

# Fabrication of Silver-Graphite Contact Materials Using Silver Nanopowders

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Silver-graphite (AgC) composites are used in electrical switchgears as arcing as well as sliding contacts. AgC composite powders for electrical contact applications are conventionally prepared using micron-size silver powder. Present investigation is aimed at exploring the effect of nanosize silver powder, made by colloidal synthesis route, on the processing and properties of AgC contact materials. The AgC composite powders synthesized from micron-size and nanosize silver powders, respectively, are characterized for particle size distribution by dynamic light scattering technique, x-ray diffraction, and scanning electron microscopy. The bulk solid compacts produced by conventional powder metallurgy process of pressing, sintering, and repressing of AgC composite powders are evaluated for their density, microhardness, electrical conductivity, and microstructure. The study reveals that the use of nanosize silver powder not only leads to reduction in sintering temperature but also contributes in improving the properties of the AgC contact materials.

**Keywords** composite materials, electrical contact material, nanocomposites, powder technology, silver-graphite contacts, sintering

## 1. Introduction

Electrical contact materials are used as contact members in a variety of switchgear applications, such as electrical switches, contactors, circuit breakers, relays, etc. (Ref 1, 2). The materials employed as contact members usually consist of markedly two different components, namely, matrix that provides good electrical conductivity and the dispersed phase which determines the switching behavior in terms of resistance to arcing and contact welding during *make and break* operations. In silver-graphite (AgC) contacts, the silver acts as the matrix and the graphite is employed as a dispersed phase. The AgC compositions with graphite in the range of 2 to 5 weight percent (9–20% by volume) are popularly used as arcing or *make and break* contacts, whereas those with greater than 5 wt.% graphite find applications as sliding contacts (Ref 3, 4).

AgC contact materials are manufactured from a blend of micron-size silver and graphite powder particles using one of the two powder metallurgy processing routes namely, press-sinter-extrude route to form wrought AgC strips or wires (from which contact pieces are either punched out or cut) or

press-sinter-repress route for piece by piece production on a relatively small scale (Ref 5, 6). The physical mixing of silver and graphite powder particles in a blender/mixer carried out for the starting powders in both these routes usually leads to problems like segregation and nonuniform dispersion on account of large difference between the densities of the constituent powders. In turn, the morphology of graphite phase in silver matrix and the resultant microstructure of AgC bulk solid affects the electrical contact properties namely, the resistance to arc erosion, the resistance to contact welding, and the over-temperature behavior (Ref 7, 8).

More recently, there has been a growing interest in the direction of application of nanotechnology to produce novel materials (Ref 9, 10). Techniques like sol-gel synthesis, colloidal synthesis, microemulsion, etc. have been developed to synthesize nanopowders (Ref 11–15). Such powders are found to offer a significant improvement in processing and properties of the bulk solids produced therefrom compared to conventional micron-size powders. For instance, nanoparticles with the particle size less than 100 nm have a large specific surface area and hence high reactivity accounting for an additional driving force during sintering. Such powders exhibit enhanced sinterability compared to conventional micron-size powder particles. The onset of sintering for nanopowders is found to take place at a significantly lower temperature compared to conventional micron-size powders. The sintering of nanopowders is found to start at temperatures as low as 0.2 to 0.4  $T_m$  ( $T_m$  = melting temperature in Kelvin) as against 0.5 to 0.8  $T_m$  for conventional powders (Ref 16). Apart from this, the bulk solids prepared from nanopowders possess improved properties such as the density, strength, and hardness.

An attempt has been made in this investigation to synthesize and characterize AgC electrical contact materials using silver nanopowders produced by colloidal synthesis route. The synthesized powders are subsequently consolidated to bulk solid compacts by powder metallurgy process and subjected to evaluation of physical properties and microstructure.

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## 2. Experimental Procedure

Two different types of silver powders, namely micron-size and the nanosize silver powders, were used during this investigation to produce Ag-3wt.%C composite powders. The source for micron-size silver powder was the analytical reagent grade silver powder (–43 micron size) from Sisco Research Laboratory (SRL), Mumbai; whereas the nanosize silver powder was prepared by colloidal synthesis route reported earlier (Ref 12), wherein an aqueous salt of silver such as silver nitrate is subjected to controlled precipitation using tri-sodium citrate and sodium formaldehyde sulfoxylate as the precipitating/reducing agents to yield silver nanoparticles.

Micron-size silver powder was used to synthesize AgC composite powders by blending route. Accordingly, the AgC composite powders as per the blending route were prepared by subjecting the stoichiometric amounts of micron-size silver powder and the graphite powder particles to blending/mixing operation in a cylindrical blender for 30 min at 130 rpm using a roller mill.

Likewise, for preparing AgC nanocomposite powders as per colloidal synthesis route, the stoichiometric amount of graphite was mixed with silver nanopowder particles prepared by colloidal synthesis and was subjected to sonication for 30 min.

In view of the dependence of the arc erosion and welding behavior of AgC contact materials on the particle size of graphite (Ref 17), the electrolytic graphite powders of two different average particle size were used. The coarse graphite powder has the mean diameter of 21.7  $\mu\text{m}$ , whereas the fine graphite powder has the corresponding value as 13.8  $\mu\text{m}$ .

The powders synthesized by above two routes were characterized by using techniques like particle size analysis, scanning electron microscopy (SEM), and x-ray diffraction (XRD). The particle size analysis of silver powders was carried out by dynamic light scattering technique using NICOMP (Santa Barbara, CA) particle size analyzer. Scanning electron microscope (JEOL JSM-5610 LV) was used for morphological investigation of powder samples. The phase identification and crystallite size measurement were done with the help of XRD technique. The powder diffraction profiles were obtained using Rigaku Gieger Flex D-max model (Tokyo, Japan) of x-ray diffractometer within the  $2\theta$  range of  $20^\circ$  to  $90^\circ$  at a scan speed of  $3^\circ/\text{min}$  using Cu target and Cu-K $\alpha$  radiation of 0.15406 nm wavelength at a power rating of 30 kV and 25 mA.

The AgC composite powders were further processed to produce bulk solid compacts of 10 mm diameter and 2 mm height using classical powder metallurgy route of press-sinter-repress. The compaction was carried out at 300 MPa pressure

in single action die compaction mode, and the green compacts were sintered at various temperatures ranging from 900 to 500  $^\circ\text{C}$  in vacuum for varying length of time. The heating rate during sintering was maintained at  $8^\circ\text{C}/\text{min}$  using a micro-processor-based proportional-integral-derivative-type temperature programmer/controller. The sintered compacts were repressed at 900 MPa pressure for further densification to a level close to theoretical density of the composite. The effect of sintering temperature and time on densification behavior and properties of AgC bulk solid compacts was also examined. The repressed compacts were subjected to measurement of the properties like density, microhardness, electrical conductivity, and microstructural examination. The density of the compacts was measured as per Archimedes' principle. The results of density measurement are reported in Table 1 as actual density and percentage theoretical density. The ground and polished compacts were subjected to microhardness measurement using the microhardness attachment of Neophot-21 microscope (Carl Zeiss, Jena, Germany). The electrical conductivity of the compacts was measured using electrical conductivity meter (Type 979, Technofour Electronics Pvt. Ltd., Pune, India) which works on the principle of eddy currents.

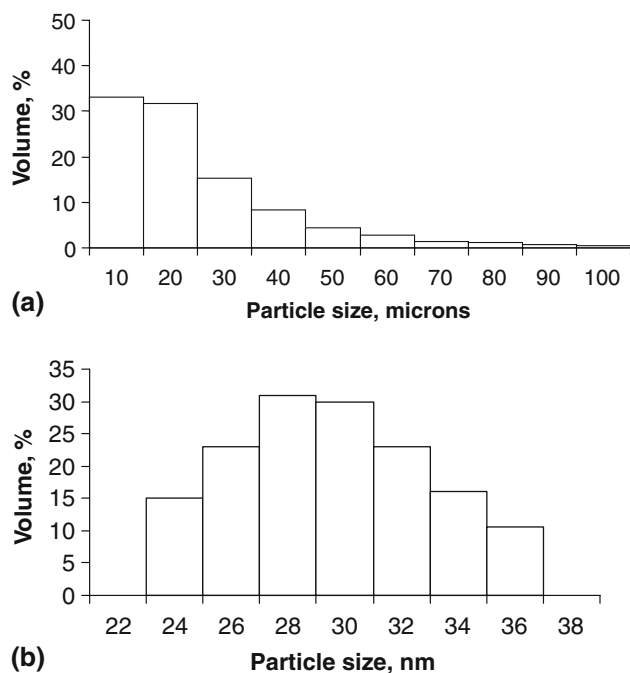
## 3. Results and Discussion

The size distribution of silver in Ag-3wt.%C composite powders synthesized by two different powder synthesis routes was examined using the particle size distribution plots given in Fig. 1(a) and (b). According to size distribution data reported in the form of histogram in Fig. 1(a), the average particle size for micron-size silver powder of blending route is coarser (most of the powder is finer than 40 microns) and the size distribution is relatively broader. Figure 1(b) shows the histogram for particle size distribution of silver nanopowders produced by colloidal synthesis route which indicates that the majority of powder particles are below 40 nm.

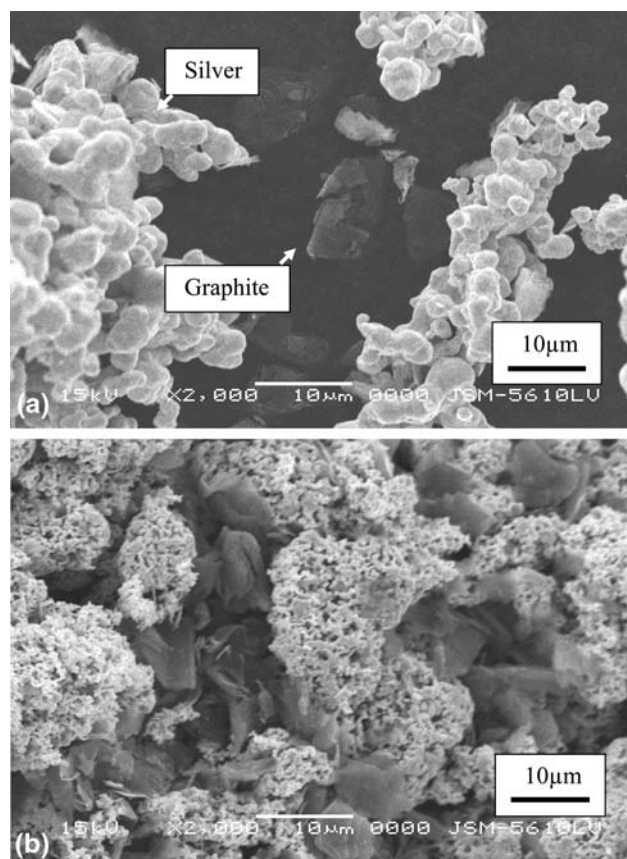
Figure 2 shows the SEM micrographs for the AgC composite powders of two different synthesis routes. The silver powder particles of blending route shown in Fig. 2(a) are relatively coarser and have a more or less rounded morphology. As against this the morphology of silver nanoparticles produced by colloidal synthesis displayed by the SEM micrograph in Fig. 2(b) is highly agglomerated or spongy with lot of inter- and intraagglomerate voids. Although the size of silver powder agglomerates is relatively coarse, the average size of individual silver nanoparticles is around 25 nm. The graphite phase in both the micrographs appears as flake-shaped particles.

**Table 1** Properties of Ag-3wt.%C bulk solid compacts produced by two different synthesis routes

Synthesis route	Sintering condition	Data on sintered compacts		Data on repressed compacts		
		Density, g/cm <sup>3</sup> (%Theoretical density)	Electrical conductivity, %IACS	Density, g/cm <sup>3</sup> (%Theoretical density)	Electrical conductivity, %IACS	Microhardness, Hv
Blending route	900 $^\circ\text{C}/60$ min	8.74 [92.4]	65	9.40 [99.4]	72	58
Colloidal synthesis route	600 $^\circ\text{C}/60$ min	7.50 [79.3]	54	9.42 [99.6]	77	76-79
	500 $^\circ\text{C}/30$ min	7.65 [80.9]	60	9.45 [99.9]	76	63-65
	500 $^\circ\text{C}/60$ min	7.91 [83.6]	59	9.45 [99.9]	76	79-81
	500 $^\circ\text{C}/120$ min	7.61 [80.4]	56	9.32 [98.5]	76	60-62
	400 $^\circ\text{C}/60$ min	7.69 [81.3]	55	9.44 [99.8]	75	76-78



**Fig. 1** Histograms showing particle size distribution for silver powders in Ag-3wt.%C composite powders produced by (a) blending route and (b) colloidal synthesis route



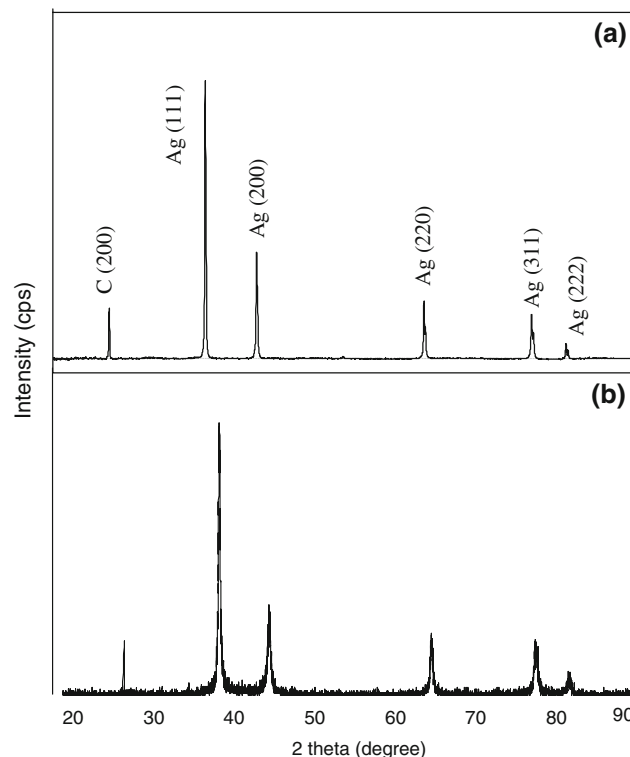
**Fig. 2** SEM micrographs for Ag-3wt.%C composite powders of (a) blending route and (b) colloidal synthesis route

The XRD profiles for AgC composite powders incorporating the micron-size and the nanosize silver powders were obtained and the respective diffraction peaks have been identified in these profiles (Fig. 3). The  $d$  values for the diffraction peaks for the powder samples under test are compared with those reported for corresponding standard material in accordance with JCPDS data files (JCPDS File nos. 4-0783 and 23-64 for silver and graphite, respectively). There is a close agreement between the measured values and the values reported in data files for standard samples. The diffraction peaks for silver in AgC composite powders of colloidal synthesis route are broader as compared to those for blending route, indicative of finer crystallite size for silver nanoparticles of the former route. To calculate the crystallite size, a mathematical analysis of the Bragg's diffraction peaks was undertaken using the Scherrer equation,

$$D = k\lambda / \beta \cos \theta,$$

where  $D$  is the crystallite size,  $k$  is a constant ( $= 0.9$  assuming the particles are spherical),  $\lambda$  is the wavelength of x-ray radiation,  $\beta$  is the line width (obtained after correction for lattice strain and the instrumental broadening), and  $\theta$  is the angle of diffraction. The average crystallite size obtained from XRD data for micron-size silver powder used in blending route is 120 nm, whereas for nanosize silver powder of colloidal synthesis route it is about 30 nm.

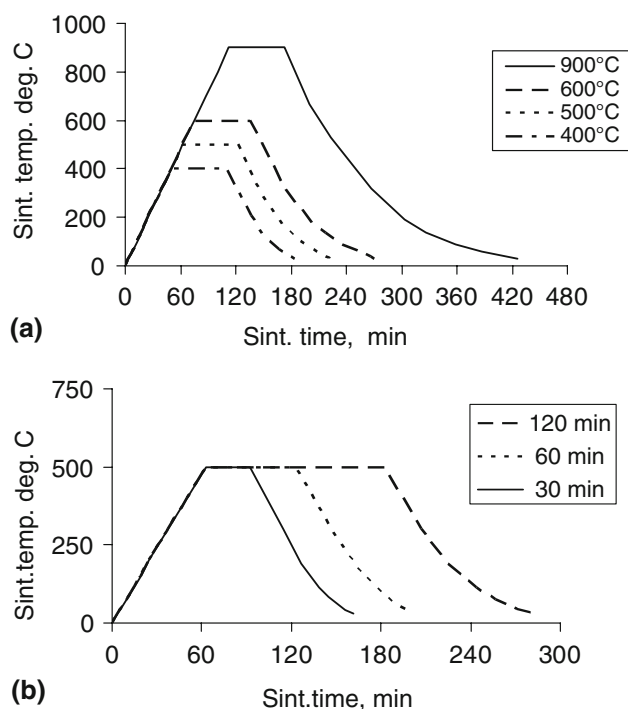
Table 1 gives the data on the properties of Ag-3wt.%C bulk solid compacts produced from powders of two different synthesis routes. For AgC compacts of blending route, it is possible to attain a density level of around 90% of theoretical density in the as-sintered condition for compacts sintered at a



**Fig. 3** XRD profiles for Ag-3wt.%C composite powders of (a) blending and (b) colloidal synthesis route

temperature of 900 °C for 60 min in vacuum and >99% after repressing at 900 MPa.

The green compacts prepared from AgC nanocomposite powders of colloidal synthesis route were sintered at three different sintering temperatures, namely 600, 500, and 400 °C for 60 min holding time to study the effect of sintering temperature on sinterability of nanocomposite powders. The sintering cycles representing different sintering temperatures and holding times are schematically shown in Fig. 4, and the properties of sintered and repressed compacts are reported in Table 1. The results clearly indicate that the sintered density in each case is around 80% of theoretical density. However, on repressing, the density significantly improves to a value greater than 99% of the theoretical density. The relatively lower as-sintered density for the AgC compacts nanocomposite powders of colloidal synthesis route with silver nanoparticles may be attributed to the higher tendency toward agglomeration of nanoparticles. The agglomeration of nanopowders is a serious problem. Very small particles are strongly influenced by the Van der Waals forces and give rise to rapid agglomeration. The green compacts prepared from such agglomerated powders generally exhibit a bimodal pore distribution: small pores within the agglomerate (interagglomerate) and large intraagglomerate pores (Ref 18, 19). The large intraagglomerate pores are not easily removed during sintering and hence account for lower as-sintered density of the material. According to a recent report, the agglomeration tendency of silver nanoparticles and the resultant porosity-related problems can be minimized by their redispersion in suitable organic/aqueous media and their subsequent loading in a water-soluble polymer like polyvinyl alcohol or polyvinyl pyrrolidone (Ref 12). However, such a treatment is not attempted in this study in view of the possible difficulty in removal of loaded polymer during sintering.



**Fig. 4** Schematic sintering cycles for sintering of AgC composite compacts sintered at different (a) sintering temperatures and (b) holding times

The density of the sintered compacts of both the routes on subsequent pressing (i.e., repressing) improves significantly. The corresponding density value for Ag-3wt.%C material reported in literature is 8.8 g/cm<sup>3</sup> (i.e., 93% of theoretical density) (Ref 20). The electrical conductivity for Ag-3wt.%C compacts of colloidal synthesis route is above 75% IACS after repressing as against the literature value of the order of 55 to 62% IACS. The average microhardness value for the compacts of colloidal synthesis route is around 78 kg/mm<sup>2</sup>.

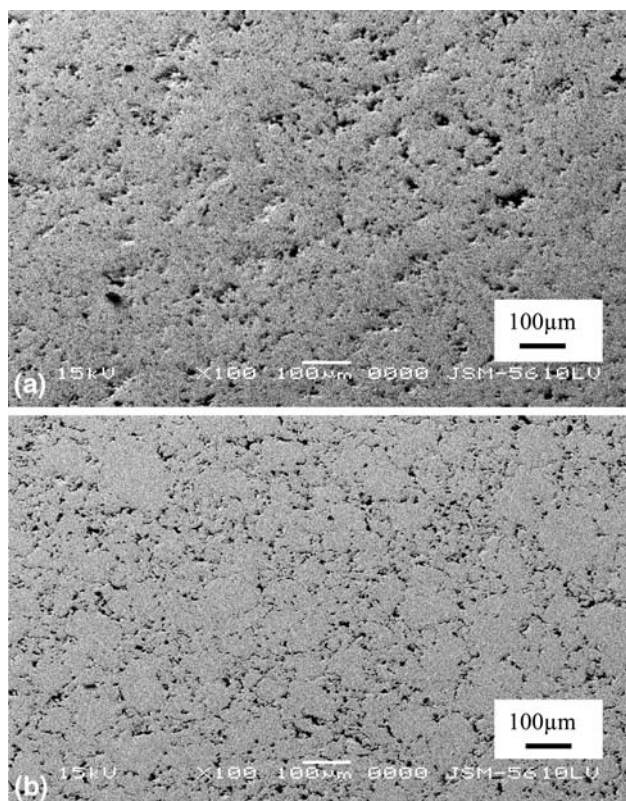
The use of nanosize silver powders in fabrication of AgC contact materials during this investigation has displayed a remarkable improvement in the microhardness of the bulk solid compacts. The microhardness for Ag-3wt.%C bulk solid compacts prepared from AgC powders of blending route is 58 kg/mm<sup>2</sup>. This is much lower as compared to values obtained for the bulk solid compacts of colloidal synthesis route. The lower hardness for compacts of blending route may be explained on the basis of the Hall-Petch relation which states that the mechanical properties (strength and hardness) of metals and alloys depend on grain size. Hall and Petch showed that the hardness or strength of polycrystalline metals increases as the grain size decreases. Materials with grain size in the submicron to nanometric order (i.e., between ~10 nm and <1 µm) have greater hardness than those with grain size equal to several tens of micrometer. The physical basis for this behavior is associated with the difficulty of dislocation movement across grain boundaries and stress concentration due to dislocation pile-up. The compacts of blending route have been sintered at 900 °C temperature which is relatively close to the melting point of silver (m.p. of pure Ag is 960 °C) and hence would have coarser grain size permitting the dislocation movement within them with ease. In turn, they offer lower hardness. As against this, the compacts of colloidal synthesis route are prepared from silver nanopowders with average particle size of the order of 40 nm and in turn nano size grains. The nanometric grain size is by and large retained in case of the bulk solid compacts of colloidal synthesis route because the sintering temperature for these compacts is between 400 and 600 °C only as against 900 °C for compacts of blending route. The nanometric dimensions of the grains for the press-sinter-repressed bulk solid compacts of colloidal synthesis route give higher grain boundary area and hence more obstacles by the grain boundaries to the movement of dislocations responsible for higher hardness.

As per the data given in Table 1, the microhardness for the bulk solid compacts of colloidal synthesis route sintered at three different temperatures, namely 600, 500, and 400 °C for a constant holding time of 60 min marginally differ from one another. The maximum hardness of 79 to 81 kg/mm<sup>2</sup> is obtained at sintering temperature of 500 °C for 60 min holding time and thus this appears to be the optimum sintering condition for this material.

Likewise, the effect of holding time at a constant sintering temperature of 500 °C on properties has also been examined. Here also sintering temperature of 500 °C and holding time equal to 60 min shows optimum behavior. Lower hardness at shorter holding time of 30 min may be attributed to somewhat undersintering, whereas that at longer holding time of 120 min may be due to grain coarsening effect associated with longer holding time.

Figure 5(a) shows the microstructure of Ag-3wt.%C bulk solid compacts prepared from AgC composite powders of blending route. The matrix in this microstructure indicates the





**Fig. 5** SEM micrographs for Ag-3wt.%C bulk solid compacts produced from powders of (a) blending route and (b) colloidal synthesis route

silver phase, whereas the black areas represent the second-phase particles of graphite. The microstructure is quite heterogeneous with the tendency to formation of islands of silver separated by the network of graphite agglomerates. Such a microstructure usually accounts for higher erosion rate and greater welding tendency for the contacts during service. The microstructures for the bulk solid compacts of colloidal synthesis route shown in Fig. 5(b) display a much uniform dispersion of the graphite powder particles compared to that seen in the case of blending route. This is a desired microstructure for improved electrical contact properties of AgC contact materials.

## 4. Conclusion

The effect of silver nanopowders on processing and properties of AgC electrical contact materials was studied. The main conclusions of this study are:

1. The conventional process of press-sinter-repressing of a blend of micron-size silver and graphite powders offers a heterogeneous microstructure with a network of graphite surrounding the silver islands responsible for inferior bulk properties which, in turn, affect the electrical performance of the AgC contact materials adversely.
2. The colloidal synthesis route for AgC nanocomposite powders using silver nanopowders provides improved

microstructure in terms of fine and uniform dispersion of graphite in silver matrix and the resultant bulk properties superior to conventionally processed material. It is possible to obtain as much as 33% increase in microhardness for this material compared to that for conventional material produced by blending route. The improvement in microhardness for AgC bulk solid compacts of colloidal synthesis route can account for lesser mechanical erosion of the contact members during service.

3. It is possible to produce AgC contact materials by sintering at a temperature as low as 500 °C, and yet with superior combination of properties. The AgC nanocomposites sintered at 500 °C for 60 min holding time showed the best combination of properties, namely the final theoretical density of the order of 99.9%, electrical conductivity equal to 76% IACS, and 79 to 81 kg/mm<sup>2</sup> microhardness.
4. The properties of AgC bulk solid compacts produced from AgC nanocomposite powders of colloidal synthesis route are better than even those reported in the literature.
5. The use of silver nanopowders to manufacture AgC electrical contact materials can offer a significant reduction in sintering temperature, thereby improving the economics of the sintering process and leading to an overall reduction in the production cost.

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