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Research Article

Sintering Characteristics of Iron and Cobalt Doped Silver-tungsten Metal-matrix Composites

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Abstract: Silver-Tungsten composites are known as electrical contact materials used in circuit breakers and industrial relays. The performance of the contact during their service life depends upon high strength and anti-weld properties of these materials. Despite their promising industrial applications, the literature dealing with their production route is still limited. Therefore, a comprehensive study exploring the structure related properties with great emphasis on the sintering process of these materials is carried out. Therefore, in this study, the successful production of a homogeneous composite powder with controlled tungsten particle size using co-precipitation and two stage reduction techniques is followed by the compaction and sintering processes. Thus, high density compacts are produced from Fe and Co doped silver-tungsten powder using powder metallurgy technique. Various environments and sintering conditions, including N_2 atmosphere and temperatures up to 1000°C, to obtain successful compacts from both doped and un-doped powders, are investigated. The morphologies and the microstructures of the sintered compacts obtained under the different sintering conditions are characterized and assessed using Scanning Electron Microscopy (SEM). Results display excellent agreement with the published studies and no evidence was found for the activated sintering of silver-tungsten by Fe additions. Also, the homogeneity of silver-tungsten in compacts is completely lost in the Fe-doped powders. However, Co additions help to facilitate the sintering between silver and tungsten whilst retaining a high homogeneity between the silver and tungsten in the sintered product.

Keywords: Ag-W composite, co-precipitation method, electrical contacts production, metal composite, sintering

INTRODUCTION

Silver-tungsten composite materials have been widely used as medium duty electrical contacts since they offer the advantages of both refractory tungsten (welding and erosion resistance) and silver (high thermal and electrical conductivities). As there is no alloying between the silver and tungsten as reported early by Hansen (1958) and Walczuk (1988) and later by Karakas (2002), Özkal (2002) and Glickman *et al*. (2003), the properties of the composites depend, in direct proportion, on their composition. A high silver content offers maximum conductivity and minimum contact resistance, while high tungsten content offers maximum resistance to arc erosion and welding tendency. So for any particular application a balance must be struck between the desirable properties of the two metals. Witter and Warke (1974) investigated the welding and erosion resistance of silver-tungsten contacts and showed them to be dependent upon particle size, morphology and distribution of the phases within the composite, with finer particles potentially giving better performance. The standard production route for these materials is either a press-sinter-infiltrate or press-sinter-repress process. In the first process, the final distribution of silver and tungsten in the finished compact is largely determined by the structure of the initial tungsten compact before infiltration with the liquid silver. Although, high density compacts can be produced by this process, it also tends to produce silver rich regions which increase the welding tendency of such contacts. Because of this limitation the second process is often used in preference for the production of contacts. In this process the distribution between silver and tungsten in the sintered compact is controlled by the mixing and sizes of the elemental powders which are used to produce the powder blend for pressing. This process is limited in the variety of microstructures that are available particularly when uniform distributions of submicron tungsten particles in a silver matrix are required, as recognized by Gáuchowski and Rdzawski (2008), Bhagat *et al*. (2008) and Bukaluk *et al*. (2008).

In previous work by Walkden and Sale (1982) on the single stage reduction of silver tungstate at high

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temperature, gross segregation of the silver phase was observed, in the early stages of reduction. To overcome this segregation problem, a controlled two stage reduction process was designed in which the first stage was carried out at low temperature (where the liberation of silver from silver tungstate occurred without the migration of the silver phase) and the second stage was carried out at higher temperature for rapid reduction of tungsten oxides (where the coalescence of the silver phase was prevented). The reduced material was then pressed and sintered below the melting point of silver in order to preserve the homogeneity and distribution of silver and tungsten. To improve the high density of the sintered product, Fe as sinter aid is used to conduct the sintering at low temperature.

Electrical contact materials: Electrical contact materials are used in different applications and the conditions under which they operate may be expected to be different, as reported by Walkden and Sale (1982), Gáuchowski and Rdzawski (2008), Bhagat *et al*. (2008) and Bukaluk *et al*. (2008). Based on such applications they can be classified into three major groups:

- **Light duty contact materials:** Usually carry current less than 1 Amp in operation. Such applications demand that the contacts are designed in such a way to keep the contact resistance to the minimum possible. Such materials are typically platinum, palladium, gold and their alloys.
- **Medium duty contact materials:** Mainly designed for domestic appliances and for industrial relays up to a size where they effectively become small contactors. These devices usually carry current between 1 and 30 A. Under such conditions they need to have a good current carrying capacity with an excellent resistance to tarnishing. Silver, its alloys and some composite materials are preferably used for medium duty applications since they have the advantages of high conductivity without oxidation. When the contacts need to withstand quite severe arcing conditions, nickel-silver and silver-cadmium oxide are normally used as contact materials.
- **Heavy duty contact materials:** Generally used in industrial and transmission switch gear, where they meet current demands in excess of 30 A. Such applications require contacts which have resistance to severe arcing and mechanical wear. Most heavy duty contacts are based on the refractory metals or their compounds, like tungsten, tungsten carbide and molybdenum.

Contact fabrication: Powder metallurgical techniques are used for the manufacture of electrical contacts which are composed of a high conductivity metal and a refractory-based metal. The starting materials for these contacts are usually silver and tungsten powders. As indicated earlier, electrical contacts are produced by press-sinter and press-sinter infiltrate routes. These production routes may require different powder properties and compositions for optimum production, e.g., in the press-sinter process a sintering aid is generally required during the sintering process. However, to obtain a uniform microstructure in the contact with a fine tungsten particle size, a lower level of sintering aid has been recommended for their fabrication as shown by Leung *et al*. (1982). The press-sinter process is usually recommended for the production of medium heavy duty contacts as it is capable of producing a contact which contains finely dispersed silver and tungsten particles but such contacts often have lower densities than those produced by the press-sinter-infiltrate route and consequently have a higher erosion rate in service. It is now generally accepted that even at a constant chemical composition, the properties of powder metal contacts depend on the particle size, morphology and uniform distribution of the refractory phase. The amount of porosity can also affect the electrical, mechanical and thermo-physical properties of the composite materials, as reported by Bevington *et al*. (1980) and earlier by Witter and Warke (1975), as well as Gessinger and Fischmeister (1972). For silver-tungsten contacts the density is often required at the highest possible value to reduce the erosion rate and prolong their service lives. Walden *et al*. (1985) have proposed a new method for the production of silver tungsten contact materials in which they reduced the silver tungstate into elemental silver and tungsten by the controlled two stage reduction process followed by activated sintering of the compact.

For sintering of refractory metal compacts small additions of group VIII elements (enough to form a few atomic layers on the tungsten particles) increase the densification rate and lower the sintering temperature to 1100°C. German and Munir (1982) postulated that activated sintering of refractory metals occurs because the additive lowers the energy barrier for atomic transportation. The lower activation energy allows increased diffusion of metal through the additive. Therefore to obtain a high diffusion rate, the additive should remain segregated at the particle-particle contact points i.e., the refractory metal is soluble in the additive and the additive is relatively insoluble in the refractory metal. Accordingly the segregated lower melting point additive provides a rapid mass transport path for the sintering process. Kuzcynski and Leszynki (1961) and Kuzcynski (1963) and later Carpay and Amer (1977), studied the mechanism of activated sintering and reported that grain growth can reduce the densification rate in many ways. Brophy *et al*. (1962) also studied the effect of Pd, Pt, Rh, Ir, Co and Fe and found that the sintering behavior of tungsten is independent of the

concentration of the added elements beyond that concentration which is required necessary to form a continuous layer on the surface of the tungsten particles. Any additions in excess of amounts necessary to form continuous layers, may lead to successively decreases in the sintering rate. Their findings also show that the sintering behavior of tungsten with additions of iron or cobalt both of which form inter-metallic compounds with tungsten, is greatly dependent on the addition concentration.

Chaoijin and German (1983) have studied the effect of various transition metal additions on the sintering of fine tungsten powder by using both isothermal and constant heating rate experiments in the temperature range 900 to 1400°C. They found that approximately four mono-atomic layers of palladium on the surface of tungsten particles were required for optimum sintering. Gessinger *et al*. (1973) studied the sintering of tungsten powder compacts with a finer particle size at 1000 and 1100°C with and without the addition of 0.5% Ni. They found a strong effect of Ni upon the sintering rate and explained this effect by assuming the Ni diffuses over the surface of the tungsten particles and accumulates at the necks between the particles. From here the Ni penetrates the grain boundaries between the tungsten particles. The presence of Ni in the grain boundaries increases the grain boundary self-diffusion in tungsten. The rate at which tungsten atoms are transported by grain boundary diffusion through the grain boundaries and deposited at the necks of the tungsten particles is much greater for Ni-doped than for un-doped tungsten and as a result more rapid densification is obtained. Chaojin and German (1983) have also studied the activated sintering of tungsten powders with the small additions of Co, Ni, Pd and Fe. They determined the effects of processing on properties such as sintered density, grain size, hardness, strength, type of activator, amount of activator, compacting pressure and sintering temperature. They found that powder compact of fine particle size gave high density at low sintering temperature and gave increased strength and hardness of the sintered compact. Their results showed that at higher temperatures Co, Ni and Pd are equally effective in promoting densification, shrinkage and hardness. German *et al*. (1983) have summarized several criteria for enhancement in the activated sintering of refractory metals with the addition of sintering activators, see also the later studies by Da Costa *et al*. (2008), Paul (2009), Songmei *et al*. (2010), Es-Saheb (2012) and Ramadan *et al*. (2012). Therefore selection of suitable additives can be achieved by the use of phase diagrams. Earlier, Walkden and Sale (1982) and Walden *et al*. (1985) and later Sale and Albiston (1989) have studied the activated sintering in silver-tungsten composites with the addition of Ni. Their investigations were mainly focused on studying the effect of tungsten particle size, its uniform distribution and the amount of activator required for optimum sintering in the silver tungsten composite powder.

Thus, in this study the main objective is the successful production of homogeneous composite powder with controlled tungsten particle size using co-precipitation and two stage reduction techniques. Therefore, to achieve this objective, wide ranges of the sintering aids Fe and Co concentration percentages of, 0.0, 0.62, 0.83, 1.55, 2.45, 3.16 and 9.73% and 0.0, 0.14, 0.28, 0.29, 0.301, 0.51 and 1.52%, respectively are investigated. Two sets of reduction temperatures, of 250 and 750°C as well as 250 and 850°C in two separate furnaces are employed to produce reduced Fe and Co un-doped and doped silver-tungsten powders. Subsequently, high density cylindrical pellets of 5 mm diameter are fabricated from these powders using powder metallurgy techniques. Axial compaction pressures of 300, 450 and 600 MPa, respectively and two sintering temperatures of 850 and 900°C for sintering time duration of 5 h under N_2 atmosphere are employed. The morphologies and the microstructures of the sintered compacts are characterized and assessed using Scanning Electron Microscopy (SEM). The details of the preparation of the materials used and the experimental techniques adopted and results discussions are given in the next sections.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Material preparation: The present study involved the use of three different types of tungstates, namely:

- Silver tungstate (Ag_2WO_4)
- Iron tungstate doped silver tungstate ($FeWO_4$ + Ag_2WO_4)
- Cobalt tungstate doped silver tungstate ($CoWO_4$ + Ag_2WO_4)

The tungstates were prepared stoichiometrically by mixing solutions of their salts (analar grade) and allowing precipitation to occur. The pure silver tungstate and doped silver tungstates were produced from the aqueous solutions of sodium tungstate, silver nitrate, iron sulphate and cobalt sulphate. On mixing these stoichiometric quantities the following reactions occurred:

$$2AgNO_3 + Na_2WO_4 2H_2O \rightarrow Ag_2WO_4 + 2NaNO_3 + 2H_2O \quad (1)$$

$$FeSO_4 7H_2O + Na_2WO_4 2H_2O \rightarrow FeWO_4 + Na_2SO_4 + 9H_2O \quad (2)$$

Fig. 1: Two stage reduction apparatus

$CoSO_47H_2O + Na_2WO_42H_2O \rightarrow CoWO_4 + Na_2SO_4 + 9H_2O$ (3)

In each case after precipitation, the tungstate or the tungstate mixture was filtered and washed with copious amounts of distilled water, in order to remove as much of the sodium salt, from the mixture as possible. The filtered precipitate of tungstate was then dried in a drying cabinet, at a temperature of 75°C for 15 h to remove the remaining water. On drying the color of the precipitate had changed due to the evaporation of the water. The iron and cobalt tungstate doped silver tungstate was produced with various doping levels. The resultant powders were analyzed and characterized before and after reduction using:

- X-Ray Diffraction analysis (XRD)
- Scanning Electron Microscopy (SEM)

Two stage reduction of tungstate: To produce large quantities of reduced powders for subsequent pressing and sintering experiments a two stage reduction process was used, Fig. 1. It consisted of two split furnaces separated from each other by an air gap. Temperature profiles for the furnaces were determined at 250-750 and 250-850°C. Several experimental variables were required to be calibrated to ensure that the conditions for solid/gas contact remained constant in subsequent experiments. These included the powder bed depth, hydrogen flow rate and time for reduction. A constant weight of powder specimen was used to minimize the differences in powder bed depth. To determine the hydrogen flow rate required for reduction in a minimum possible time, a number of hydrogen reduction experiments were performed and the obtained products, after every reduction experiment, were characterized by X-Ray Diffraction (XRD) analyses.

The method involved in the reduction process was as follows: The powder specimen (4 g) was placed in a pyrophillite reaction boat and inserted into a gas tight tubular reaction vessel. The vessel was purged with argon gas for a period of 30 min, after which the hydrogen atmosphere was established. The time for the reaction vessel to reach the reaction temperature was found to have no significant effect on the first stage reduction product. However, as the first stage of reduction allows time for the second stage temperature to be established. The first stage must be sufficiently long enough to allow this to happen. Upon completion of first reduction stage, the specimen was pushed into the second stage temperature zone using a Wilson seal arrangement. This arrangement allowed the whole process to be completed in one operation in the hydrogen atmosphere. After the period required for second stage reduction, the reaction vessel was withdrawn from the end, to increase the cooling rate. The whole apparatus was cooled down to the room temperature under flushing argon.

Pressing and sintering of reduced silver tungsten powders: Before pressing and sintering experiments, all the reduced products were characterized with XRD to ensure that the powders were completely reduced. The powder specimens were then compacted in a single action cylindrical tungsten-carbide die with diameter of 5 mm using a stainless steel collar which allowed the production of compacts of a similar length. In all cases

Fig. 2: Dilatometer

the densities were calculated by measuring the weight, the diameter and length of the compacts. The sintering experiments were carried out in a dilatometer, shown in Fig. 2, with which any linear change in the specimen is measured on heating.

The sintering experiments were commenced from room temperature to 900°C at a constant heating rate 10°C/min. Micro-structural studies were carried out on the sintered pellets. The specimens were metallographically polished following the standard procedure, to a quarter micron diamond finish. The polished specimens were then etched in 'Murakanis' reagent (a mixture of potassium ferricyanide, sodium hydroxide and water). After etching, the specimens were examined under the microscope. Optical microscopy failed to provide the evidence of tungsten-tungsten contact in the compacts as the tungsten particle size was too fine. Thus to examine the specimen Transmission Electron Microscope (TEM) is used.

RESULTS AND DISCUSSION

Silver tungstate: The analysis of the precipitated silver tungstate is made by atomic absorption spectroscopy and the molecular formula for precipitated silver tungstate (Ag_2WO_4) is obtained (Calculated Formula = $Ag_{1.96}$ $WO_{4.01}$), Azhar and Es-Saheb (2013) and Es-Saheb and Azhar (2013). It is evident from the formula that the silver/tungsten ratio is very close to the theoretical value 2:1 and the oxygen content calculated from the total mass of specimen also agrees with the theoretical value for silver tungstate. Also, the results show that iron is present in a very small amount along

Fig. 3: Precipitated form of silver tungstate Ag_2WO_4 (x5000)

with traces of impurities, including sodium, which could originate during the precipitation from the salts used in the preparation process. However, the level of Na is found to be 0.037% which is well below the acceptable range of 0.2% Na reported by Skarsted and Geller (1975) and Bottelberg *et al*. (1976).

The powders were also characterized by XRD analysis. The diffraction patterns obtained from the precipitated powders are exclusively a silver tungstate. Morphological studies of the powders were conducted using scanning electron microscope. Figure 3 shows a typical micrograph of precipitated silver tungstate Ag_2WO_4, which indicates that it's a mixture of block-like crystals and clusters of fine needles. These blocks which seem rough and have corrugated surfaces are 20 to 30 μm in length and *5* to 10 μm in thickness.

Silver tungstate doped with iron tungstate: Silver tungstate samples doped with iron tungstate were

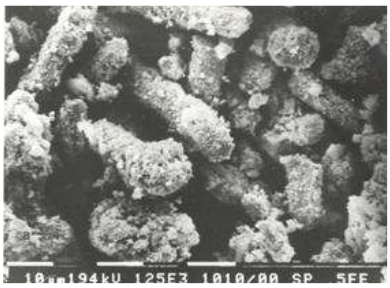


Fig. 4: Precipitated form of silver tungstate doped with iron tungstate, (0.83% $FeWO_4$ doped Ag_2WO_4)

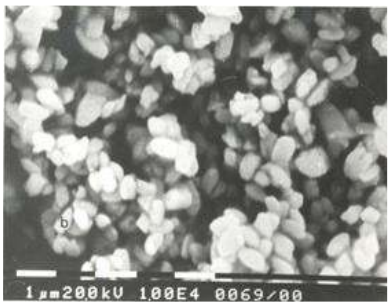
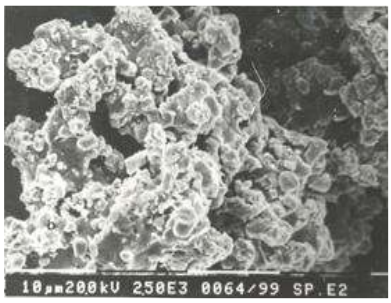


Fig. 5: Precipitated form of silver tungstate doped with cobalt tungstate, (1.52% $CoWO_4$ doped Ag_2WO_4)

prepared by co-precipitation from sodium tungstate, silver nitrate and iron sulphate solutions. The different levels of iron tungstate achieved in the composites were 0.14, 0.25, 0.35, 0.64, 1.03, 1.32 and 4.2 Wt% which may be expressed as 0.34, 0.62, 0.83, 1.55, 2.45, 3.16 and 9.73% Fe with respect to tungsten (wrt W). A typical representative micrograph of silver tungstate Ag_2WO_4, doped with iron tungstate is displayed in Fig. 4. It is noticed that with the addition of Fe the surface of the silver tungstate blocks are covered with a fine dispersion. Also, as the Fe concentration increased in the powder, the surface coverage with the fine precipitate also increased without any significant effect on the block-like morphology.

Silver tungstate doped with cobalt tungstate: Silver tungstate samples doped with cobalt tungstate were prepared by co-precipitation from sodium tungstate, silver nitrate and cobalt sulphate solutions. The various levels of cobalt concentration achieved were within the range 0.05 to 0.63 Wt% Co which could be expressed as 0.14 to 1.52% Co (wrt W). The cobalt levels produced within the powders were 0.14, 0.28, 0.29, 0.30, 0.301, 0.51 and 1.52% Co, respectively (wrt W). A typical representative micrograph of silver tungstate Ag_2WO_4, doped with cobalt tungstate is displayed in Fig. 5. It is noticed that with the addition of Co needle like crystals form which indicate a preferential growth direction. Also, as the concentration of cobalt increased to 1.52% the precipitation process was changed because of change in nucleation conditions and as a result small agglomerates of re-crystallized particles were formed.



(a)

(b)

(c)

Fig. 6: (a) Silver tungsten powder reduced from precipitated silver tungstate at 250-850°C, (b) 02.45% Fe doped Ag-W powder reduced from doped tungstate at 250°C -750°C, (c) 1.52% Co-doped Ag-W powder reduced from doped tungstate at 250-750°C

Reduction of silver tungsten, Fe-doped silver tungstate and Co-doped silver tungstate: As stated above the samples of precipitates of silver tungsten, silver tungstate doped with iron tungstate and silver tungstate doped with cobalt tungstate, produced in the previous step, are then reduced by dry hydrogen at two stages in two separate split furnaces kept at two different sets of temperatures (250-750 and 250-850°C). Morphological studies of the reduced powders were conducted using scanning electron microscope. Typical representative micrographs for the reduced silver tungsten, Fe-doped silver tungsten and Co-doped silver tungsten are displayed in Fig. 6a to c, respectively.

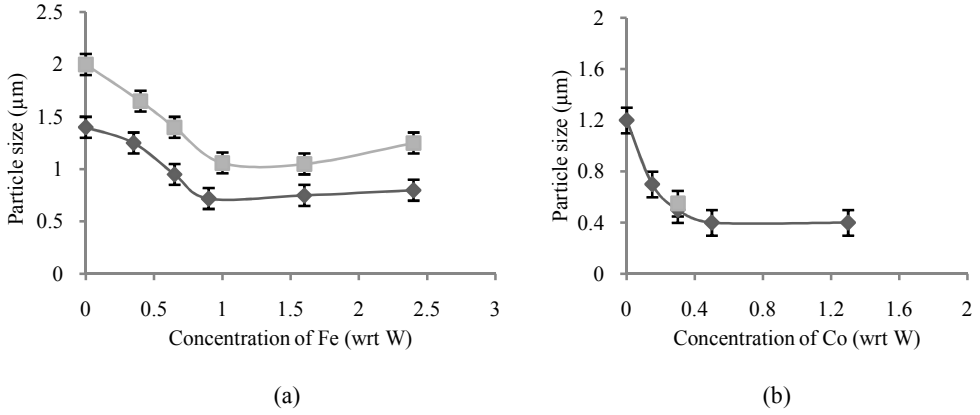


Fig. 7: (a) The effect of Fe concentration on the Ag-W particle size in the produced powders at temperature sets of 250-750°C (○) and 250-850°C (□) and (b) the effect of Co concentration on the Ag-W particle size in the produced powders at temperature sets of 250-750°C (□)

The representative micrograph in Fig. 6a shows the morphology of powder produced at 250-850°C. It is evident from the micrograph that the pseudo-morph morphology of the powder is still retained, but in a less well-defined manner. However, the size of the re-crystallized tungsten particles has increased from approximately 1 to 2 pm average with the increase in reduction temperature. The microscopy of the powders thus indicates that a finer tungsten particle size is obtained by processing at temperatures of 250-750°C than at 250-850°C. Figure 6b, shows the morphology of 2.45% Fe-doped silver-tungsten powder. It is evident that interlocking between the re-crystallized tungsten particles seems to have occurred and thus helped to decrease segregation. Meanwhile, Fig. 6c shows the morphology of 1.52% Co-doped silver-tungsten powders produced at 250-750°C have identical morphologies. The micrograph indicates that a small particle are more spherical in shape and are 0.5 µm in size while the large particles are 2 µm are different in shape and composed of several small particles which are sintered together. The large particles are sintered as a result of the higher thermal energy available for diffusion of silver phase in the second stage of the reduction process.

Pressing of silver-tungsten powders: As stated above it is clear that the morphology as well as particle size are highly affected by the powders production process and subsequently affect the pelleting process (i.e., compaction including sintering) and ultimately the final electrical contact produced. Thus to achieve this goal (i.e., the successful production of homogeneous composite powder with controlled tungsten particle size using co-precipitation and two stage reduction techniques) and obtain the optimal contact, huge number of parameters involved in the process must be controlled. This covers the initial conditions of producing the correct powder morphology and particle sizes, reported earlier, including in particular the use of different concentrations of sintering add elements, such like Fe and Co and subsequent pressing and sintering conditions such like the pressing pressures as well as the sintering temperature, time and atmosphere. Thus, at this stage of the work and following the initial huge efforts concentrated on the production of the suitable Ag-W powder composites, reported above, an intensive experimental program is carried out to investigate the effect of the other pressing and sintering vast parameters. A summary of the most important findings and related issues are presented below. However, for more details, information and analyses of the materials, measurements and experimental techniques involved refs (a, b, c) can be consulted. In this section typical examples of the main data and findings related to pressing and sintering are presented. This covers the effect of Fe and Co percentage additions on the particle size distributions, pressing pressures and densities as well as the effect of sintering temperatures up to 1000°C for 5 h under N_2 atmosphere.

The particle size of the reduced powder plays a vital role in obtaining a high density and uniform distribution of the phases within the compact. The effect of the different concentration additions of both Fe and Co on the particle size of the reduced powders produced at the reduction furnaces at temperature sets of 250-750 and 250-850°C are shown in Fig. 7a and b respectively. Meanwhile, the relationship between the pressing pressure and densities for the powders obtained at 250-750 and 250-850°C are shown in Fig. 8. It is clear from the graph that at three different pressing pressures, the 250-750°C powder always produces lower density compacts than equivalent 250-850°C powders. At a pressing pressure of 600 MN/mm^2 the maximum density obtained for the 250-750°C powder was 69% theoretical whereas the 250-850°C powder yielded a maximum density of 80% theoretical. Thus it is clear that powder having the finer particle size always produces a lower density. Although both

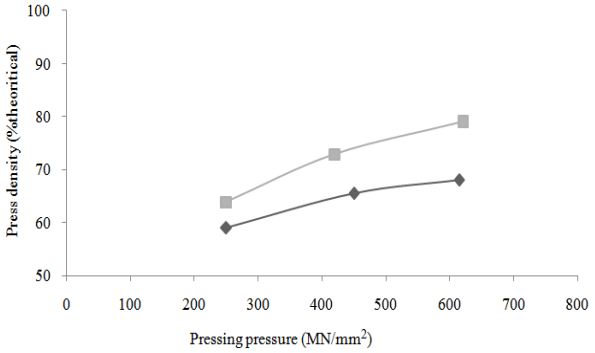
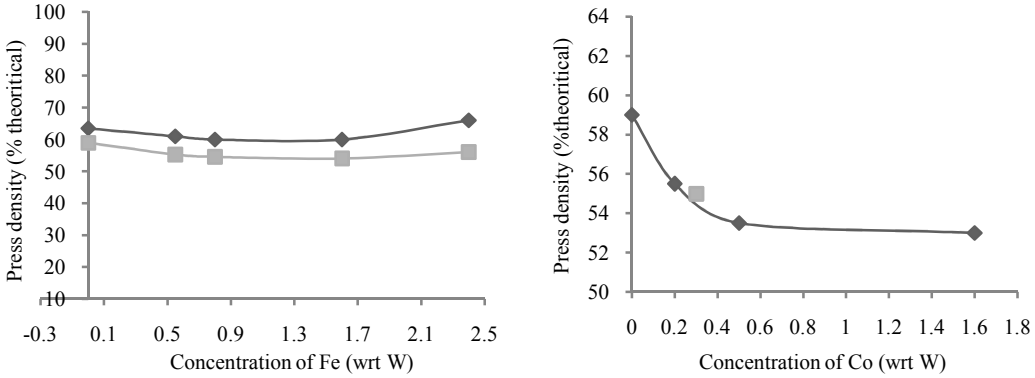


Fig. 8: Typical pressing characteristics of Ag-W powders produced by the two stage reduction process at temperature sets of 250-750°C (○) and 250-850°C (□)

reduced powders retained to some extent a pseudomorphic morphology of the silver tungstate agglomerates, the difference in powder behavior could be attributable to the flow and die filling properties of the powder. Therefore, the present study gives strong support to the hypothesis of Albiston (1989) that the press density depends upon the powder morphology of the starting materials.

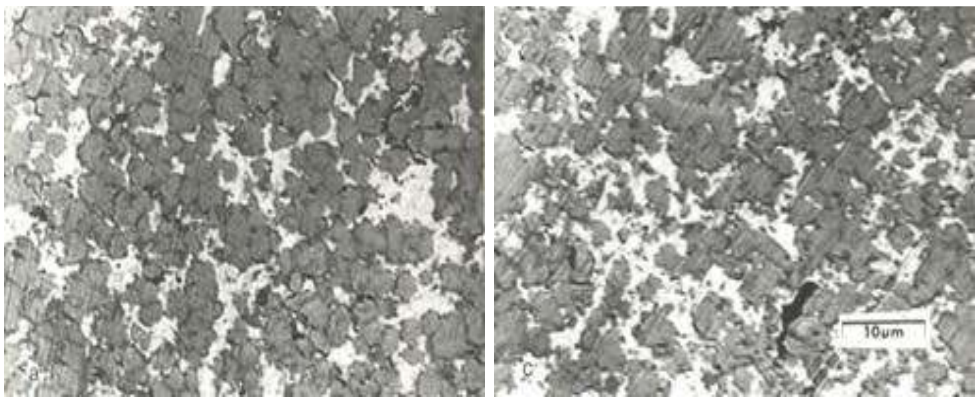
Furthermore, Fig. 9a and b shows the pressing characteristics for both Fe and Co-doped Ag-W powders produced in the reduction furnaces at temperature sets of temperature sets of 250-750°C (○) and 250-850°C at a pressing pressure of 300 MPa respectively. Also, Figure 10 show typical representative optical photomicrographs of compacted powder reduced at 250-750°C of Ag-W and 0.83% Fe-doped Ag-W.

However, to improve the density and quality of the produced compacts, from the various reduced powders, different pressing pressures are employed. Also, sintering is carried out on all the compacts at four sintering temperatures of 850, 875, 900 and 1000°C, respectively for 5 h in N_2 atmosphere. All the compacted samples are sintered using the dilatometer and then tested as reported above. Typical graphs



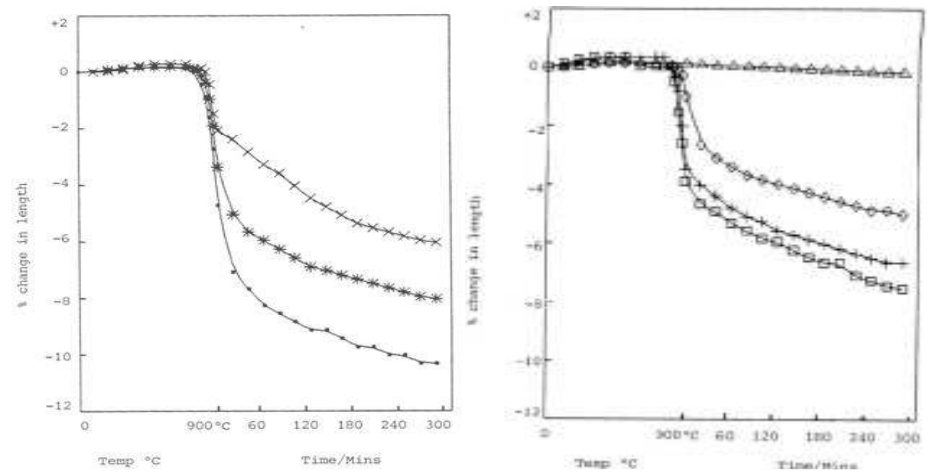
(a) (b)

Fig. 9: Typical pressing characteristics at pressing pressures of 300 MPa for, (a) Fe-doped and (b) Co-doped Ag-W, powders produced at temperature sets of 250-750°C (○) and 250-850°C (□)

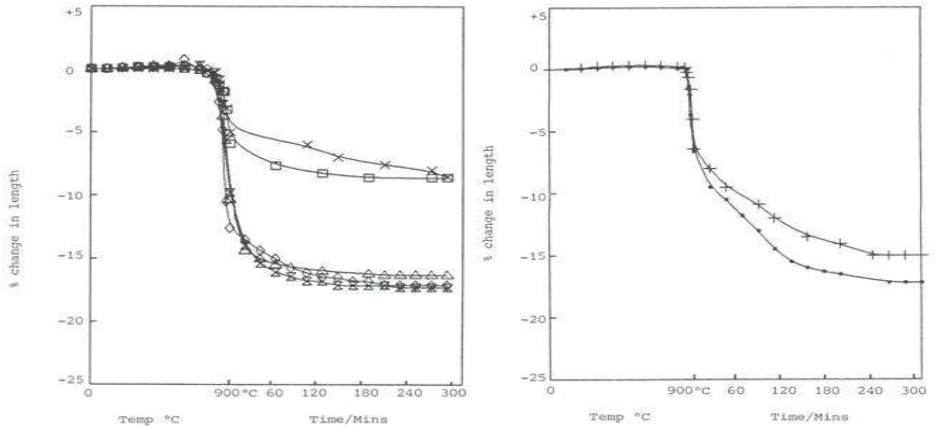


(a) (b)

Fig. 10: Typical optical photomicrographs of compacted powder reduced at temperature sets of 250-750°C, (a) Ag-W, (b) 0.83% Fe-doped Ag-W



(a)



(b)

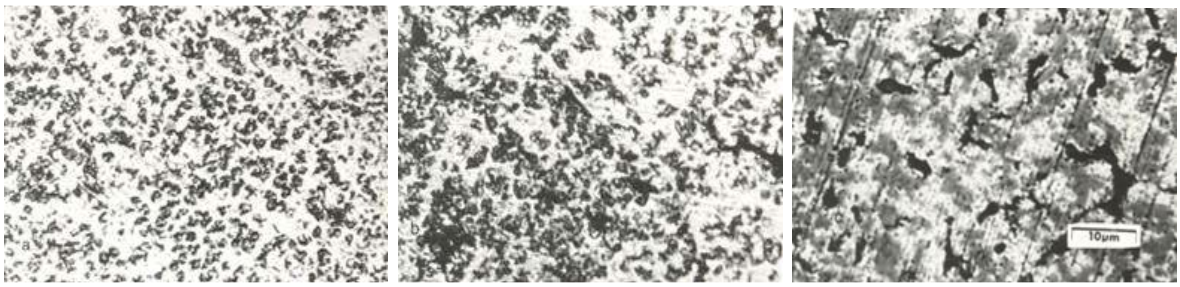
Fig.11: The change in length of powder compacts during isothermal sintering at 900°C for 5 h for (a) % Fe-doped Ag-W; ▪ 0.0, * 0.62, x 0.83, □ 1.55, + 2.45, ◊ 3.16, Δ 9.73%, (b) % Co-doped Ag-W; x 0.14, □ 0.28, Δ 0.29, ◊ 0.30, x 0.301, + 0.51, ▪ 1.52%

Table 1: Densification behavior of Fe and Co-doped Ag-W powder compacts, pressed at 300 MPa and sintered at 900°C for 5 h

Materials wt % (wrt W)	Initial density (%)	Sintered density (%)	Attainable change in density (%)
Un-doped Ag-W	57.30	69.59	28.78
wt % Fe 0.620	58.12	64.79	15.92
wt % Fe 0.830	58.40	63.72	11.70
Wt % Fe 1.550	55.34	62.82	16.78
wt % Fe 2.450	56.70	64.00	17.00
wt % Fe 3.160	56.11	60.45	9.880
wt % Fe 9.730	53.77	57.23	7.48
wt % Co 0.140	56.90	65.50	20.10
wt % Co 0.280	56.20	63.50	16.66
wt % Co 0.290	54.40	74.30	43.50
wt % Co 0.300	54.80	75.00	45.69
wt % Co 0.301	53.60	77.50	49.90
wt % Co 0.510	53.30	80.30	57.80
wt % Co 1.520	52.20	90.40	79.91

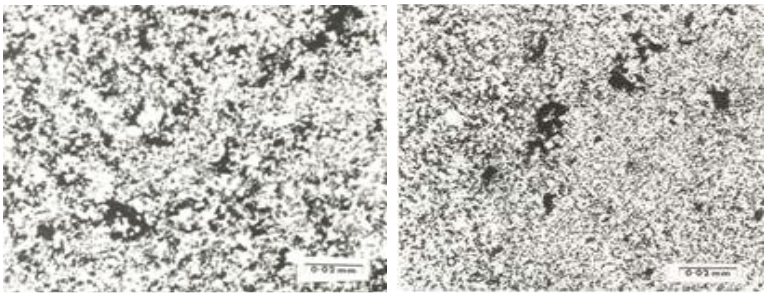
showing the change in length of powder compacts during isothermal sintering at 900°C for 5 h of the various Fe and Co-doped Ag-W samples are shown in Fig. 11. Meanwhile, Figure 12 display typical photomicrographs for the sintered Fe and Co-doped Ag-W samples at 900°C showing the resulted morphology and structure of the Ag-W composite electrical contacts. Finally, in Table 1 the densification behavior of Fe and Co-doped Ag-W powder compacts, pressed at 300 MPa and sintered at 900°C for 5 h.

Table 1 gives the data obtained for Co-doped powders sintered at 900°C for 5 h. It includes the initial and final densities along with the percentage change in densities. Figure 11 shows some sintering curves for compacts produced from Co-doped powder which were pressed at 300 MPa. Several observations may be made from these curves. Of prime interest is the fact that shrinkage is greater for powders with high cobalt content when compared with those containing less cobalt. The curves can be seen to fall into two distinct groups. One group consists of powder compacts with a lower level of cobalt, less than 0.29 wt%, while

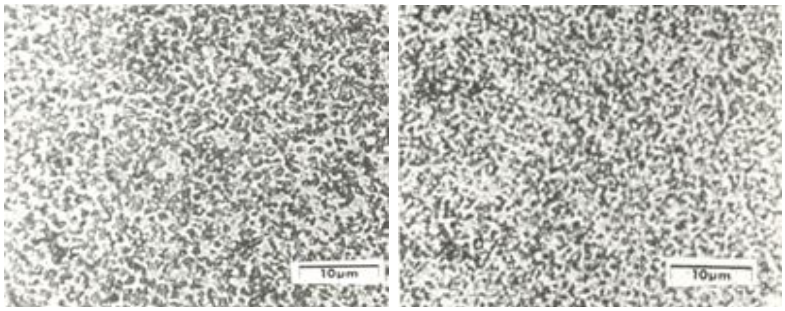


0.0% Fe-doped Ag-W 0.83% Fe-doped Ag-W 2.45% Fe-doped Ag-W

(a)



0.14% Co-doped Ag-W 0.30% Co-doped Ag-W



0.51% Co-doped Ag-W 1.52% Co-doped Ag-W

(b)

Fig.12: Typical photomicrographs for the sintered Fe and Co-doped Ag-W samples at 900°C for 5 h for, (a) Fe-doped Ag-W, (b) Co-doped Ag-W

the other group consists of powders with higher levels of cobalt. A similar trend was observed in the case of the 1.52 wt% Co-doped powder; however, the amount of densification was slightly higher and completed with a sinter density of 93% theoretical. Optical microscopy was carried out on some of the powder compacts to evaluate the distribution between silver and tungsten phases. Figure 10, shows the photomicrographs of the compacted powders. In the micrographs, there are three different areas, light area (silver phase), grey area (tungsten phase) and black area (porosity). Figure 12 gives a series of optical micrographs of Co-doped compacts. These specimens showed maximum density after sintering at 900°C for 5 h. It is evident that both phases are present in a highly homogeneous state and little porosity is present. Optical microscopy indicated that the sintered compacts retained their high homogeneity at 900°C. It also revealed that the amount of porosity was visibly reduced when compared to the pressed powders.

Finally, in brief a mixture of block-like crystals with clusters of fine needles of silver tungstate were produced by mixing an aqueous solution of silver nitrate and sodium tungstate. The morphology of tungstate was highly dependent upon the level of impurities present in the solutions. Very fine particulates of $FeWO_4$ were obtained on the surface of the silver tungstate lock, when $FeSO_4$ solution was mixed simultaneously with $AgNO_3$ and Na_2WO_4 solutions during precipitation. The amount of fine

particles on the tungstate blocks increased with the increase in the $FeSO_4$ solution. Eventually, with the addition of 9.73 wt% Fe, a very fine precipitate was obtained which was amorphous as indicated by XRD. It was then apparent that such a high level of Fe addition caused the growth of the block-like crystals to be modified. Similarly, the addition of $CoSO_4$ solution into the $AgNO_3$ and Na_2WO_4 solution completely changed the growth morphology from the block-like crystals into needles of $CoWO_4$ doped Ag_2WO_4 precipitate. However, as the concentration of $CoSO_4$ in the solution was increased up to I 0.52 wt% Co, agglomerates of equiaxed particles were produced as a precipitated tungstate. It was suggested that silver tungstate precipitated before iron tungstate and so true co-precipitation did not occur in this case, whereas in the case of the cobalt tungstate doped silver tungstate, simultaneous precipitation occurred.

In an attempt to reduce the sodium impurity to the minimum possible, some loss of $FeWO_4/CoWO_4$ in the silver tungstate was observed during repeated washing of precipitate. An intimate mixture of silver and tungsten was yielded by two stage reduction processes at 250-750 and 250-850°C. It was also observed that the size of tungsten particle was dependent on the higher temperature stage of the reduction process. During reduction process, both additives (Fe/Co) showed a similar effect on the particle size and produced submicron tungsten particles at 250-750°C. The press density of the reduced powder showed a significant dependency upon the tungsten particle size. The powder produced at 250-750°C, which contained fine particles, gave lower press density whereas the powder produced at 250-850°C, which contained coarse particles, gave higher press density.

During scanning dilatometric sintering experiments it was observed that undoped silver-tungsten powder densified to a smaller extent than the doped powders. The densification process always finishes just below the temperature at which liquid silver appeared (i.e., 960°C). As the highest densification was obtained in the powder which contained fine particles, this suggested that densification occurred mainly due to particle rearrangement and also indicated the importance of particle size to achieve high density of the powder compact. Optical microscopy showed that most compacts, on heating up to 1000°C, lost their homogeneity as the liquid silver flowed towards the bottom edge of the compact due to immiscibility with tungsten and gravitational force.

No evidence was found from the isothermal sintering experiments for the activation of the sintering of silver-tungsten composite powders by additions of iron. It was suggested that this effect could be because of the non-uniform coverage of tungsten particles with Fe/Fe_7W_6, the formation of an excess amount of stable inter-metallic compound and the non-reduction of some of the iron tungstate. These observations were confirmed by the transmission electron microscope. Evidence was found for the presence of some unreduced $FeWO_4$ particles which were entrapped in the silver matrix. Cobalt addition showed a significant enhancement of the sinter-ability of the silver-tungsten composite which was linked with the level of the cobalt addition. It was found that 6 to 7 mono-layers coverage of cobalt on the tungsten particles was required to activate the sintering process at 900°C.

Optical microscopy of the sintered specimens indicated that in the case of Fe-doped materials homogeneity between silver and tungsten was completely destroyed whereas in the case of the Co-doped powders a uniform distribution of tungsten particles was obtained in the silver matrix and both phases were present in a highly homogeneous state. Transmission electron microscopy of the sintered compacts showed that contact between tungsten particles existed and that the tungsten particles were wetted with the silver phase. Analysis of some regions of the compact demonstrated that in the case of Fe-doped powder, the percentage of iron varies from 0.25 to 3.5 wt% Fe and confirmed its none-uniform distribution. No such evidence was found in the case of the Co-doped powder. Microscopy also showed that the wetting conditions of tungsten with silver were improved with the addition of cobalt rather than iron to the silver-tungsten composite. No significant difference between the two methods of additions of iron in the powder was observed. Whereas in the case of Co-doped powder the densification was dependent upon the method of addition of dopant to the powder. In the sulphate processed powder, the densification decreased more than 50% which indicated that the method of addition was very vital in that case where the morphology of the powder was changed during co-precipitation by the addition of the dopant.

CONCLUSION

From the intensive experimental investigation carried out on Ag-W composite materials to produce homogeneous composite powder with controlled tungsten particle size for electrical applications, it is possible to draw the following conclusions:

- The production of a homogeneous composite powder with controlled tungsten particle size using co-precipitation and two stage reduction techniques followed by compaction and sintering processes to produce electrical contacts is successfully achieved.
- No evidence was found for the activated sintering of silver-tungsten by Fe additions.
- The homogeneity of silver-tungsten in compacts is completely lost in the Fe-doped powders.

- Cobalt additions help to facilitate the sintering between silver and tungsten whilst retaining a high homogeneity between the silver and tungsten in the sintered product.
- It is anticipated that the sintered compact will have improved erosion resistance and anti-weld properties.
- Finally, this promising success of the sintering process to fabricate electrical contact with a homogeneous structure is believed to have a big impact on the electrical industries.

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