. J-C. Kim, S-S Ryu, and I-H. Moon, J Advanced Mater., Vol. 31, No. 4, 1999, pp. 37.
7. M. Nicholas and D. M. Poole, J. Mater. Sci., Vol. 2, 1967, p. 269.
8. V. I. Kornilova, L. D. Konchakovskaya, V. V. Panichkina, P. Ya. Radchenko, and V. V. Skorokhod, Soviet Powder Metallurgy and Metal Ceramics, Vol. 24, No. 3, 1985, pp. 197.
9. ASTM E 1461-01, Standard Test Method for Thermal Diffusivity of Solids by the Flash Method, Annual Book of ASTM Standards, Vol. 14.02, ASTM, West Conshohocken, PA, 2002, p. 462.

10. ASTM E 1019-00, Standard Test Method for Determination of Carbon, Sulfur, Oxygen and Nitrogen in Steels and in Iron, Nickel and Cobalt Alloys, Annual Book of ASTM Standards, Vol. 3.05, ASTM, West Conshohocken, PA, 2002, p. 766.
11. J. L. Johnson, R. M. German, Metall. Trans. A, Vol. 24, 1993, p. 2369.
12. R. M. German, Sintering Theory and Practice, Wiley-Interscience Publication, John Wiley and Sons, Inc., New York,NY, 1996, p. 54.
13. H. Taimatsu, Y. Ikeda, N. Nemoto, T. Kimura, and H. Kaneko, Zeitschrift fuer Metallkunde, Vol. 81, No. 8, 1990, pp. 588.
14. S. Sridhar, Du Sichen, and S. Seetharaman, Met. Mater. Trans. B, Vol. 25B, 1994, pp. 391.
15. Z. Zhang, Y. Zhang, and M. Muhammed, Intl. J. Refrac. Metals and Hard Mater., Vol. 20, 2002, pp. 227.