Research Article
Homogenous Silver-Tungsten Composite Production for Electrical Contacts

[1]Shahid M. Azhar and [2]Mahir Es-saheb
[1]CEREM, Advanced Manufacturing Institute,
[2]Mechanical Engineering Department, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

Abstract: 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 (efficient electro-thermal conductivities). Since there is no alloying between the two elements (Ag and W), the properties of the composite depends on their composition. So for any particular application, a balance must be struck between the desirable properties of the two metals. Both welding and erosion resistance properties of silver-tungsten contacts depend on particle size, morphology and distribution of both elements within the composite, with finer W particles in Ag matrix give better performance. The main objective of this study is to produce an intimately mixed silver-tungsten powder with homogeneous distribution of both phases (silver and tungsten) in the composite. Thus, to produce homogenous elemental silver-tungsten powder, the reduction behavior of each tungstate is studied at various reduction temperatures using TGA technique. Based on the results obtained from TGA, the reduction of silver tungstate carried out in two stage reduction process for producing elemental silver-tungsten powder with controlled particle size of tungsten. Also, small quantities of Fe and Co as sinter aids are introduced into tungstates by co-precipitation technique. However, the precipitated Fe and Co doped silver tungstates are reduced to yield Iron and cobalt doped silver-tungsten powders. The effect of Fe and Co on the morphology and particle size of the tungsten is studied using SEM. The reduced products will be used for subsequent sintering experiments to produce high density sintered compact for contact fabrication.

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 by Hansen (1958), Karakas (2002) and Costa *et al*. (2008) 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 (Karakas, 2002; Glickman *et al*., 2003). So for any particular application a balance must be struck between the desirable properties of the two metals, as reported by Özkal (2002) and later by Bhagat *et al*. (2008) and Bukaluk *et al*. (2008). 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.

Meanwhile, the performance of these materials as electrical contacts is investigated lately by Slade (2009) and Bukaluk *et al*. (2008). 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 (Es-Saheb, 2012; Ramadan *et al*., 2012). 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.

The controlled reduction of mixed oxides has been shown to yield intimate mixtures of metals by a number

Corresponding Author: Shahid M. Azhar, CEREM, Advanced Manufacturing Institute, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

of investigators, such like Basu and Sale (1978) as well as Bracconi and Dufour (1976). As one of these investigations, a study has been made of the hydrogen reduction of silver tungstate in which both silver and tungsten are mixed on an atomic scale within the tungstate lattice. It was shown that oxygen could be removed from the tungstate lattice by the controlled reduction to produce an intimate mixed powder. In previous work by Walkden and Sale (1982) on the single stage reduction of silver tungstate at high 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 by Walkden and Sale (1982), 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). Pressing and sintering experiments will be conducted on the powder produced with the two stage reduction process. Other techniques to obtain homogeneous Ag-W structures are used by many investigators; amongst them Sun *et al.* (2010). Theyutilized ordered mesoporous approach. Though this approach is very promising, more work still is needed. Recently, Azhar and Es-Saheb (2013) as well as Es-Saheb and Azhar (2013) adopted successfully the controlled two stage reduction process, as recommended by Walkden and Sale (1982).
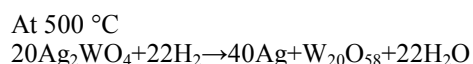
MATERIALS AND METHODS

Reduction of tungstate: Guerassimov (1957) studied the reduction behavior of various bivalent metal tungstates with H_2/H_2O gas mixtures up to a temperature of 1100ºC and concluded that the reduction behavior may be classified into two extreme types such as:

a) $MWO_4(s)+3H_2(g)\rightarrow MO(s)+W(s)+3H_2O(g)$
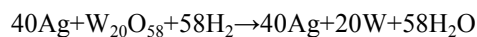b) $MWO_4(s)+(4-x)H_2(g)\rightarrow M(s)+WO(s)+(4-x)H_2O(g)$

In the first case the metal tungstate is reduced to form a metal oxide and tungsten, whereas, in the second case, the metal is formed along with a tungsten oxide in the initial stages of reduction and then the tungsten oxide is subsequently reduced into tungsten, as the reduction reaction proceeds. Intermediate behavior between these two extremes may occur such that mixtures of tungsten and an alloy or tungsten alloys and tungsten oxides are produced. They reported that the metals which have a high affinity for oxygen such as Mg, Ca, Sr, Br and Mn behave according to extreme (a) while the metals which have a low affinity for oxygen such as Cu, Cd and Pb behave as extreme (b). Other metals such as Fe, Co and Ni are found to behave in an intermediate manner between the two extremes and produce mixtures of tungsten and tungsten alloys on their reduction.

Reduction of silver tungstate: Silver and tungsten have no mutual solubility in either the molten or in the solid state hence, no silver tungsten alloys are found to exist in silver-tungsten-oxygen system. In addition, only one stable ternary compound based on the formula Ag_2WO_4 is found in the system. Walkden and Sale (1982) carried out an investigation on hydrogen reduction of silver tungstate. They concluded that Ag and $W_{20}O_{58}$ were produced during the initial reduction of silver tungstate and its subsequent reduction was very similar to the reduction behavior of copper tungstate studied earlier by many investigators including Guerassimov (1957) as well as Basu and Sale (1977, 1978, 1979). They summarized the reduction mechanism for silver tungstate as follows:
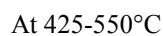
At 500 °C
$$20Ag_2WO_4+22H_2\rightarrow 40Ag+W_{20}O_{58}+22H_2O$$

Followed by:

$$40Ag+W_{20}O_{58}+58H_2\rightarrow 40Ag+20W+58H_2O$$

They found that at temperatures up to 500°C, W was present in the fully reduced form whilst at 600°C and above, silver and α-W were produced. The reduction rate was found to double approximately for every hundred degree rise in reduction temperature from 500 to 900°C. The morphologies of reduced powders changed with an increase in the reduction temperature from 500 to 900°C. At low temperatures, with the resultant low rates of reduction, gross segregation of phases was obtained in the totally reduced powders giving silver rich areas and tungsten rich interiors of very fine particles. They concluded that if these materials were held for longer periods of time at these temperatures, the silver rich clusters of large dense silver particles produced. Rabes *et al.* (1949) investigated the reduction of Ag_2WO_4 in controlled CO/CO_2 gas mixtures first produce metallic silver and tungsten oxide which could be subsequently reduced to tungsten metal.

Reduction of cobalt tungstate: Bracconi and Dufour (1976) and Bevington *et al.* (1980) studied the reduction behavior of $CoWO_4$ in hydrogen at a temperature between 440 to 1100°C and observed that reduction at temperatures lower than 550°C produced $CoW_{2.5}O$ whilst the remaining tungsten which was not retained in this phase appeared in the form of β-W. An amorphous phase was formed by the further reduction of $CoW_{2.5}O$. They found that the reduction of $CoWO_4$ in hydrogen could be summarized as:
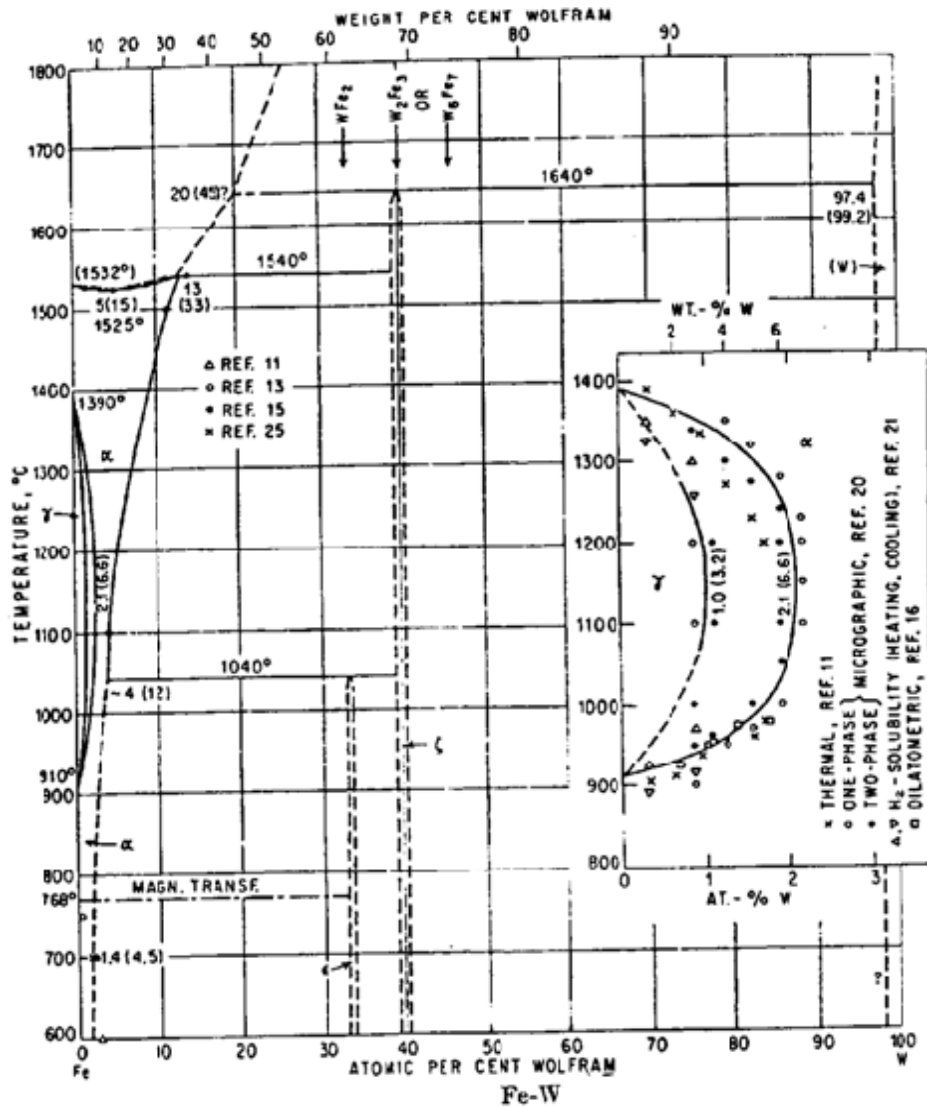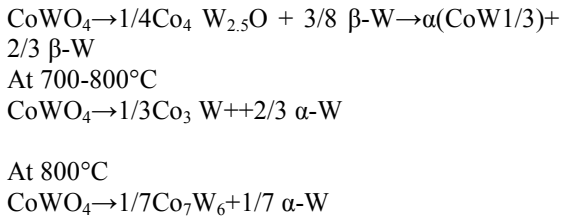
At 425-550°C

Fig. 1: Fe-W system (Arnfelt, 1928)

$CoWO_4 \rightarrow 1/4Co_4 \ W_{2.5}O + 3/8 \ \beta\text{-}W \rightarrow \alpha(CoW1/3) + 2/3 \ \beta\text{-}W$

At 700-800°C

$CoWO_4 \rightarrow 1/3Co_3 \ W + +2/3 \ \alpha\text{-}W$

At 800°C

$CoWO_4 \rightarrow 1/7Co_7W_6 + 1/7 \ \alpha\text{-}W$

French and Sale (1985) investigated the reduction of $CoWO_4$ with hydrogen; they concluded that the reduction process occurs via the formation of an amorphous phase which contains cobalt, tungsten and oxygen. The amorphous phase becomes unstable and precipitates out as Co_3W or Co_7W_6 depending on the degree of cobalt enrichment of the amorphous phase. They also found that at low temperatures Co_3W produced whereas at higher temperatures, Co_3W decreases and the amount of Co_7W_6 increased.

Reduction of iron tungstate: In the Fe-W binary system (Fig. 1), two intermediate phases WFe_2 and W_2Fe_3 exist in the narrow range of homogeneity. Later investigations showed that WFe_2 formed at temperatures between 1000°C and 1450°C. Based on x-ray data reported by Amfelt (1928), Sykes (1926, 1929) and Arnfelt and Wetsgren (1935), it was determined that the ideal composition for the compound called W_2Fe_3 is W_6Fe_7 (73.84 wt% tungsten). W_6Fe_7 is therefore, not stable at low temperatures. The phase diagram for the Fe-W system confirmed the existence of WFe_2 and W_2Fe_3 (Sykes and Van-Horn, 1933). The phase diagram showed that the solubility of tungsten in solid iron decreases with temperature, with its value 2.6 at % W in the temperature range 600-700°C. The solubility of iron in solid tungsten was determined by Chartkoff and Skyes (1930) to be 1.2 wt% at 1600°C.

EXPERIMENTAL PROCEDURE

Material preparation: The present work involved the use of following 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 and iron sulphate. On mixing these stoichiometric quantities the following reactions occurred:

- $2AgNO_3+Na_2WO_4.2H_2O \rightarrow Ag_2WO_4+2NaNO_3+ 2H_2O$
- $FeSO_4.7H_2O+Na_2WO_4.2H_2O \rightarrow FeWO_4+Na_2SO_4+ 9H_2O$
- $CoSO_4.7H_2O+Na_2WO_4.2H_2O \rightarrow CoWO_4+Na_2SO_4 +9H_2O$

In each case after precipitation, the tungstate mixture was filtered and washed with copious amounts of distilled water 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 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. Following the method described the iron tungstate doped silver tungstate with various doping levels of iron were produced using the appropriate amounts of their salts.

Material characterization: The resultant powders before and after reduction was analyzed using the following analytical techniques.

Differential thermal analysis: To study the possible reactions between silver, iron and tungsten and the decomposition on heating, "DTG-H60; Simultaneous DTA-TG Apparatus, SHIMADZU" was used for study the reduction of silver tungstate. A powder sample of known weight (100 mg) was heated to the desired temperature at constant rate of 10°C/min in a nitrogen atmosphere and then furnace cooled to room temperature. Calcined alumina powder was used as a reference material.

X-ray diffraction analysis: X-ray Diffraction Analysis (X-RD) on the powders produced was carried out with a BRUKER, D8-DISCOVER. The powder specimens in the diffractometer scanned over the range of 10 to 90° at a scan rate 6°/mm.

Scanning electron microscopy: Starting materials and reduced powders were examined for the morphological information and particle size using a SEM. The EDAX system used to gain an overall chemical composition of the specimens.

Two stage reduction experiment: To produce large quantities of reduced powders for subsequent pressing and sintering experiments a two stage reduction process was used. The apparatus consisted of two tube furnaces separated from each other by an air gap (Fig. 2). Temperature profiles for the furnaces were determined at 250-750°C. Several experimental variables were calibrated accurately 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

Fig. 2: Two stage reduction process based on the two STF1200–tube furnaces

differences in powder bed depth. To determine the hydrogen flow rate required for the best possible 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 XRD. 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 nitrogen gas for a period of 30 minutes, 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 (higher temperature) to be established. The first stage must be sufficiently long enough to allow this to happen. On completion of the first stage reduction, the specimen was then pushed in to 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 nitrogen.

RESULTS AND DISCSSION

Silver tungstate: The analyses of the precipitated silver tungstate by atomic absorption are presented in Table 1. Using these results the molecular formula for precipitated silver tungstate has been established. It is evident from the formula that the silver/tungsten ratio is very close to the theoretical value 2: The results show that Fe is present in a very small amount along with traces of impurities which could originate during the precipitation process. The most likely origin is the salts used in the preparation process. The Na level present in the tungstate is also of special interest because the

Table 1: Analysis of precipitated Ag_2WO_4 by AA spectrometry

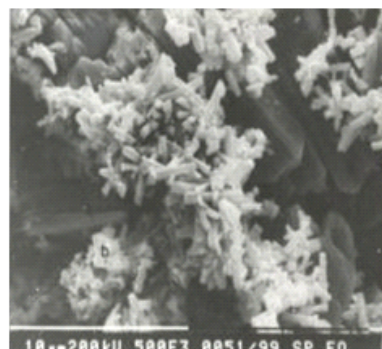| Element	% Wt
W	39.970
Ag	46.073
Cu	0.0350
Na	0.0370
Fe	0.0130
Co	0.0050
Ni	0.0170
O	13.870

Calculated formula of silver tungstate = $Ag_{1.96}WO_{4.01}$; Theoretical formula of silver tungstate = Ag_2WO_4

contamination of ammonium para-tungstate with Na is known to cause rapid grain growth of tungsten at elevated temperature as reported by Skarsted and Geler (1975). This investigation showed that 0.2% Na addition in tungsten caused increases in the crystal size of tungsten. As the properties of electrical contacts depend upon the grain size of tungsten, the level of sodium impurity in the tungstate must be controlled. In present study, repeated washing of the precipitate allowed to reduce the sodium content to the acceptable range. The results in Table 1, show that the precipitated tungstate sample contains 0.037% Na which is less than 0.2% Na reported by Skarsted and Geler (1975).

The powder samples were characterized by XRD technique. The diffraction pattern obtained from the precipitates corresponded to the d-spacing of JCPDS card 32-1028 and identified it as exclusively silver tungstate. A morphological study of the precipitated silver tungstate showed a mixture of block-like crystals and clusters of fine needles as it can be seen in Fig. 3. These blocks which seem rough and have corrugated surfaces are 20 to 30 µm in length and 5 to 10 µm in thickness. This morphology of the silver tungstate is different from the morphology studied by several investigators, such like Walkden (1981) and Albiston (1989). Skarsted and Geller (1975) reported two different forms of silver tungstate and explained the effect of temperature on the silver tungstate morphology. They indicated that subtle differences in pH and heating of the solution appeared to modify the
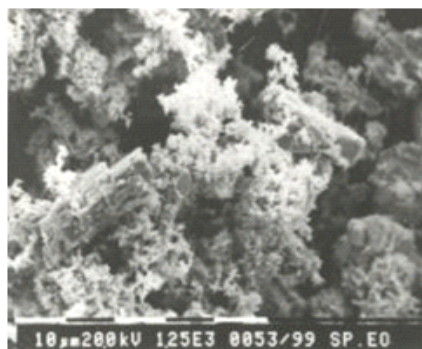
(a)   (b)

Fig. 3: Precipitated form of silver tungstate

Table 2: Chemical analysis of FeWO$_4$ doped silver tungstate conducted by atomic absorption spectroscopy

Element	Wt %						
W	41.2	40.26	42.17	41.42	41.880	41.67	43.15
Cu	0.02	0.008	0.006	0.007	0.0030	0.007	0.012
Na	0.03	0.018	0.084	0.015	0.0400	0.090	0.070
Fe	0.14	0.250	0.350	0.640	1.0300	1.320	4.200
Co	0.07	-	0.003	-	0.0002	-	-
Ni	-	-	0.010		0.0050	-	-
Fe (wrt W)	0.34	0.620	0.830	1.550	2.4500	3.160	9.730

precipitates. The transition occurred from one silver tungstate phase to another as it was heated from 90 to 250°C. Albiston (1989) studied the morphology of silver tungstate and reported several factors could effect on the powder morphology, i.e., temperature of solution, pH of solution, method of mixing solution and purity of solution. Walkden (1981) studied the morphology of silver tungstate and found that at low temperature, needle-like crystals of silver tungstate were obtained which again reflects the temperature dependency. In the present work, the silver tungstate was prepared at low temperature; therefore, a mixture of block-like crystals with cluster of fine needles was anticipated.

Iron tungstate doped silver tungstate: Silver tungstate doped with iron tungstate was prepared by co-precipitation from sodium tungstate, silver nitrate and iron sulphate solutions. The precipitated tungstates were grey in color and turned dark grey as the amount of iron sulphate solution was increased in the mixture. The elemental compositions of all the doped tungstates were analyzed by atomic absorption spectrometry. The results showed in Table 2, that sodium is the only trace element which varies over a wide range from powder to powder. The variation arises from the washing of the precipitated tungstates and so indicates the importance of this stage of the process. It is evident from the results that the concentration of Fe is increased with increased addition of iron sulphate.

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 %, respectively which may be expressed as 0.34, 0.62, 0.83, 1.55, 2.45, 3.16 and 9.73%,

respectively Fe with respect to tungsten. A calibration chart for these Fe levels is presented in Fig. 4 which gives the relationship between the addition of iron sulphate solution and Fe concentrations achieved in the tungstate powders. It is evident from Fig. 4 that the experimental values of iron are much lower than the expected ones. The possible reason for this could be partial solubility of tungstates in water. As the precipitated tungstates required washing several times in order to control the sodium impurity, it is likely that some loss of iron would occur. Alternatively, it could be possible that all of the iron added initially does not precipitate out. Experimental evidence shows that a combination of these explanations applies. Albiston (1989) work gave a strong support to the above explanation, where he explained that due to partially
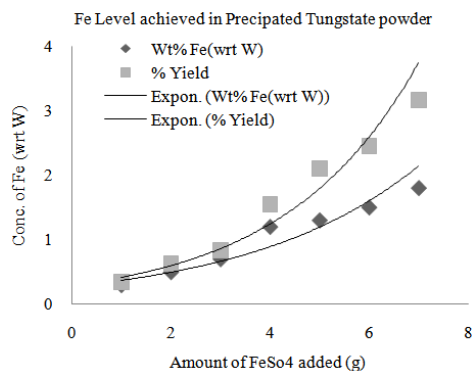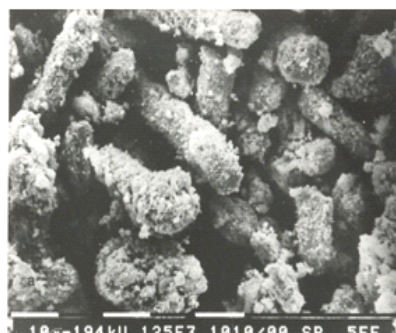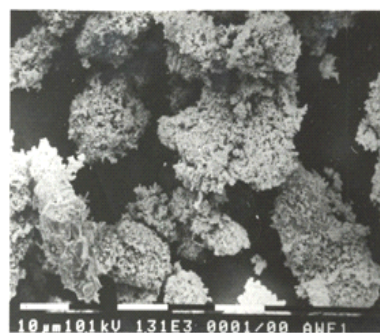
Fig. 4: Graph showing the concentration of Fe achieved in the composites by the addition of FeSO$_4$ solution to the silver nitrate and sodium tungstate solutions

(a)

(b)

Fig. 5: Precipitated iron tungstate doped silver tungstate; (a) 0.83% FeWO4 doped Ag$_2$WO$_4$; (b) 2.45%FeWO$_4$doped Ag$_2$WO$_4$

Table 3: Chemical analysis of $CoWO_4$ doped silver tungstate conducted by atomic absorption spectroscopy

Element	Wt %						
W	39.770	39.25	41.18	40.00	39.84	41.45	41.430
Cu	0.0030	0.004	0.005	0.003	0.004	0.003	0.0025
Na	0.1600	0.017	0.030	0.080	0.020	0.020	0.0200
Fe	0.0600	0.060	0.070	0.040	0.030	0.050	0.0700
Co	0.0056	0.110	0.114	0.120	0.120	0.210	0.6300
Ni	-	-	-	-	-	-	-
Co (wrt W)	0.1400	0.280	0.290	0.300	0.301	0.510	1.520

solubility of tungstates and fine particle size of dopant, it was difficult to collect 100% concentration of the dopant because of repeated washing and filtering of the precipitate.

The XRD of the precipitates indicated that most of the powders have different relative intensities for the same lines. To investigate the effect of Fe concentrations on the powder, the ratio of the relative intensity of two major peaks, 2.83°A d-spacing and 2.71°A d-spacing, were taken in each case. It is clear from the results that no significant effect of Fe was observed on the relative intensity ratio except for 3.16% Fe addition and above. To ascertain whether the large difference in ratio was associated with the morphology of the doped powders SEM studies were conducted. The representative micrograph in Fig. 5a shows that with the addition of 0.83% Fe (wrt W), the surface of the silver tungstate blocks are covered with a fine dispersion. As the Fe concentration increased to 2.45% in the powder, the surface coverage with the fine precipitate also increased (Fig. 5b), without any significant effect on the block-like morphology. The dispersion on the block surface was so fine that it was difficult to analyze with the EDAX. The possible explanation for these observations is that the Na_2WO_4 first reacts with $AgNO_3$ to form crystals of $AgWO_4$ and then $FeSO_4$ reacts sequentially and deposits iron tungstate on the surface of these blocks. This explanation of sequential precipitation is substantiated by the observation that when the concentration of iron sulphate in the solution is increased, the surface coverage of the silver tungstate crystals was also increased. As the addition of Fe reaches 3.16% (wrt W) a different morphology was obtained. The reason for this could be due to the presence of excess Fe during reaction and growth such that extra nucleation and favored growth directions have resulted in the large number of needles and whiskers of $AgWO_4$ (Fig. 4b) which are covered with iron tungstate precipitate.

Silver tungstate doped with cobalt tungstate: The cobalt tungstate doped silver tungstate samples were prepared by the co-precipitation from cobalt sulphate, sodium tungstate and silver nitrate solutions. The precipitated tungstates were obtained with a light yellow color which turned into off-white on drying. The precipitates were analyzed by atomic absorption spectrometry. The results shown in Table 3, indicate

that the impurity traces particularly Na, are in the acceptable range. It is evident from the results that the cobalt concentrations of the powders were increased with increasing the additions of cobalt sulphate in the 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 I.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 (wrt W). A calibration chart in Fig. 6 gives the relationship between Co and sulphate addition. The graph shows the concentration of cobalt obtained in the powder specimen was much lower than the expected value. The possible reason could be the partial solubility of CoWO4/Ag2WO4 in water during washing.

The tungstates were characterized by XRD. The effect of cobalt concentration on the powder was studied by taking the ratio of relative intensity of the four major peaks, 2.85, 2.74, 2.01 and 1.67 A d-spacing for each case. The relative intensity ratio slightly decreased in the case of 2.85/2.74 A with the addition of cobalt in the powder which could be related to the change in powder morphology. Therefore, to this effect, the powder morphologies were studied by SEM and photomicrographs are shown in Fig. 7. The electron micrograph in Fig. 7a reveals the morphology of 0.51%
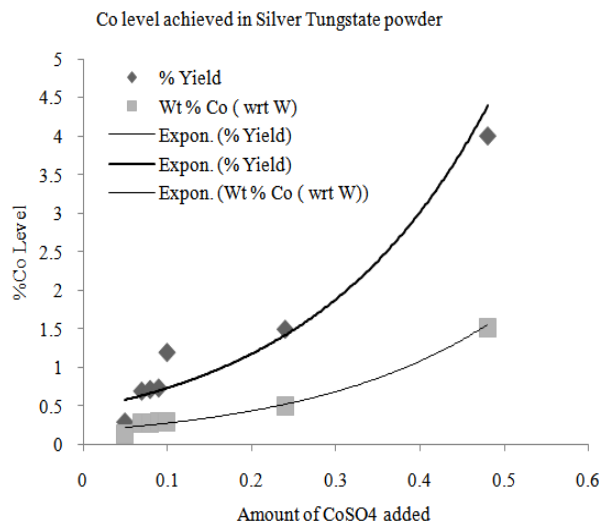

Fig.6: Graph showing the concentration of Co achieved in the composites by the addition of $CoSO_4$ to the silver nitrate and sodium tungstate solutions

(a)   (b)
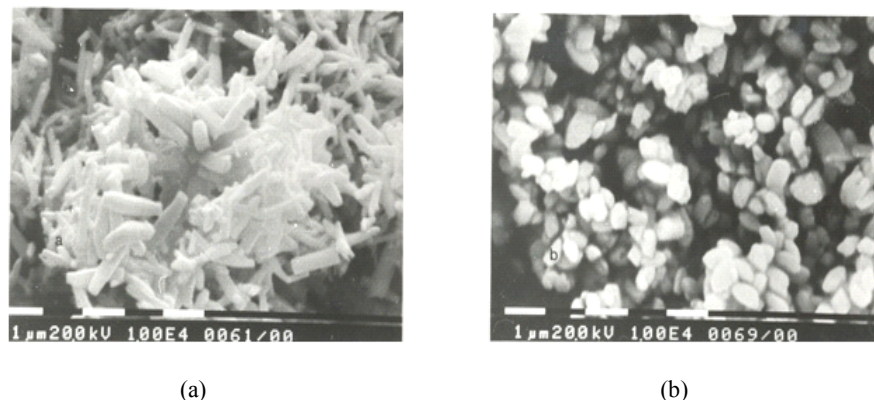
Fig. 7: Precipitates of AgWO4 dope with CoWO4; (a) 0.51% Co- doped silver tungstate; (b) 1.52%Co-doped sliver tungstate

Co doped silver tungstate. The powder specimen has needle like crystals which indicate a preferential growth direction. In Fig. 7b, the micrograph shows that 1.52%Co addition in the powder, the morphology of the powder changed from needle like crystals to the agglomerates of small equi-axed particles. It is believed that Cobalt tungstate provide a large number of small nuclei on which the needles of silver tungstate formed. However, 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.

Reduction of silver tungstate: The microscopy of the powders thus indicates that a finer tungsten particle size is obtained by processing at temperatures of 250-750°C (Fig. 8). This observation, that the higher temperature in the second stage of reduction showed a significant effect on the growth of tungsten particle size, is in agreement with previous workers. The reason for this effect on tungsten particle size is associated with the breakdown of WO_2 on reduction at 750°C. When WO_2 is reduced into O-W, the growth of primary tungsten nuclei may be limited and lead to the production of a large number of nuclei and, as a result, the formation of a large number of tungsten particles takes place. But as the reduction temperature increases in the second stage both the reduction kinetics and the diffusive mobility of the metal product atoms increase. The end result is that the nuclei tend to grow more rapidly giving a large particle size. Walkden and Sale (1982), Walkden *et al.* (1985) and Bottelberg *et al.* (1976) investigated the controlled two stage reduction of silver tungstate and observed a similar effect of higher temperature on the tungsten particle size. They observed that the temperature of the first stage of reduction either 200 or 300°C showed little effect upon the powder morphology and the size of the incompletely reduced oxide product obtained at these temperatures. However, the temperature of the second stage 700 or 900°C had a marked effect upon the tungsten particles
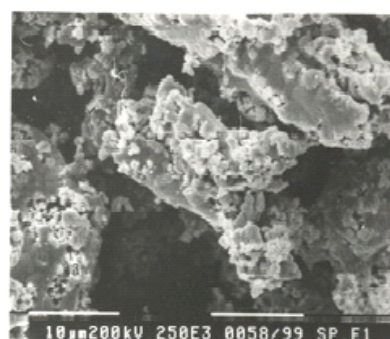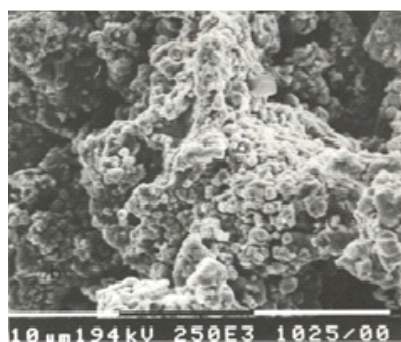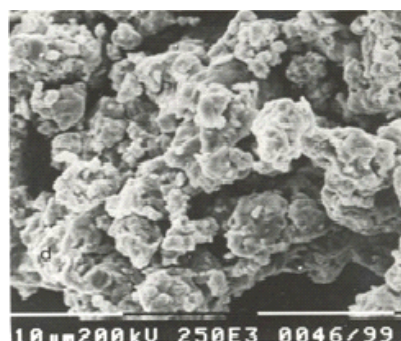

Fig. 8: Reduced Ag-W powder

with sub-micron particles being produced at 700°C where as at 900°C the particle size was up to 2 µm average. The effect of temperature on the tungsten particle size obtained in the present study agrees generally with the observations of Walkden and Sale (1982), however, sub-micron particles were not obtained at 250-750°C. It is possible that the difference is related to the small change in temperature, or it may be due to the presence of impurities. As mentioned earlier, the production of electrical contact materials requires considerable analytical control of Na impurity which can affect the growth of tungsten particle size at higher temperature. In the present study this effect could be well explained by comparing the results with the previous work reported by several investigators Walkden (1981) and Albiston (1989). As the 1 µm tungsten particles obtained at 250-750°C are found with this low level of Na impurity it seems that the only possible reason could be the effect of the marginally higher temperature. The above explanation reflects the importance of the reduction temperature in the second stage for the control of particle size.

Reduction of Fe-doped silver tungstate: Figure 9 gives scanning electron micrographs which demonstrate the morphologies of Fe doped powders produced at 250-750°C. The morphology of 0.62% Fe-doped silver-

(a)

(b)

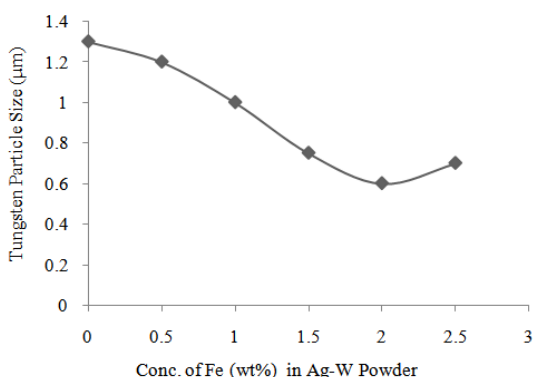Fig. 9: Reduced Fe-doped Ag-W powders; (a) 0.62% Fe-doped Ag-W; (b) 0.83% Fe-doped Ag-W

Fig.10: Graph showing the effect of Fe addition on tungsten particle size in the reduced Ag-W powders produced at 250-750ºC.

tungsten powder is shown in Fig. 9a where it can be seen that the agglomerates are segregated into fine and coarse particles. The fine particles tend to accumulate in certain regions, leaving a lot of porosity and result in segregation between coarse and fine particles. The fine particles are tungsten of approximately 1 μm diameter and the coarse particles are silver in the size range 5 to 10 μm. The photomicrograph 9b, shows the morphology of 0.83% Fe-doped silver-tungsten powder. It is evident from the micrograph that as the

original tungstate lattice collapsed, small agglomerates formed. The average size of the tungsten particles reduced to 0.7 μm and the interlocking between the recrystallized tungsten particles seems to have occurred.

The decreases in tungsten particle size observed as a function of iron addition are shown in Fig. 10. Every point shows an average tungsten particle size which was obtained for each powder from 30 mean linear intercept measurements of the appropriate scanning electron micrographs. The maximum effect of iron on the tungsten particle size was obtained with additions up to 0.83 Wt% Fe in reduction processes. After this addition the curve shows no significant effect of iron on the tungsten particle size.

These fine particles were suspected to act as nucleation sites for the growth of tungsten particles during the reduction process. As a result large numbers of small recrystallized tungsten particles were obtained within the framework of the original tungstate particles. This effect was observed up to 1.55 Wt% Fe addition. After this level of addition for the 250-750°C powders, it appears that the surface coverage was such that as extra nucleation sites could be created so that the further addition of iron had no significant effect on the reduction of tungsten particle size. The present results agree with the previous investigation Albiston (1989) used the nickel as dopant for tungsten particles and also observed that nickel inhibits the grain growth of tungsten even at higher reduction temperature. As the iron acted in similar ways to nickel during the precipitation of silver tungstate, therefore, it was also expected to act as a grain growth inhibitor. Bottelberg *et al*. (1976) observed that the doping element inhibits grain growth of tungsten at higher temperature. Morcom *et al*. (1976) also studied the effect of various doping elements on the reduction of tungsten trioxide and showed mechanism in that the temp noted for the stability of certain oxides varied as a function of doping element. This inturn produced a change in both particle size and morphology.

Reduction of Co-doped silver tungstate: The cobalt doped silver-tungsten powders were produced at 250-750°C with different levels of cobalt concentration. Figure 11a gives a series of photomicrographs which demonstrate the morphologies of 0.14% Co-doped powder. It is evident that the two different types of particles are present in the powder. The small recrystallized particles of tungsten have a well faceted morphology and the larger particles in the background and sometimes surrounding the tungsten are silver. The tungsten particle size is 1 μm (average) while the silver particle size is 3 μm (average). Figure 11b shows the morphology of 0.3% Co-doped silver-tungsten where it can be seen that the particle size of the tungsten is reduced to 0.6 μm and the silver particles are in the size
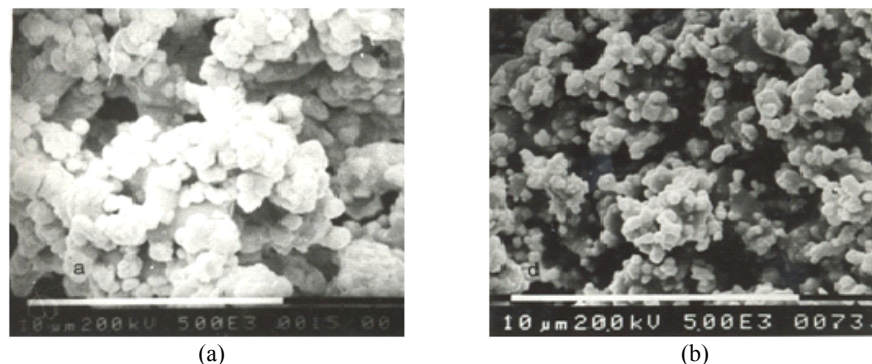
(a)   (b)

Fig. 11: Co-doped Ag-W powders; (a) 0.14% Co-doped Ag-W; (b) 0.30%Co doped Ag-W
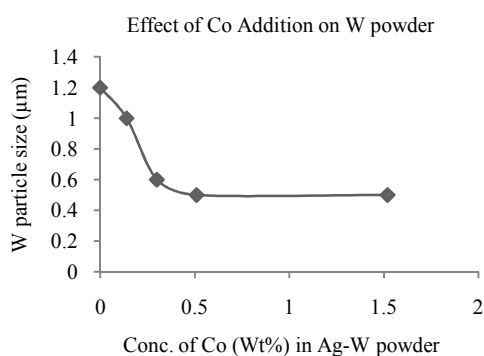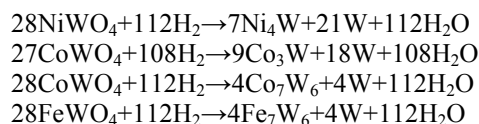

Fig. 12: Effect of Co addition on W particles

range 2-3 μm. From the micrograph a significant dispersion of the recrystallized tungsten particles can be observed.

Effect of cobalt addition on tungsten particle: Figure 12 shows the relationship between the cobalt content and the tungsten particle size, where it can be seen that as the cobalt concentration increased there is a decrease in tungsten particle size. The maximum effect of cobalt was observed at 0.51 Wt% Co (wrt W), where the minimum particle size 0.5 μm (average) was obtained. After this level, no significant reduction in the tungsten particle size was obtained. It is clear that the effect of cobalt addition on the tungsten particle is similar to that of iron in the powder. However, the effect of cobalt is rather more pronounced than that of iron. Initially it was expected that cobalt would behave in a different manner to iron during the reduction process because during precipitation, it was observed that the addition of cobalt changed the precipitation sequence of the tungstates and gave different powder morphology to that of Fe-doped powder. Therefore, it was expected that the growth of tungsten particles could occur in a different way in the presence of cobalt rather than iron. As both powders (iron and cobalt-doped powders) showed a similar behavior, therefore, the effect of morphology of the starting material on the growth of tungsten particles during reduction process seems negligible. During reduction process when WO_2 breaks

down into α-W, these fine particles of $CoWO_4$ would provide nucleation sites for the growth of tungsten particles. The observations in Fig. 11, indicates that cobalt has a rather more pronounced effect on the tungsten particles than iron. This effect may be explained in terms of the formation of their intermetallic compounds (Fe_7W_6, Co_7W_6 or Co_3W). Elements Fe, Ni and Co form inter-metallic compounds with W, during the reduction of their tungstates at temperatures above 700°C.

The following reactions occur:

$$28NiWO_4+112H_2 \rightarrow 7Ni_4W+21W+112H_2O$$
$$27CoWO_4+108H_2 \rightarrow 9Co_3W+18W+108H_2O$$
$$28CoWO_4+112H_2 \rightarrow 4Co_7W_6+4W+112H_2O$$
$$28FeWO_4+112H_2 \rightarrow 4Fe_7W_6+4W+112H_2O$$

According to these reactions if tungsten produced from these tungstates acts as nuclei for tungsten obtained from silver tungstate then the nuclei density could be considered according to the following sequence if the number of nuclei were simply dependent upon the relative amount of free tungsten produced on reduction of the respective metal tungstate:

$$Ni > Co \geq Fe$$

This shows that Ni could give higher nuclei density during reduction of its tungstates than either Co andFe. The above order reflects the effect of elements on the production of tungsten particles based on this assumption that all the powders reduce in a similar manner. Albiston (1989) studied the reduction behavior of Ni-doped silver tungstate. His investigations showed that nickel has a greater effect on the reduction of tungsten particle size than that observed in the present study for cobalt and iron which gives a strong support to the observation made above.

CONCLUSION

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 block, 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. It was then apparent that such a high level of Fe addition caused the growth of the block-like crystals to be modified. In an attempt to reduce the sodium impurity to the minimum possible, some loss of $FeWO_4$ in the silver tungstate was observed during repeated washing of precipitate. An intimate mixture of silver and tungsten was yielded by reduction process at 250-750°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 and Co showed a similar effect on the particle size and produced submicron tungsten particles at 250-750°C.

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