EFFECT OF COATING AND ACTIVATORS ON SINTERING OF W-Cu ALLOYS

A. Upadhyaya, C. Ghosh

Abstract

This study investigates the effect of Ni and Co addition on the sintering of W-Cu alloys sintered at temperatures ranging from 1000 to 1400°C. Tungsten-copper alloys containing 10, 25, and 40 weight percent copper were prepared by mixing and by coating route. Owing to lack of solubility of tungsten in copper, it is very difficult to achieve full density during sintering in W-Cu alloys having starting W powder size ≥ 4 μm. The role of transition metal elements Ni and Co in activating the densification during sintering has been critically examined vis a vis the solubility effects.

Keywords: coating, densification, liquid phase sintering, W-Cu alloys

INTRODUCTION

In recent years, considerable attention has been directed to the thermal management materials for microelectronic applications [1-3]. The requirement for such high performance materials is necessitated due to the miniaturization of the semiconductor devices, which imposes restriction on convective cooling media [4, 5].

The high heat generated in the limited cross-section area requires heat dissipation in a predominantly conductive mode through the surrounding thermal management device. Thus, for better heat dissipation, materials that offer a combination of high thermal conductivity (>200 W/mK) and low thermal expansion coefficient

($<7 \times 10^{-6}$/K) matching that of the Si-chip are required [6, 7]. It is very difficult to achieve this combination through monolithic materials and therefore composite/alloy design is desired [8]. Tungsten-copper alloys are such candidate materials for these applications wherein the high thermal conductivity of Cu dissipates heat and the low thermal expansion coefficient of the W-skeletal structure provides the hermetic sealing between the microelectronic circuitry and the heat sink.

Because of the refractory nature of tungsten (m.p. 3420°C), W-Cu alloys are fabricated by powder metallurgy (P/M) route. One such variant involves infiltration of Cu-melt into partially sintered tungsten powder compacts having interconnected porosity [9-11]. Alternatively, the W and Cu powders are mixed together and shaped by either pressing the compacts or by powder injection molding (PIM) [12, 13]. The latter is employed for complex shaped components and/or when finer powders are used, which pose problem during compaction [14]. The as-pressed or as-molded compacts are subsequently sintered. The W-Cu alloys are typically liquid phase sintered. The relatively lower fusion temperature of copper (1083°C) coupled with its good wetting behaviour towards W makes W-Cu alloys amenable to liquid phase sintering [15]. Conventionally, rearrangement and solution-reprecipitation processes are predominant mechanisms that lead to densification

Anish Upadhyaya, Chiradeep Ghosh, Materials & Metallurgical Engineering Indian Institute of Technology, Kanpur, INDIA

during liquid phase sintering [16]. However, there is no intersolubility between tungsten and Cu in both solid and liquid-state [17]. Hence, solution-reprecipitation is non-existent in W-Cu alloys. This puts constraint on achieving full density in W-Cu system. Another processing difficulty during liquid phase sintering is the sensitivity of Cu-melt wetting tungsten to the oxygen content. Huppmann and Riegger [18] have shown that the wetting angle of Cu-melt in the W-Cu system may vary from 8° to 85°. Consequently, densification in the W-Cu system through capillary stress-induced rearrangement is highly dependent on the purity of powders and of the atmosphere [19, 20]. To achieve full densification, the W-Cu alloys are milled or very small W particle size is used to enhance the solid-state densification [21, 22]. Researchers have used sub-micron to nano-sized tungsten powders for this [19, 23]. Another variant of the P/M processing involves using WO_3 and CuO as starting powders, which are milled together. Subsequently, the powders are co-reduced and sintered to near full density [23-25].

An alternate approach for attaining full density in W-Cu alloys is by adding small quantities of transition elements, such as Ni, Fe, Co, and Pd [26-29]. These additives either segregate at the W-W grain boundary, forming intermetallic phases at the grain boundaries, or dissolve in the Cu-melt, thereby providing a short-circuit diffusion path.

For optimum properties, W-Cu must contain about 20 to 60 (vol.%) of copper [4]. A high volume fraction of Cu in turn results in inhomogeneous microstructure and restricts rearrangement, which further limits densification. One of the objectives of this research is to investigate the effect of Cu content on the densification of W-Cu alloys both during solid-state as well as liquid phase sintering. Özkal *et al.* [30] chemically coated the tungsten powder with copper to further enhance densification. This study investigates the effect of Ni and Co additions on the sintering response of both uncoated and coated W-Cu alloys.

EXPERIMENTAL PROCEDURE

The W powder (grade: M55), supplied by Osram Sylvania (Towanda, PA, USA) was manufactured by reduction and had an average size of 5.4 μm with minimum and maximum size of 4.3 and 5.7 μm, respectively. The Cu powder (grade: 635) was supplied by ACuPowder International (Union, NJ, USA). The Cu powder was prepared by gas atomization and had a rounded shape with the average size of 13 μm in as-received condition. Figure 1 shows the SEM micrograph of the Cu powder.

In the present study W-Cu alloys containing 10, 25 and 40 wt.% Cu were investigated. In one set of experiment, the compositions were prepared by mixing the constituent W and Cu powders in requisite proportion for 30 min in a Turbula mixer.

In the second set, the same compositions were prepared by chemically coating copper on to the tungsten powders so as to yield the required composition [30]. The coated powders were supplied by Osram Sylvania Ltd. The details of the coating process are summarized elsewhere [30-32]. The W powder was first coated with $CuCl_2$ to the requisite requirement. The solution is then dried by baking. The $CuCl_2$ coated W powder is then reduced in a fluidized bed. Figures 2a and 2b show the SEM micrographs of W and W-10Cu (coated powders). The W powder shows a faceted, polygonized morphology, whereas that coated with Cu shows a relatively more rounded surface.

The powders were compacted at 200 MPa using a 20-ton uniaxial hydraulic press (Apex Construction Ltd., UK). To facilitate pressing, zinc-stearate was used as die-wall lubricant. The compacts were pressed in cylindrical pellet form with diameter of 12.7 mm and height of about 5 mm. Both the coated and uncoated compositions resulted in similar green density [33]. The green density of the W-Cu compacts was found to increase slightly

with increasing Cu content. The W-10Cu compacts had a green density of 57% of the theoretical, whereas the W-40Cu compacts were pressed to 62% of the theoretical density.

In a separate set of experiment, Ni and Co was added to both the coated and the uncoated (as-mixed) powders. The activator amount was restricted to 1 wt.%. The Ni and Co was blended with W-Cu powder mixture using Turbula mixer.
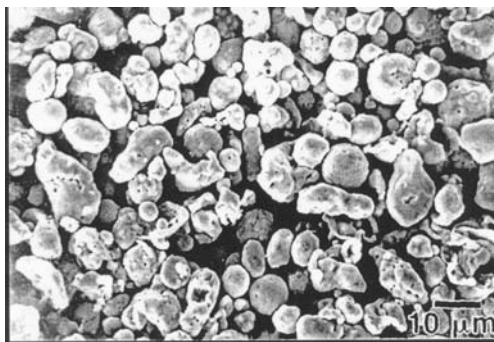

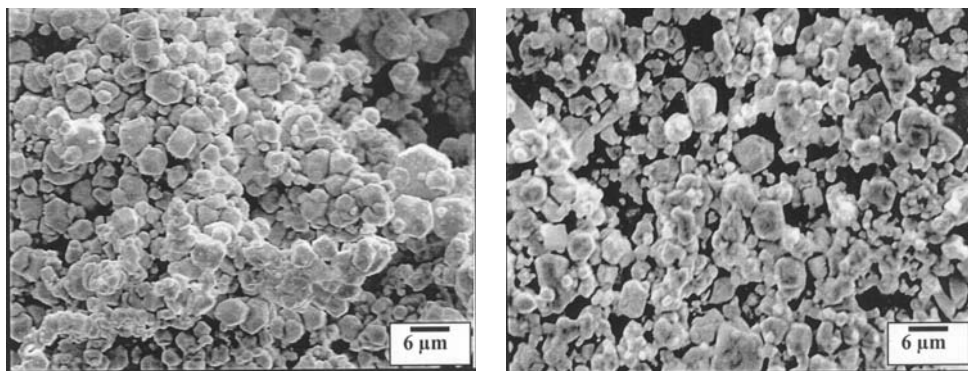Fig.1. SEM micrograph of the Cu powder in as-received condition.

Fig.2. Micrograph of (a) W powder and (b) W powder coated with Cu (W-10Cu).

The W-Cu compacts were solid-state sintered at 1000°C. Liquid phase sintering of the compacts was carried out 1200°C and 1400°C. Sintering was done in a super-Kanthal heated tubular furnace (model: OKAY 70T-4) supplied by Bysakh & Co., Kolkata, India. The furnace had an alumina muffle of diameter 7.5 cm. The sintering was done in hydrogen (dew point: -35°C). The flow rate of hydrogen was maintained at 1 liter/min. The compacts were heated at 5°C/min and the samples were held at the sintering temperatures for 60 min. Subsequently, the samples were furnace cooled.

The sintered samples were quantified for density, hardness, and electrical conductivity. The hardness measurements were performed at 5 kg load using a Leco hardness tester (model: V-100-C1). The electrical conductivity of the sintered samples was measured using conductivity-meter (model: 757) supplied by Technofour Ltd., Pune, India. The conductivity was measured relative to that of an international annealed copper standard (IACS).

RESULTS

Densification Behavior

Figures 3a to 3c show the variation in the density with varying Cu content and sintering temperature for coated as well as uncoated W-Cu alloys without activators; and with Co and Ni as activators, respectively.
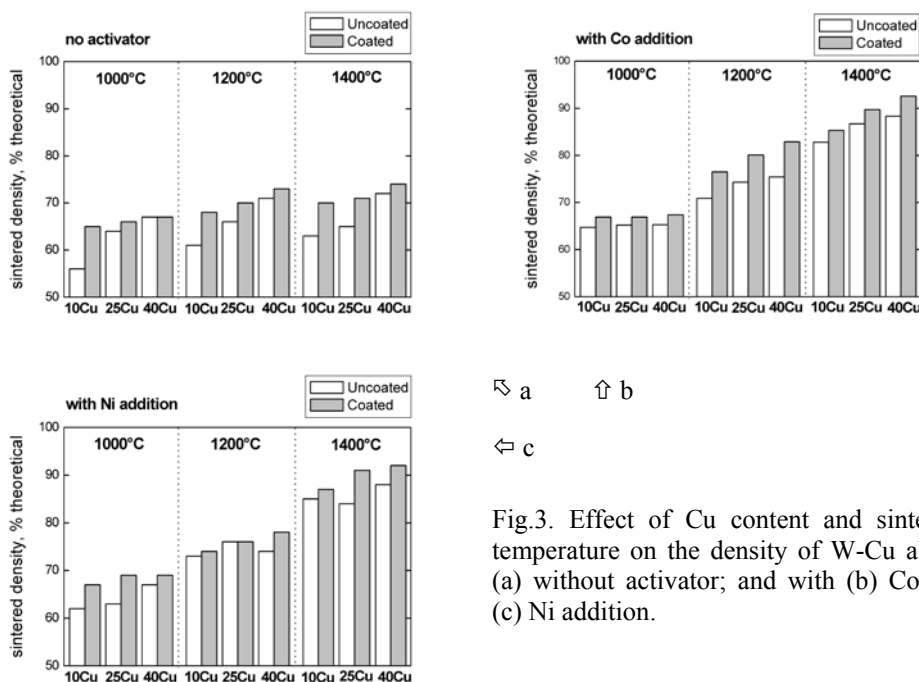
⬊ a   ⇧ b

⇦ c

Fig.3. Effect of Cu content and sintering temperature on the density of W-Cu alloys (a) without activator; and with (b) Co and (c) Ni addition.

From Fig.3, it is obvious that an increase in the copper content and an increasing sintering temperature enhances the density of W-Cu alloys. In addition, for both solid-state (1000°C) as well as liquid phase sintering conditions (1200 and 1400°C), coated powders give marginally higher densification.

From Fig.3b, one can infer that 1wt.% Co addition has limited effect on densification enhancement in solid-state sintering condition (1000°C). However, Co acts as a potent activator in enhancing the densification of W-Cu alloys during liquid phase sintering at 1200 and 1400°C. The density enhancement due to Co addition is more in coated samples and increases with increasing Cu content and increasing temperature.

Figure 3c shows the sintered density variation with Cu content, coating, and temperature in W-Cu alloys with Ni addition. The trend with Ni-addition is similar to W-Cu samples with Co (Fig.3b). As in the previous case, Ni too enhances the sintered density in W-Cu alloys irrespective of the Cu content. As compared to the uncoated samples, the Ni-containing coated W-Cu alloys undergo higher densification during sintering.

Hardness

Figures 4a to 4c compare the effect of activator addition on W-Cu alloys with varying Cu contents on the hardness at 1000°C, 1200°C, and 1400°C, respectively. For all

compositions, the hardness of the compacts increases with increasing sintering temperature. However, for a particular sintering temperature, the hardness decreases as the Cu content is increased, irrespective of the activator addition. As compared to the uncoated samples, the coated samples in general have a marginally higher hardness. It is interesting to note that for both coated and uncoated samples, addition of activators significantly enhances the hardness. The positive role of activators in hardness enhancement is more pronounced during liquid phase sintering (1200°C and 1400°C).


↘ a   ⇧ b

⇦ c
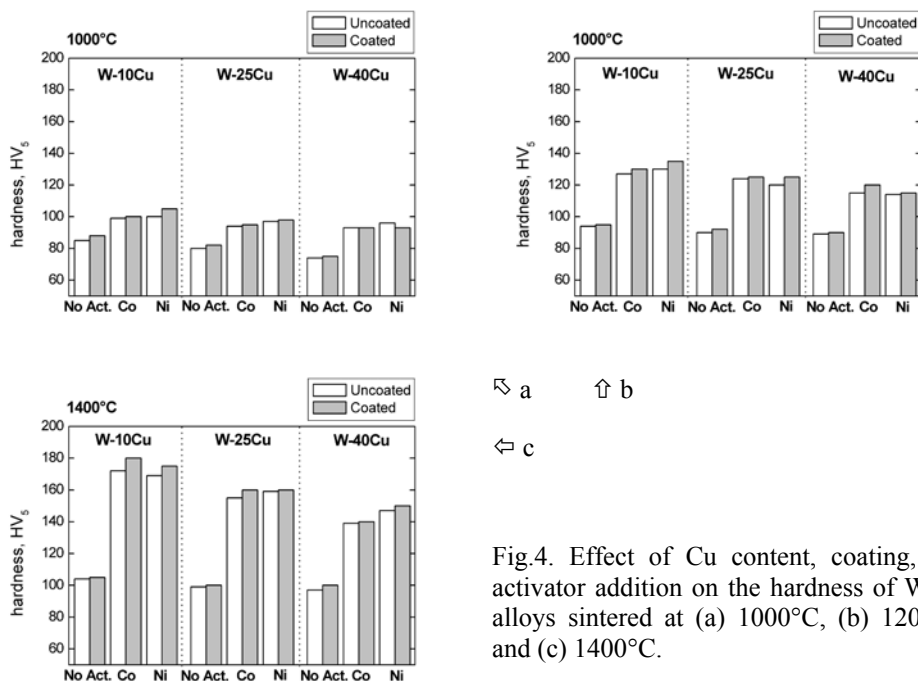
Fig.4. Effect of Cu content, coating, and activator addition on the hardness of W-Cu alloys sintered at (a) 1000°C, (b) 1200°C, and (c) 1400°C.

Electrical Conductivity

Figures 5a to 5c compare the effect of activator addition on the electrical conductivity of W-Cu alloys sintered at 1000°C, 1200°C, and 1400°C. For all conditions, the conductivity of the coated samples is higher than that of uncoated ones. The electrical conductivity of both coated and uncoated W-Cu compacts increases with Cu content and sintering temperature. As compared to the uncoated W-Cu alloys, no discernible trend in conductivity was observed by additions of Ni and Co activators.
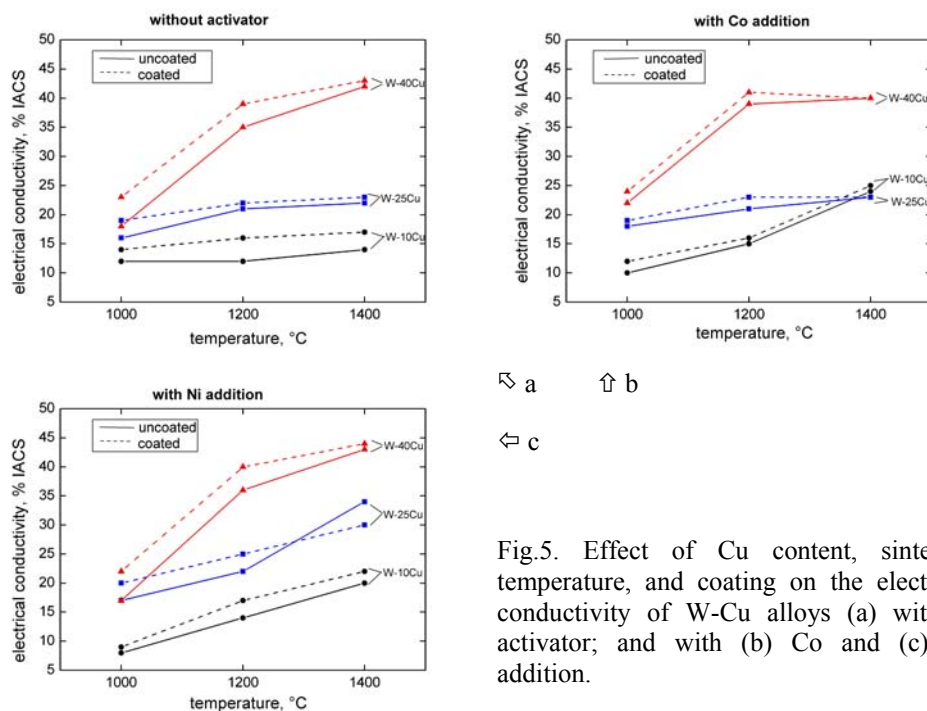
Fig.5. Effect of Cu content, sintering temperature, and coating on the electrical conductivity of W-Cu alloys (a) without activator; and with (b) Co and (c) Ni addition.

DISCUSSION

The average tungsten powder size used for the present investigation varied between 5 to 8 μm. For such sizes, the W-Cu compacts normally do not undergo much densification in either coated or uncoated forms, even when sintered up to 1400°C. In fact, there is not much difference in the sintered density of W-Cu compacts when sintered at solid-state (1000°C) and liquid phase (1200 and 1400°C) conditions (Fig.3a). This is in line with the reported observations in the literature [34,35]. The negligible solubility of tungsten in copper obviates solution-reprecipitation as densification mechanism. Hence, densification occurs predominantly by solid-state sintering and capillary-induced rearrangement of tungsten grains during liquid phase sintering [20]. Rearrangement will be more pronounced in case of coated alloys because of homogeneous melt distribution. As indicated in Fig.3, coated W-Cu samples always yield higher sintered density as compared to their uncoated counterparts. Elsewhere, Özkal *et al.* [30] too reported similar observation.

The coated W-Cu alloys result in higher sintered density even with Ni and Co activator addition. Figure 6 compares effect of activator addition and coating on the density of W-10Cu and W-40Cu compacts solid-state sintered at 1000°C. For lower Cu content, the coated sample with activator gives higher sintered density as compared to uncoated ones. For W-10Cu, Ni and Co addition does not appreciably contribute towards densification at 1000°C. In contrast, the uncoated W-10Cu samples show significant densification enhancement by Ni and Co addition. This can be inferred by the interaction mechanism of Ni and Co with the W-Cu system. .Cobalt has little solubility in Cu and negligible solubility in W. Consequently, cobalt enhances the density of tungsten compacts by segregating at the W-W interface and by forming an intermetallic phase (Co_7W_6) which

provides short-circuit diffusion path [29]. However, in case of coated samples, cobalt does not come in contact with tungsten and has therefore no effect on densification (Fig.6). Addition of less than 1 wt.% Ni has shown to result in full densification of W compact even when sintered below 1500°C [34,36]. This has been attributed to the very low solubility of Ni in W. Thus, Ni which remains segregated at the W-W particle interface provides a short-circuit path for enhanced diffusion during sintering. For W-Cu alloys though, the mechanism of densification enhancement by Ni addition is different. Nickel has complete solid-solubility with copper. Hence, during sintering, rather than remaining segregated at the W-W interface, Ni preferentially forms solid-solution with Cu [37]. At the sintering temperature, W has limited solubility in the Cu-Ni matrix which depends on the Ni content [38-40]. This leads to solution-reprecipitation mechanism during sintering which enhances densification. In case of uncoated samples, it is likely that there are some W-Co and W-Ni contact surfaces initially which contribute to densification enhancement. Of course, as the sintering progresses, Ni dissolves into Cu, whereas Co remain segregated. This explains the higher sintered density with Co addition in uncoated W-10Cu as compared to Ni addition.
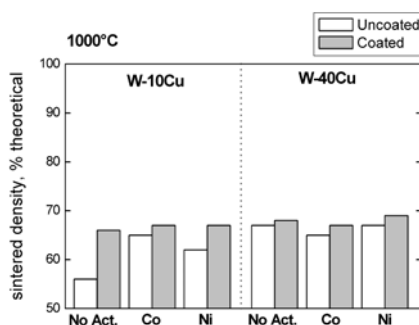

Fig.6. Effect of activator addition on the sintered density of coated and uncoated W-10Cu and W-40Cu alloys. The compacts were solid-state sintered at 1000°C.
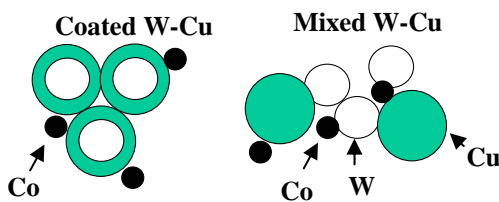

Fig.7. Schematic representation of the effect of Co-activator addition on the microstructural evolution of coated and uncoated (mixed) W-Cu alloy. The sketch shows the configuration W, Cu, and Co in green condition. As sintering progresses, Co remains segregated at the W-W and W-Cu particle interfaces.
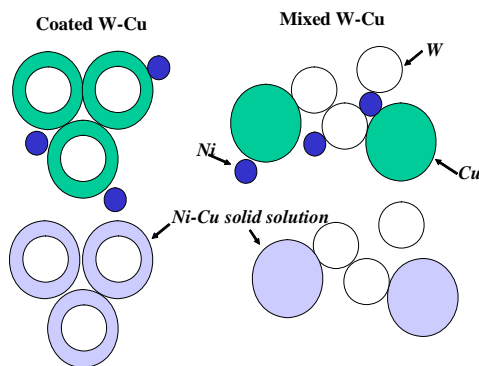
Fig.8. Schematic representation of the effect of Ni-activator addition on the microstructural evolution of coated and uncoated (mixed) W-Cu alloy. The sketch shows the configuration W, Cu, and Ni in (a) green condition and (b) prior to melt formation. As sintering progresses, Ni preferentially forms solid-solution with Cu.

The probability of W-Ni or W-Co contacts being formed is reduced as the Cu content increases. Consequently, at 1000°C, there is no significant effect of either activator in both coated as well as uncoated W-40Cu alloy, as shown in Fig.6. Figures 7 and 8 schematically show the effect of Co and Ni addition, respectively, on the microstructural evolution in both coated and uncoated W-Cu alloys.

Figure 9 compares the effect of activator addition and coating on the sintered density of W-10Cu alloys liquid phase sintered at 1200°C and 1400°C. As shown in Fig.9, when liquid phase sintered at 1200°C, Ni and Co significantly enhance densification in both uncoated as well as coated compacts. For coated W-10Cu, Co is a better activator, whereas, Ni addition leads to more densification enhancement for uncoated ones at 1200°C. At 1400°C, the potency of both the activators becomes even more pronounced with Ni being a better activator in both coated as well as uncoated conditions.
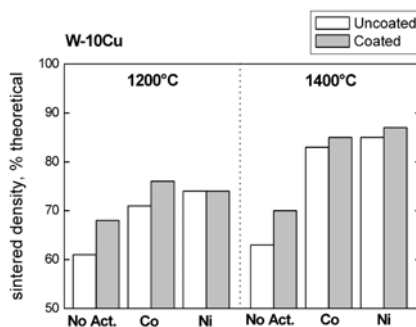

Fig.9. Effect of activator addition on the sintered density of coated and uncoated W-10Cu alloys. The compacts were liquid phase sintered at 1200°C and 1400°C.

Besides the wetting angle, dihedral angle is another parameter that influences the densification behavior during liquid phase sintering [41]. The dihedral angle represents the

balance between the solid-solid and solid-liquid interfacial energies; and is also expressed as the interparticle neck size to the grain size ratio. The higher the dihedral angle, the larger is the interparticle neck size that forms. The W-Cu system has a high dihedral angle ranging between from 85 to 95° [42,43]. In case of uncoated W-Cu compacts prepared by mixing the constituent powders, prior to Cu-melt formation, the W-W particle contacts will form by solid-state sintering. Because of the high dihedral angle the network of W-W interparticle contacts remain stable even on Cu-melt formation. Figures 10a and 10b show the SEM micrograph of W-40Cu alloy sintered at 1400°C for 1h [20]. The Cu has been selectively dissolved chemically to reveal the interconnected W-W skeletal structure. The network of W grains form a contiguous structure. It has been shown that because of the high dihedral angle the W-Cu compacts with up to 80 vol.% of Cu can be liquid phase sintered without distortion [44-46]. However, the conditions that promote structural rigidity hinder densification through capillary-induced rearrangement [47].
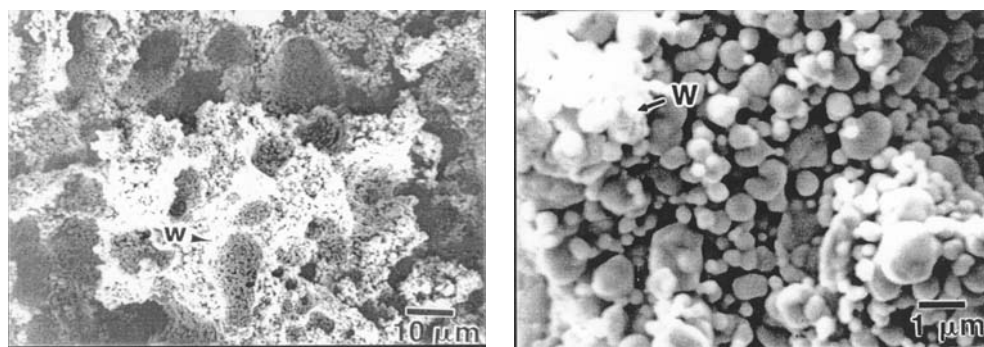

Fig.10. SEM micrographs of W-40Cu alloy at (a) low and (b) magnifications. The alloy was liquid phase sintered at 1400°C for 1h. The Cu has been chemically dissolved to reveal the contiguous W-W skeletal structure.

Figure 11 shows the schematic microstructure of coated W-Cu alloy in unsintered and liquid phase sintered condition. Initially, the Cu-coated W powders correspond to a zero-degree dihedral angle configuration. This condition persists till melt formation. When the coated W-Cu compacts are liquid phase sintered, the Cu-melt will retract partially from the W surface in order to attain the non-zero dihedral angle configuration. Eventually, the microstructure of liquid phase sintered coated W-Cu compacts will become similar to that of uncoated (mixed) compacts. Nickel addition to the W-Cu system reduces the dihedral angle [44-45]. However the amount of Ni relative to Cu is too low to cause any significant reduction in the dihedral angle. Unlike Ni, Co addition is not expected to have any effect on the dihedral angle as it is not soluble in either W or Cu. However, Co does indeed segregate at the W-W interface and forms an intermetallic phase (Co_7W_6) [29]. The critical content of Co required to form this intermetallic phase and whether or not Co_7W_6 -if it forms- occurs as a continuous thin layer will influence the dihedral angle of W-Cu system. Elsewhere, in hardmetals, Henjered *et al.* [48] have shown a continuous sub-monolayer of Co segregated at the WC grain boundaries using high-resolution microanalytical techniques. Similar in-depth studies are required to understand the nature of segregation of Co at the W-W interface and its effect thereof on the dihedral angle of the W-Cu system.
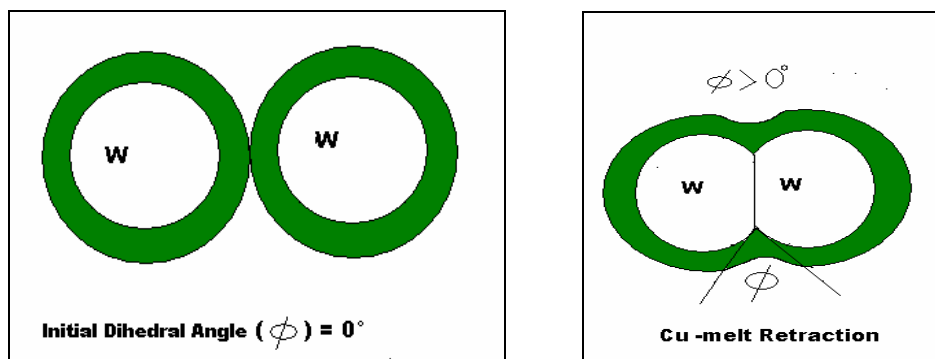
Fig.11. Schematic representation of the microstructure of coated W-Cu system (a) prior to sintering and (b) after liquid phase sintering. The high dihedral angle in W-Cu system favors Cu-melt retraction, thereby reducing the effective coverage of Cu on to W-grains and favoring W-W contacts.

The lower sintered density of uncoated W-Cu sample can also be attributed to the disparity in size and size distribution of Cu powder relative to W, which causes inhomogeneous melt formation. During liquid phase sintering, the Cu-melt diffuses into the smaller pore regions and leaves behind large pores corresponding to the prior location of coarse Cu powder. Consequently, the larger pores will be more difficult to eliminate by further sintering. Panichkina and Filipov [20]; and Upadhyaya and German [35] have reported an increase in the pore size in W-Cu compacts during sintering. Elsewhere, similar result has been shown by Debata and Upadhyaya [49] on W-Cu system containing Sn. Figure 12 compares the characteristic features between the green and sintered (at 1400°C) 80W-17.5Cu-2.5Sn alloy. In Fig.12, pores in the microstructure of green sample are smaller and are barely visible, while the sintered sample shows relatively larger pores corresponding to the location of Cu powders before melting.
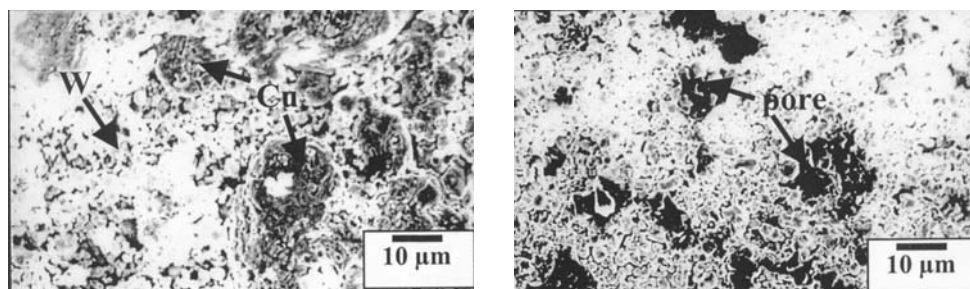

Fig.12. SEM micrographs of green and sintered (at 1400°C) 80W-Cu alloy containing 2.5 wt.% Sn. The green compact was 62% dense whereas the sintered compact had about 64% of the theoretical density [48].

The hardness of W-Cu alloys decreases with increasing Cu content which is the softer phase as compared to W. Alternatively, for a particular composition, hardness increases with increasing sintering temperature and coating, both of which result in lower porosity. Figure 13 replots the hardness of the W-Cu alloys, both with and without activators, sintered at various temperatures, as function of the sintered density. As shown in

Fig.13, the hardness increases with increasing sintered density. Thus, conditions that lead to an increase in sintered density, such as activator addition and sintering temperature increase, enhance the hardness. It is interesting to note that the W-Cu alloys without any activator addition have very little difference between their hardness. However, there is significant enhancement in the hardness with activator addition, particularly at 1200°C and 1400°C. Furthermore, irrespective of activator addition, the hardness is higher for high W-Cu alloys with lower Cu contents.
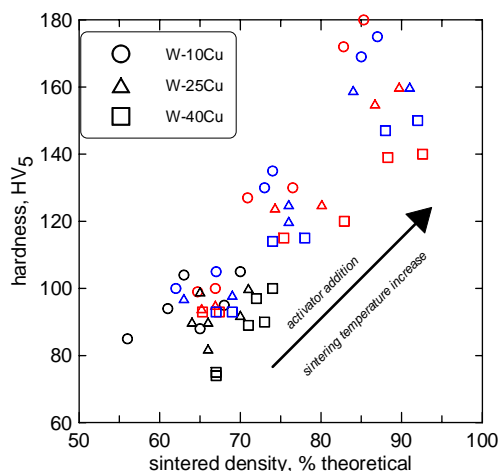

Fig.13. Variation in the hardness of W-Cu alloys with and without activator addition plotted against the sintered density. The symbols in red and blue colors signify 1 wt.% Co and Ni addition, respectively, to the W-Cu alloys.
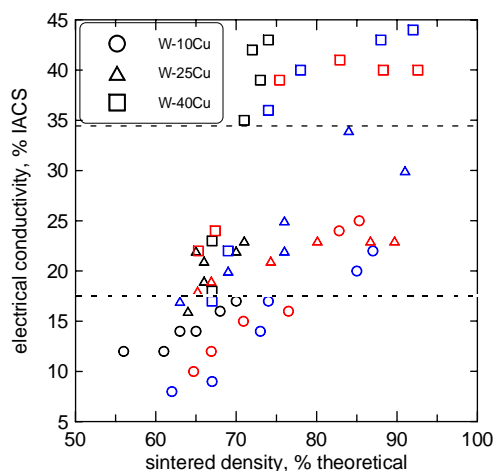
Fig.14. Variation in the electrical conductivity of W-Cu alloys with and without activator addition plotted against the sintered density. The symbols in red and blue colors signify 1 wt.% Co and Ni addition, respectively, to the W-Cu alloys.

Just like hardness, the electrical conductivity too increases as the conditions that decrease porosity prevail. In general, the electrical conductivity is directly proportion to the thermal conductivity (Wiedemann-Franz law) and the same has been shown to be valid for sintered W-Cu system as well [50,51]. In coated W-Cu alloys, there is a relatively more contiguous path of Cu-Cu contact which results in slightly higher conductivity as compared to the uncoated alloys. It has been reported that the addition of transition metal activators drastically reduces conductivity of W-Cu alloys [29,50]. However in the present study, no such trend was observed. It is likely that the decrease in conductivity is proportionately compensated by the corresponding increase in the sintered density by activator addition. This is evident by replotting the conductivity data against the sintered density (Fig.14). As shown in Fig.14, the electrical conductivity increases with increasing sintered density. Also, there seem to be three distinct regions, with the W-40Cu alloys lying in the topmost region (highest conductivity) and W-10Cu alloys being in the region with lowest conductivity. Furthermore, addition of Ni and Co activator only shifts the sintered density and does not result in much variation in the electrical conductivity.

CONCLUSIONS

This study shows that densification in W-Cu alloys increases with increasing copper content and with powder modification by coating copper on to tungsten. The W-Cu

system sinters predominantly by a solid-state mechanism, and there is not much density enhancement (over the alloys solid-state sintered at 1000°C) even when these alloys are liquid phase sintered at 1200 and 1400°C. For all cases, the coated W-Cu alloys yield higher sintered density than the uncoated ones. Significant densification enhancement occurs with the addition of Ni and Co activators. The choice of activator depends on the Cu content, state of the powder (coated *vs.* uncoated), and the sintering temperature.

Acknowledgement

REFERENCES
[1] German, RM., Hens, KF., Johnson, JL.: Int.J.Powder Metall., vol. 30, 1994, no. 2, p. 205.
[2] Kirk, TW., Caldwell, SG., Oakes, JJ.: Adv.Powder Metall., 1992, vol. 9, p. 115.
[3] Sepulveda, JL., Jech, DE. In: Tungsten Refractory Metals and Alloys- 4. Eds. A. Bose, R.J. Dowding. Princeton : MPIF, 1998, p. 393.
[4] Anon.: Int.J.Ref.Hard Metals, vol. 7, 1988, p. 134.
[5] Moon, IH., Lee, JS.: Powder Metall., vol. 9, 1977, no. 1, p. 23.
[6] Johnson, JL., German, RM.: Adv.Powder Metall., vol. 4, 1993, p. 201.
[7] Brush Wellman Engineered Materials, Tucson, Arizona, USA, www.brushwellman.com
[8] Gotoh, S., Hara, N., Kai, Y.: Nippon Tungsten Rev., vol. 28, 1996, p. 12.
[9] Lezanski, J., Rutkowski, W.: Powder Metall.Int., vol.19, 1987, no. 2, p. 29.
[10] Wang, WS., Hwang, KS.: Metall.Mater.Trans.A, vol. 29, 1998, p. 1509.
[11] Yang, B., German, RM.: Adv.Powder Metall., vol. 5, 1993, p. 105.
[12] German, RM.: Powder Injection Molding. Princeton : MPIF, 1990.
[13] Yang, B., German, RM.: Int.J.Powder Metall., vol. 33, 1997, no. 4, p. 55.
[14] Kim, JC., Ryu, SS., Lee, H., Moon, IH.: Int.J.Powder Metall., vol. 25, 1999, no. 4, p. 47.
[15] Moon, IH., Kim, EP., Petzow, G.: Powder Metall., vol. 42, 1998, no. 1, p. 51.
[16] Huppmann, WJ. In: Sintering and Catalysis. Ed. G.C. Kuczynski. New York : Plenum Press, 1975, p. 189.
[17] Subramaniam, PR., Laughlin, DE. In: Binary Alloy Phase Diagram, 2nd ed., vol. 2. Metals Park, OH : ASM, 1990.
[18] Huppmann, WJ., Riegger, H.: Acta Metall., vol. 23, 1975, p. 965.
[19] Yang, B., German, RM.: Adv.Powder Metall., vol.2, 1993, p. 203-216.
[20] Upadhyaya, A., German, RM.: Int.J.Powder Metall., vol. 34, 1998, no. 2, p. 43.
[21] Upadhyaya, A., German, RM.: Adv.Powder Metall., vol. 1, 1997, p. 7.41.
[22] Panichkina, VV., Sirotyuk, MM., Skorokhod, VV.: Sov.Powder Metall.Metal Ceramics, vol. 21, 1982, p. 447.
[23] Lee, JS., Kim, TH. In: Proc.Fourth Nisshin Engg.Particle Tech.Int.Seminar NEPTIS-

IV. Ed. K. Niihara. Osaka : Nisshin Engg.Co., 1995, p. 59.

[24] Sebastian, KV., Tendolkar, GS.: Int.J.Powder Metall., vol. 15, 1979, p. 45.
[25] Jech, DE., Sepulveda, JL., Traversone, AB.: U.S. Patent 5686676, 1997.
[26] German, RM., Ham, V.: Int.J.Powder Metall.Powder Tech., vol. 12, 1976, p. 115.
[27] Johnson, JL., German, RM.: Adv.Powder Metall., vol.3, 1992, p. 35.
[28] German, RM., Johnson, JL.: Int.J.Powder Metall., vol. 30, 1994, no. 1, p. 91.
[29] Ihn, TH., Lee, SW., Joo, SK.: Powder Metall., vol.37, 1994, no. 4, p. 283.
[30] Özkal, B., Upadhyaya, A., Ovecoglu, ML., German, RM. In: Proc.2nd Turkish National Powder Metall.Conf.. Ed. S. Saritas. Ankara : Türk Toz Metalurjisi Derneği, 2000, p. 185.
[31] Houck, D., et al.: U.S. Patents 5,439,638 (1995) and 6,103,392 (2001).
[32] Liu, L.: MS Thesis. University Park : Penn State, 1998.
[33] Ghosh, C., Upadhyaya, A.: Trans.PMAI, 2002 (in press).
[34] Johnson, JL.: PhD Thesis. University Park : Penn State, 1994.
[35] Panichkina, VV., Filipov, NI.: Sci.Sintering, vol. 20, 1994, no. 3, p. 269.
[36] Hayden, HW., Brophy, JH.: J.Electrochem.Soc., vol. 110, 1963, p. 805.
[37] Johnson, JL., German, RM.: Adv.Powder Metall., vol. 3, 1994, p. 267.
[38] Eremenko, VN., Minakova, RV., Churakov, MM.: Sov.Powder Metall.Metal Ceram., vol. 15, 1976, p. 283.
[39] Upadhyaya, A., Johnson, JL., German, RM. In: Tungsten and Refractory Metals -1995. Ed. A. Bose, R.J. Dowding. Princeton : MPIF, 1995, p. 3.
[40] Sailland, F., Chaix, JM., Allibert, CH. In: Proc.Colloq.Controlling Properties of Powder Metallurgy Parts Through their Microstructure. Paris : Societe Francaise de Metallurgie, 1990, p. 4.1.
[41] German, RM.: Liquid Phase Sintering. New York : Plenum Press, 1985.
[42] Upadhyaya, A.: MS Thesis. University Park : Penn State, 1996.
[43] Upadhyaya, A.: PhD Thesis. University Park : Penn State, 1998.
[44] Upadhyaya, A., German, RM.: Adv.Powder Metall., vol. 5, 1996, p. 18.107.
[45] Upadhyaya, A., German, RM. In: Proc.14th Int.Plansee Seminar, vol. 2. Eds. G. Kneringer, P. Rödhammer, P. Wilhartitz. Reutte : Plansee AG, 1997, p. 68.
[46] Marcondes, PVP., Upadhyaya, A., German, RM.: J.Adv.Mater., vol. 32, 2000, no. 4, p. 10.
[47] German, RM.: Mater.Trans.JIM, vol. 42, 2001, no. 7, p. 1409.
[48] Debata, M., Upadhyaya, A.: Trans.PMAI, 2002 (in press).
[49] German, RM.: Metall.Trans.A, vol. 24, 1993, p. 1745.
[50] Yang, B., German, RM.: Adv.PowderMetall., vol. 5, 1994, p. 317.