JMME. Vol. 13, April, 2021
pp. 29 – 38

ISSN: 2006-1919

DENSIFICATION BEHAVIOUR OF W-Cu COMPOSITE COMPACTS PRODUCED BY LIQUID PHASE SINTERING AND CONTACT INFILTRATION PROCESSES

N.I Amalu [(1)], B. I. Onyia [(1)], and B.A. Okorie [(2)]
[(1)] Projects Development Institute (PRODA), Enugu
[(2)] Department of Metallurgical and Materials Engineering, Enugu State University of Science and Technology

ABSTRACT

Sintered compacts of W-Cu composites containing 20 – 50wt%Cu have been produced using liquid phase sintering (LPS) and contact infiltration processes. The compaction pressures used to produce the starting green compacts ranged from 100MPa to 300MPa, and the sintering and infiltration temperatures ranged from 1150^{0}C to 1250^{0}C. The selected sintering time was one hour. The relative densities of all green compacts and sintered/infiltrated specimens were determined. For the specimens produced by the LPS process, the relative density values ranged from 90% to 93%, while for the infiltrated specimens, the relative densities ranged from 96.4% to 97.8%. Cobalt coating of tungsten particles prior to sintering was found to be beneficial to densification, with the optimal amount of cobalt coating in the range of 0.45 to 0.50 wt% cobalt. Higher sintering temperatures in the range of 1200^{0}C to 1300^{0}C also resulted in increased densification. The results generally show that the infiltration process results in more efficient filling of pores and better densification than the LPS process.

Key Words: *Sintering, Infiltration, Density, porosity, capillarity.*

1.0 INTRODUCTION

Solidification processing is the most common method used for obtaining metallic alloys and compounds. However, the method is not suitable for producing cermets or for producing mixtures of metals which will not mix together when melted. Tungsten is a refractory metal with a very high melting point of about 3410^{0}C. Because of the difficulty in melting tungsten, alternative processing techniques are required for producing tungsten – based alloys and compounds. These techniques include powder metallurgy (P/M), Powder Injection Moulding, and High Energy Ball Milling or Mechanical Alloying (MA), among others. Of these techniques, powder metallurgy processing is the most commonly used.

In the powder metallurgy process, the material, in the form of powder or a mixture of powders, is brought to the desired final shape by placing it in a die and compressing it to obtain a green compact. The green compact is then sintered in a furnace and subjected to some desired secondary operations.

During compaction using a die of the single punch design, the density of the green compact obtained is higher in the part close to the "upper" punch, with the density diminishing progressively away from it. Thus, the portion closest to the "Lower" punch (which is the support base of the die), will not be sufficiently dense. Improvements in punch and die design will often yield more uniform densification, but generally the density of the green compact is found not to be perfectly uniform. The sintering process further reduces the porosity, but generally, the final sintered specimen contains some residual porosity.

Sintering of W-Cu green compacts may be achieved by placing the specimen in a furnace at a temperature well above the melting point of copper (1083^0C), such as 1150^0C or 1200^0C. The molten copper then flows to fill the pores in the compact giving the final dense composite. This is liquid phase sintering. Alternatively, a green compact of pure tungsten is first obtained and then sintered to obtain a porous tungsten skeleton. This is then placed in a furnace, with solid copper placed on top of it in an amount enough to fill the pores. On heating, the copper melts and is drawn by capillary forces through the specimen to fill the pores. This is the infiltration process.

This paper presents the results of an investigation of the efficiency of pore-filling and densification using the liquid phase sintering and infiltration processes. Enhanced efficiency of densification is desirable, as it imparts desirable mechanical, electrical, thermal and acoustical properties to the composite.

2.0 EXPERIMENTAL

2.1 Materials and Equipment

The materials used for this work include powder specimens of tungsten, cobalt and copper obtained from vendors in the United States and United Kingdom, a 5mm diameter rod of pure copper obtained from Cutix Ltd, Nnewi, Anambra State of Nigeria, and stearic acid and paraffin wax purchased from Conraws Nigeria Ltd, Enugu. The equipment used include a rigid metal die, a digital microbalance, a turbular mixer for powder specimens, a controlled atmosphere furnace, an optical microscope, and a scanning electron microscope.

2.2 Preliminary powder characterization

The starting powder materials were characterized with the aid of the scanning electron microscope. The mean particle sizes and the tap densities of the powders were determined.

2.3 Production of Green and Sintered Compacts

2.3.1 Press Sinter Consolidation (Liquid phase sintering)

For the W-Cu system under investigation, the press sinter consolidation process is essentially a liquid phase sintering (LPS) process. The melting point of tungsten is 3410^0C while that of copper is only 1083^0C, so that sintering of green compacts at temperatures above 1083^0C will result in molten copper flowing to fill the voids in the compact, provided that a low contact angle is maintained between the molten copper and solid particles of tungsten.

In the present work, powder mixtures of tungsten and copper of composition W-20%Cu, W-30%Cu, W-40%Cu, and W-50%Cu, were carefully mixed together, with about 0.5wt.% paraffin wax, and subjected to prolonged tumbling (for about 2 hours). The paraffin was added to act as a lubricant to reduce the friction during compaction. After the mixing process, a determined quantity of each powder mix was poured into the rigid metal die (Figure 1) for cold pressing so as to get green compacts measuring approximately 15mm diameter and 5mm thick. Compaction pressures of 100, 150, 200, 250 and 300 MPa were used. Green compacts of pure tungsten were also produced from the same set of compaction pressures.

To study the effect of cobalt coating on the tungsten particles, the procedure was repeated for mixtures of composition W-30Cu-0.2Cu, W-30Cu-0.3Co, W-30Cu-0.4 Co, W-30Cu-0.5Co, W-30Cu- 0.6 Co, and W-30Cu-0.8 Co. In this case, the tungsten and cobalt were first mixed together and tumbled for at least one hour before

introduction of 30% Copper and 0.5% paraffin wax for another one hour of tumbling.

After measurements of green density, the various compacts were placed in a nitrogen atmosphere sintering furnace and sintered for one hour at 1200^0C. To study the effect of sintering temperature, green compacts of W-30Cu (produced using a compaction pressure of 300MPa) were sintered at 1150^0C, 1200^0C, and 1250^0C, and their relative densities determined.

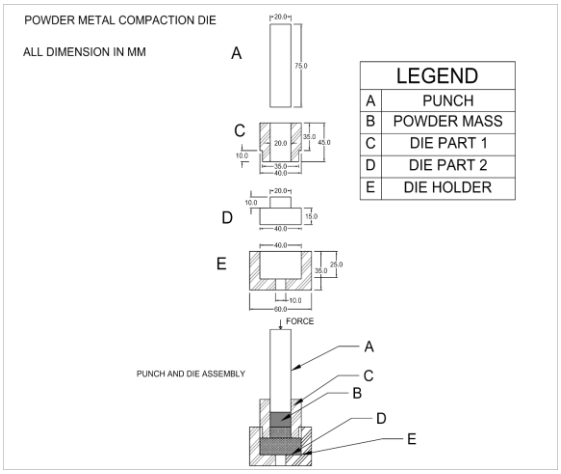

Figure 1: Rigid metal Die with punch (Schematic).

2.3.2 Press-Sinter Infiltration Process

For the infiltration process, sintered porous skeletons of tungsten were first obtained and the required amounts of pure copper were then contact infiltrated into them to fill the pores.

In this work, green compacts of pure tungsten were obtained using the various compaction pressures (100, 150, 200, 250 and 300MPa), and then sintered at 1200^0C for one hour in a nitrogen atmosphere sintering furnace. The weight percentage of copper required for each specimen in this process depends on the percentage of pores in the sintered skeletons of tungsten, which in turn depends on the compaction pressure used to obtain the starting green compacts. It is thus necessary to obtain a calibration curve of pore percentage versus compaction pressure. From this curve, the compaction pressures required to obtain the desired pore percentages are obtained. Since these pore percentages are equal to the volume percentages of copper required for infiltration, the weight of copper required for infiltration is calculated for each specimen.

For infiltration, the sintered skeletons of tungsten were placed on steel plates in the furnace and the amounts of copper required by each specimen were placed on top of them. Selected infiltration temperatures were 1200^0C and 1250^0C, and the infiltration time was one hour. After infiltration, the surfaces of the specimens were machined.

The true, apparent and relative densities of all the green and sintered specimens were determined.

3.0 RESULTS AND DISCUSSION

3.1 Powder Characteristics

Selected properties of the powders used for this work are shown in Table 1 below.

The particle sizes and shapes varied considerably. Table 1 above shows that the tungsten particles are fairly larger than the others. The cobalt particles are particularly small (between 200 and 500 nanometers in size), and their gumminess and stickiness tend to promote particle agglomeration. The particle shapes of the Cu and Co particles vary from acicular to dendritic and to fragmented irregular. For the tungsten, the particles used were generally spherical smooth, spherical rough, and polygonal in shape. Figure 2 presents scanning electron micrographs of the starting powder materials used.

3.2 Dependence of Green Density of Tungsten Compacts on Compaction Pressure

The effect of compaction pressure on the green density of pure tungsten is shown in Figure 3.

Table 1: Selected Properties of Powders used

Powder Material	Particle Size (μm)	Purity (%)	Tap Density (gm/cm^3)	Theoretical Density (gm/cm^3)	Melting point (^0C)
W	5-10	99.90	2.81	19.30	3410
Cu	2.0-4.0	99.50	2.50	8.96	1083
Co	0.2-0.5	99.00	-	8.85	1498

(a) (b) (c)

Figure 2 Scanning Electron micrographs of (a) Tungsten powder, (b) Copper powder, and (c) Cobalt powder.

It is seen that the green density shows a particular linear dependence on compaction pressure, varying from about 47.2% of theoretical density for a compaction pressure of 100MPa to about 67% of theoretical density for a compaction pressure of 300MPa.

Heckel's equation (equation 1) (Heckel, 1962) may be used for an approximate estimate of the relationship between compaction pressure and green density of metal powder compacts.

$$P = \frac{\ln\left[1/(1-D)\right]-A}{K} \qquad (1)$$

Where P = applied pressure, D= Green Density as percentage of theoretical density, K = proportionality constant related to the yield strength of the metal, and A is a material constant. Using the data obtained in this work and plotting P against $\ln\left[1/(1-D)\right]$, figure 4 below is obtained. From this plot, the values of K and A are obtained as 1.8 x $10^{-3}MPa^{-1}$ and 0.023 respectively for the pure tungsten powder used in this work.

3.3 Relative Densities of Green and Sintered Composites obtained by Liquid Phase Sintering (LPS)

The relative densities of green and sintered pure W and W-Cu composites of various compositions obtained by the LPS technique are presented in Figure 5. The green compacts were obtained using a compaction pressure of 300MPa, and were then subsequently sintered at 1200^0C for one hour.

The relative density values do not show any remarkable trend, for both the green and sintered specimens, but it is noted that the green densities (relative densities) ranged from 56% to 58%, while the

densities of the sintered specimens ranged from 90% to 93% for the W.Cu specimens of copper contents from 20%to 50%.

3.3.1 Effect of sintering temperature on density of sintered compacts.

The effect of variation of sintering temperature on the density of sintered W-Cu compacts produced using various compaction pressures is shown in figure 6.

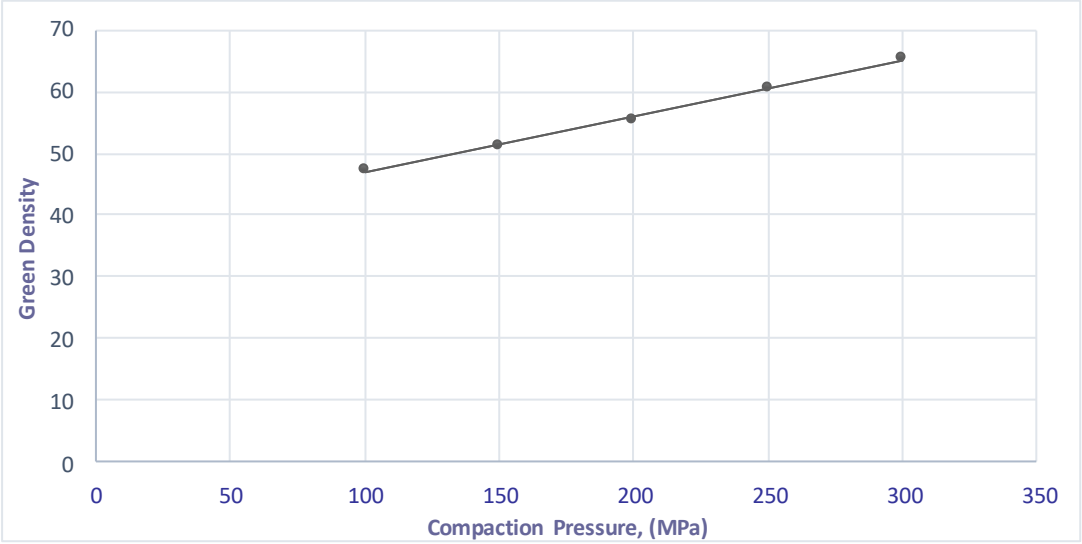

Figure 3: Effect of compaction pressure on green density of pure tungsten

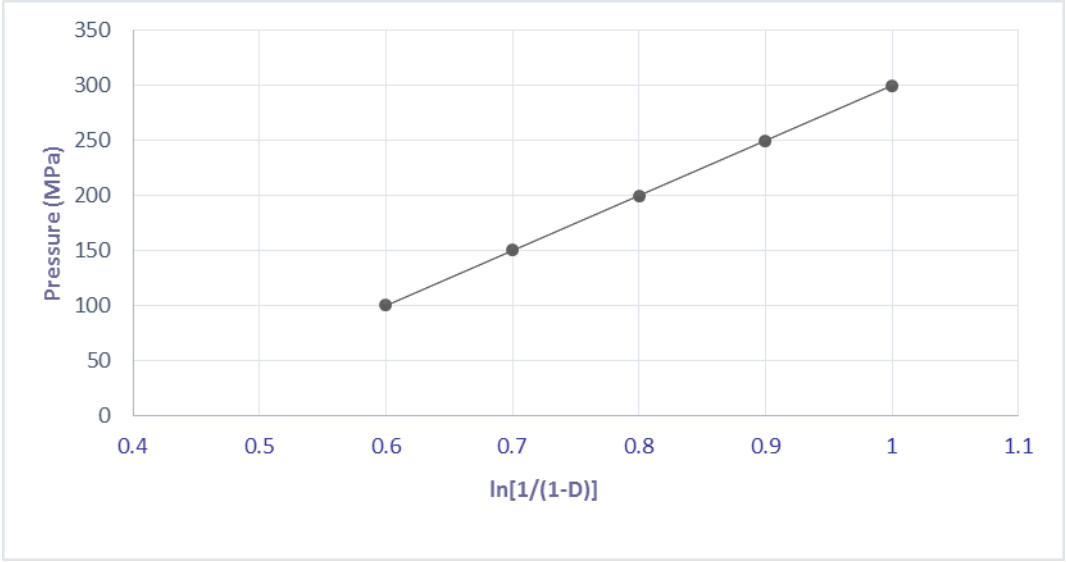

Figure 4: Plot of compaction Pressure P against ln $\left[{}^{1}/_{(1-D)}\right]$.

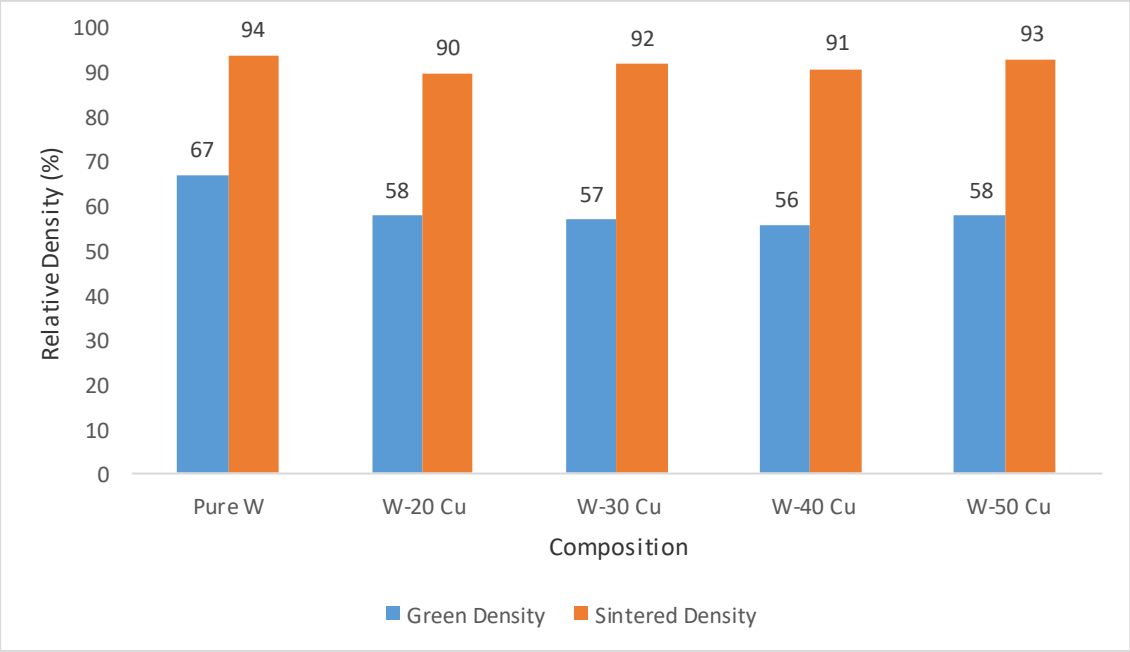

Figure 5: Green and sintered densities of pure W and W-Cu compacts of various compositions (compaction pressure = 300MPa; sintering temperature = 1200^{O}C, for 1 hour).

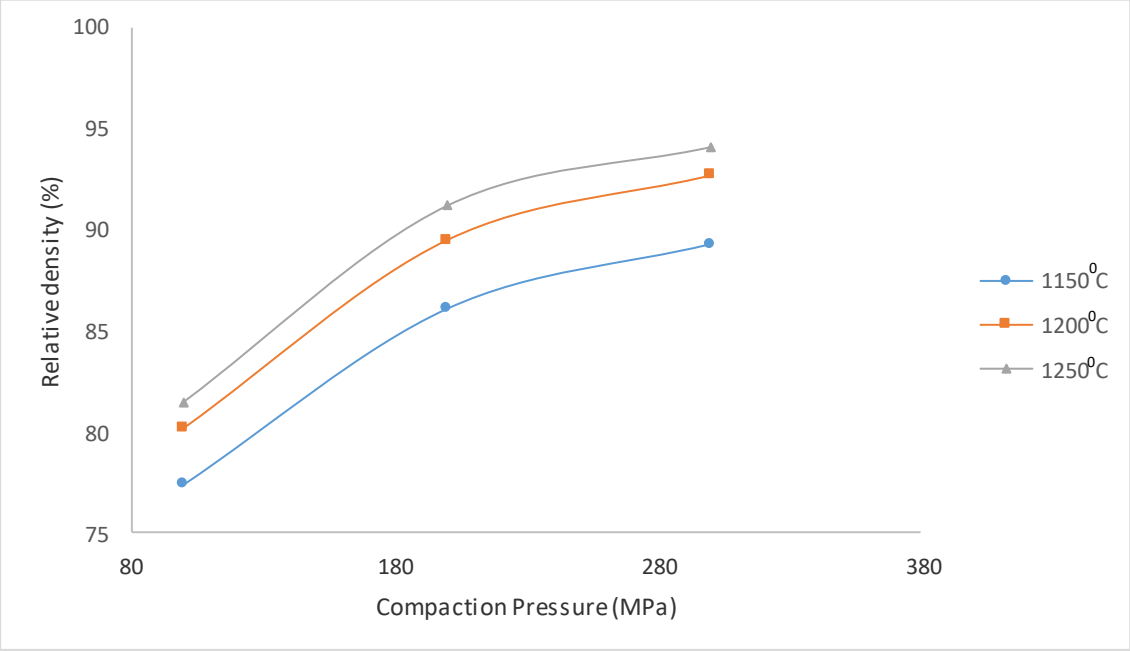

Figure 6: Dependence of relative density of sintered W-30Cu composites on sintering temperature and compaction pressure.

The figure shows that with increase in sintering temperature and compaction pressure, the relative densities of the compacts increase. The dependence of relative density on temperature is as a result of decrement in percentage porosity as sintering temperature is increased. This may be explained by considering the effect of sintering temperature on the viscosity of molten copper during the liquid phase sintering process. With increase in temperature well above $1083^{O}C$ (the melting point of copper), the copper melt becomes less viscous and flows to fill the pores in the composite mixture, with accompanying changes in specimen dimension. The wetting of the tungsten particles by the molten copper is affected by changes in the viscosity of the melt.

From figure 7, which presents the schematic of a drop of liquid material (such as molten copper) on a substrate (the solid tungsten particles), it can be seen that the contact angle Θ made by the molten metal on the substrate must be less than 90^0 for the melt to wet the substrates; otherwise there will be no wetting. From the figure, we have from resolution of forces horizontally.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \Theta \qquad (2)$$

Where γ is interfacial energy, and the subscripts SG, SL and LG stand for solid-to-gas (vapour), solid-to-liquid, and liquid-to-gas respectively. The vertical component $\gamma_{LG} \sin \Theta$ is balanced by the energy of adhesion, E_{ad}, between the molten droplet and the substrate.

Higher sintering temperatures will lower the viscosity of the molten copper, decrease the contact angle Θ, and enable the melt to flow more freely and fill the pores. Thus, higher temperatures will favour wetting of the tungsten particles, filling of porosity, and enhanced densification of the sintered compacts. However, there is a limit to the temperature level appropriate for use in liquid phase sintering. Figure 6 shows that the gain in density is far less between 1200^0C and 1250^0C than between 1150^0C and 1200^0C. This strongly suggests that beyond a certain temperature of sintering, there may be little or no further gain in density. The sensitivity of densification to sintering temperature observed here has been reported by other workers (Davis, 2001; Baker and Okamoto (1992); German and Olevsky [1998]; and Nikolic [1999]).

It is also worthy of note that the high liquid formation and rapid liquid diffusion and migration that accompany sintering at higher temperatures can result in compact shape distortion, less dimensional precision, and microstructural changes (Liu et al, 1999; Marchi et al, 2000). Another factor to consider is that without careful control of the process, gravity assisted downward flow of the molten metal may result in graded densification. Other workers (Azadbeh et al, 2011) have reported the need for careful control during their work on the sintering of Cu-20Zn brass alloyed powder compacts.

3.3.2 Effect of Cobalt Addition on Densification of W-Cu Compacts

The effect of addition of small amounts of cobalt to the tungsten on the relative density of W-Cu composite compacts is shown in figure 8, for specimens sintered at 1200^0C and 1250^0C for one hour.

The figure shows that cobalt addition substantially increases the relative density of the sintered compacts. The specimens were compacted using a compaction pressure of 300MPa, so that the results for the specimens sintered at 1200^0C may be compared with the data presented in figure 5 for the W-30Cu sintered compacts.

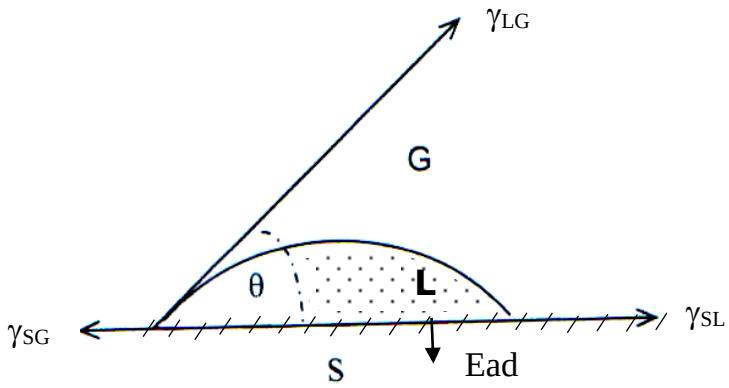

Figure 7: Schematic of a sessile drop illustrating the wettability of a substrate by a liquid droplet.

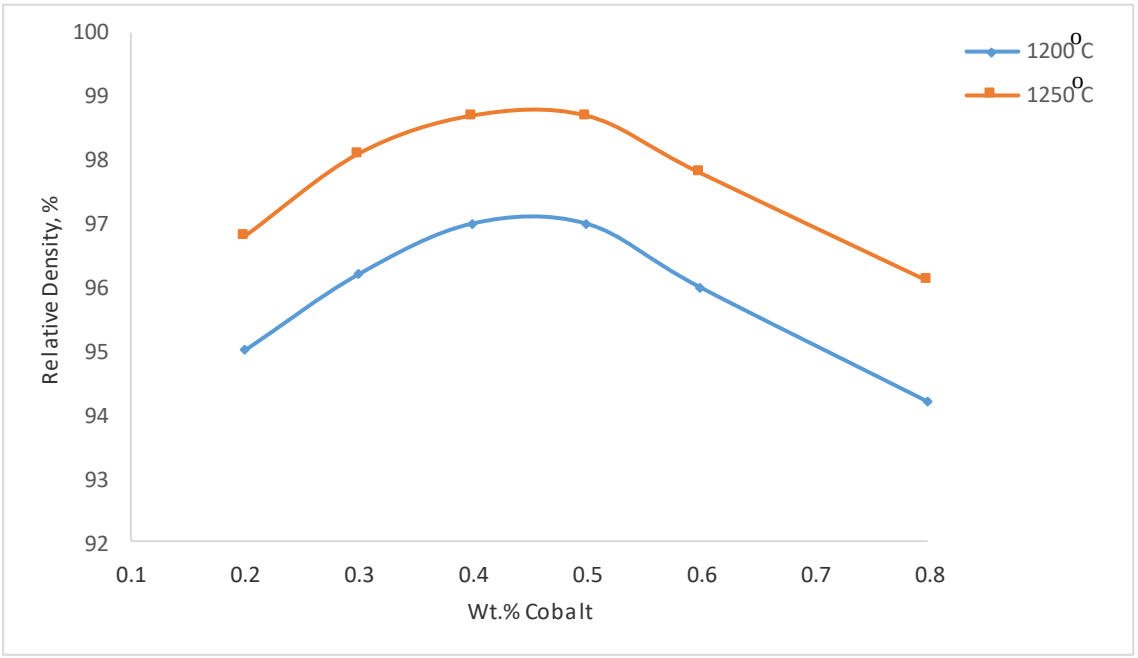

Figure 8: Effect of cobalt coating of W-particles on density of sintered W-xCo-30Cu composite compacts

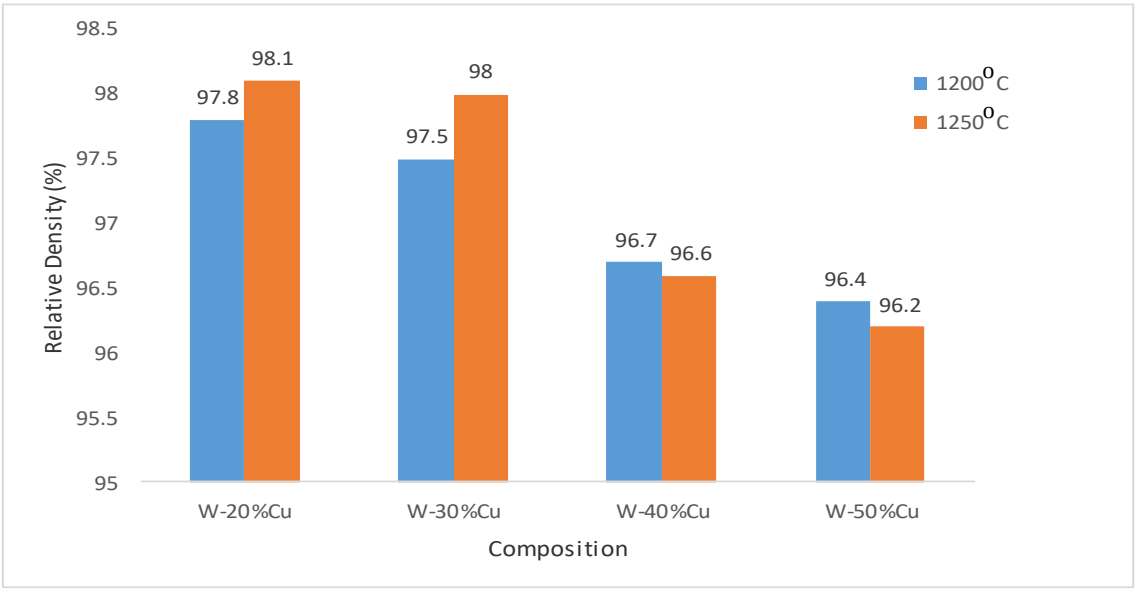

Figure 9: Relative Densities of infiltrated W-Cu specimens versus composition for infiltration temperatures of 1200^{0}C and 1250^{0}C.

Whereas figure 5 shows a relative density of 92% we have in figure 8, relative densities of 95%, 96.2%, 96.8%, 97.0%, 96.0% and 94.2% for the compacts with cobalt coatings on tungsten of 0.2wt.%, 0.3 wt.%, 0.4 wt.% 0.5wt.%, 0.6 wt.% and 0.8 wt.% respectively.

The cobalt coating results in the formation of a thin film of the intermetallic compound Co_7W_6 on the tungsten particles, and this promotes the wetting of the particles by molten copper during sintering. This enhancement of wetting leads to increase in relative density. The figure shows that the optimal value of cobalt addition for the W-Cu composites is 0.45-0.5 wt%. Beyond this value, there is a decline in density, probably because the thickness of the film of the intermetallic compound has increased to the extent that there is reduction in the diffusion of the tungsten atoms to the surface of the particles where wetting by molten copper takes place. This report is in agreement with other reports in the literature (Moon and Retzow, 1998). From their work on cobalt additions to tungsten-silver (Ag-W) composites, however, Es-Saheb et al (2015) have reported that the optimal addition of Co for activated sintering of the system is about 0.3 wt. % cobalt.

3.4 Relative Densities of W-Cu Composites Obtained By The Infiltration Process.

The values of the relative density of specimens infiltrated with 20 wt.%, 30 wt.%, 40wt.% and 50 wt.% copper are presented in fig 9.

The Figure shows a definite trend with relative density values decreasing as the weight percent copper in the specimen increases. This behaviour differs markedly from that shown in Figure 5 for liquid phase sintered specimens. Whereas the relative densities obtained for the W-20Cu, W-30Cu, W-40Cu and W-50 Cu specimens are 90%, 92%, 91% and 93% respectively for the specimens obtained by liquid phase sintering at 1200^0C, the corresponding values for the specimens obtained by infiltration are 97.8%, 97.5%, 96.7%, and 96.4% respectively. These results show that the infiltration process results in significantly better densification than the LPS process. Figure 9 also shows the effect of an increase in infiltration temperature (from 1200^0C to 1250^0C) on the relative densities of the specimens.

The effect of cobalt-coating of the tungsten particles has been presented in section 3.3.2 and figure 8, for the LPS process. Clearly, cobalt-coating will result in relative intensities well above 98.0% for the infiltration process.

The need for good wetting of the tungsten particles and for selection of appropriate sintering temperature is important in infiltration just as it is in the LPS process. Consideration must be given to the melt viscosity (at the selected temperature) and capillary flow of the melt in both cases, but this is much more important in the case of infiltration. In the LPS process, molten copper evolves from copper powder particles located more or less evenly throughout the volume of the compact, and flows to fill neighbouring voids. This results in re-orientation of the solid particles of tungsten, and a net change in dimension of the composite compact. In infiltration, little or no dimensional change of the porous sintered skeleton is expected, but considerable capillary pressure is required to draw the molten copper over long distances to fill the inter-connected porosity in the already sintered skeleton. The need for a threshold capillary pressure requirement is supported in the literature (Fletcher et. al 1990); Maxwell et al. (1990); Mortensen and Cornie (1987); and Mortensen and Wong (1990). In the present work, no pressure was used to support or assist the infiltration process because of the excellent wettability of tungsten by molten copper.

4.0 CONCLUSION

From the results and discussion presented above, the following conclusions may be drawn

1) The infiltration process results in significantly better densification of the sintered W-Cu composites than the liquid phase sintering (LPS) process.
2) In both the infiltration and LPS processes, there is need for careful consideration of factors such as wettability, sintering temperature, and infiltration temperature and time.
3) For the W-Cu system, a high sintering temperature within the range 1200^0C to 1300^0C is recommended. The higher the sintering temperature (within this range) the more efficient will be the densification.
4) Cobalt coating of the tungsten particles prior to sintering results in enhanced wetting and densification.
5) Generally, the infiltration process will often require the application of capillary pressure to draw the molten metal down through the sintered metal skeleton to fill the inter-connected pores.

REFERENCES

Azadbeh M., Danninger H., and Gierl C, "Euro PM 2011 International Powder Metallurgy Congress and Exhibition", European Powder Metallurgy Association, 2011.

Baker, H., and Okamoto H., "ASM Handbook, Vol. 3, 'Alloy Phase Diagrams'" ASM International, Materials Park, Ohio, 501, (1992).

Davis, J.R., "Copper and Copper Alloys", Materials Park, Ohio, ASM Specialty Handbook (2001).

Es-Saheb, Mahir; Azhar Shahid M; and Khan, Sohail M.A., "Effect of Co addition on the Densification Behaviour of Ag-W composite Powder Compacts at various sintering Temperatures". International Conf., Data Mining, Civil and Mechanical Engineering (ICOMCME, 2015), Bali, Indonesia, Feb. 1-2, (2015).

Fletcher T.R., Cornier J.A. and Russell K.C., in "Proceedings of Innovative processing of Inorganic composites", TMS Fall Meeting, Detroit (1990).

German, R.M. and Olevsky, E.A., "Modeling Grain Growth dependence on the Liquid content in liquid phase sintered materials", Metall. Mater, Trans. A, 29, 3057 (1998).

Heckel, R.W., "A normalized density-pressure curve for powder compaction", Trans. Met, Soc., AIME, 884, 1073 – 1074 (1962).

Liu J., Lal A., and German R.M., "Densification and Shape Retention in Supersolidus Liquid Phase Sintering", Acta Mater, 47, 4615 (1999).

Marchi C.S., Felbarbaum L., and Mortensen A, "The Effect of Gravity on Solution Precipitation during Liquid Phase Sintering", Metal Mater Trans. A. 31, 397, (2000).

Maxwell P.B., Martins G.P., Olson D.L. and Edwards G.R., Metallurgical Transactions, 21B, pp. 475 (1990).

Moon, L.H. and Retzow, G., "Full Densification of Loosely-packed W-Cu Composite Powder", Powder Metallurgy, No. 1, p.51 (1998).

Mortensen A. and Wong T., Metallurgical Transactions, 21A, pp. 2257 (1990)

Mortensen A., and Cornie, J.A., Metallurgical Transactions, 18A, pp. 1160 (1987).

Nikolic, Z.S., "Computer Simulation of Grain Growth by Grain Boundary Migration during Liquid Phase Sintering", J. Mater, Sc., 34, 783 (1999).