Turkish J. Eng. Env. Sci.
26 (2002) , 285 – 291.

Effect of Oxygen Content on the Sintering Behaviour of Silver Nanopowders Produced by Inert Gas Condensation

Mehmet TÜRKER
Gazi University, Technical Education Faculty, Metallurgy Department,
Beşevler, Ankara-TURKEY
e-mail: mturker@tef.gazi.edu.tr

Received 24.05.2001

Abstract

Polymer-based materials are made electrically conductive by combining with a particulate conductive material. Instead of using high aspect-ratio conventional fillers, such as fibres and flakes, highly porous silver nanopowders were produced for using in polymer matrix composites. Such powders were produced by inert gas condensation (IGC) in a helium atmosphere with or without additional oxygen. The effect of oxygen content on the size, morphology and specific surface area of the particles were determined. In addition, powders were annealed at 100, 150, 200 and 300°C for 60 minutes and the sintering behaviour of particles depending on oxygen content was assessed.

Key words: Inert gas condensation, Ag nanopowders, Sintering.

Introduction

Interest in a wide variety of nanostructured materials, with average grain or other structural domain size below 100 nm, has increased during the last decade with the anticipation that their properties are different from, and often superior to, those of conventional materials that have phase or grain structures on a coarse scale (Siegel, 1993; Einar *et al.*, 1988). These materials are characterized by a large number of grain boundary interfaces in which the local atomic arrangements are different from those of the crystal lattice. Due to their high surface area, small nanoscaled particles generally showed a strong interaction (Nieman *et al.*, 1991).

Ding *et al.*, (1996) stated that nanostructured materials are now widely used in different parts of industry. It is possible to use silver powders as a reinforcement material in polymer matrix composites (PMCs) to make them electrically conductive due to their high electrical conductivity and relatively good stability against oxidation during application. According to Günther (1999), highly porous silver nanopowders are potentially useful as filler material in PMCs due to improvements in thermal cycling properties as compared to composites filled with commercially available flake powders or fibres. Such nanopowders can be produced by inert gas condensation (IGC), where Ag is evaporated from a tungsten crucible in an inert gas atmosphere (Siegel, 1993). This process allows the production of very pure nanopowders. However, residual oxygen impurity in the gas atmosphere also exists throughout the process at concentrations in the ppm range. This may lead to the formation of a tungsten oxide or surface oxide layer on Ag particles. If the oxygen level is too high, this oxide sublimes around 850°C and is introduced into the powder product as an integral component that cannot subsequently be removed. It is believed that the residual oxides adversely affect the properties of silver nanopowders.

In this work, an investigation was carried out to determine whether there was a critical concentration of tungsten oxide, above which the shape, size and the morphology and also the sintering behaviour of particles was affected. Thus, the oxygen concentra-

tion in the carrier gas was increased to very high levels during the production of particles and the behaviours mentioned above were investigated.

Experimental Procedures

Powder preparation and characterization

Silver nanopowders were produced by IGC in a reduced pressure helium atmosphere with or without the addition of a small amount of oxygen. Helium gas was generally used as both a cooling agent and a carrier gas for the nucleating metal particles. However, in some experiments, in order to see the effect of oxygen on the properties of Ag nanopowders, a small amount of oxygen was added to the helium and then powders were produced in a helium atmosphere together with 1, 2, 5, 10 and 20 sccm/min (standard cubic centimetre/min) oxygen.

The Ag powder deposits produced were then sieved with 0.5 mm grit. The powders were put in a Pyrex container and annealed at 100, 150, 200 and 300°C (373, 423, 473 and 573 K) for 60 minutes to see the effect of annealing temperature on the sintering behaviour of the Ag nanopowders. Characterization of powders, especially the coarsening behaviour and sinter neck features of the particles, was carried out by scanning electron microscopy (SEM). A Leitz field emission scanning electron microscope with a nominal resolution of about 3 nm range was used. The specific surface area of the powders was determined by volumetric nitrogen adsorption performed with Nova 2200 (Quantachrome) equipment based on the Brunauer, Emmett and Teller (BET) method (Heimenz, 1986). After each process, the particle size was determined using the mean linear intercept (MLI) method. The amount of tungsten and oxygen in the powders was determined by atomic emission spectroscopy and hot extraction, respectively.

Results and Discussion

Effect of oxygen flow on the amount of tungsten and oxygen in Ag nanopowders

Ag nanopowders were produced in a pure helium atmosphere with or without additional oxygen flow and its effect on the amount of (wt%) tungsten and oxygen in the Ag nanopowders was determined by atomic emission spectroscopy.

As expected, there was a direct relation between the oxygen content and the amount of tungsten in the Ag nanopowders (Fig. 1). In the Ag powders produced in a "pure" helium environment, it was observed that the powders contained about 0.3 wt% tungsten. This was due to residual oxygen in the chamber. Increasing the oxygen content from 1 sccm/min to 20 sccm/min, the amount of W in Ag nanopowders also increased from 1.91 wt% to 12.6 wt%. Similarly, increasing the oxygen flow during the production of particles, the amount of (wt%) O_2 in Ag nanopowders increased (Fig. 1). With increasing oxygen content, the size, morphology and sintering behaviour of particles are affected.

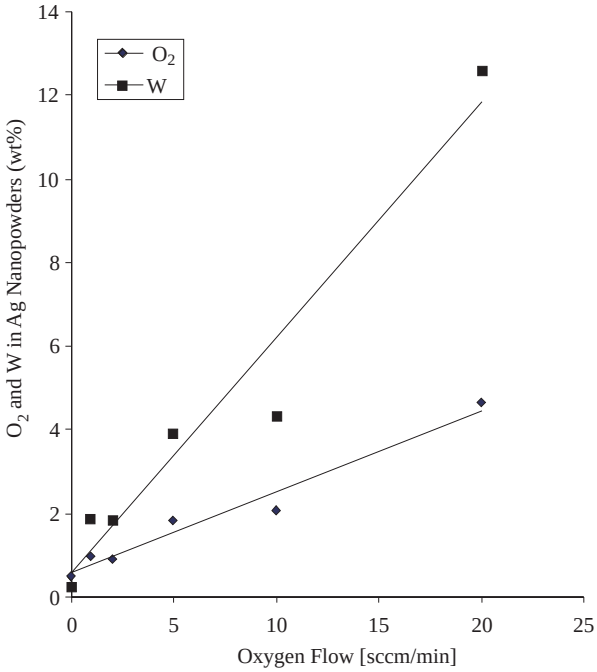


Figure 1. Effect of oxygen flow on the amount of (wt%) tungsten and oxygen in Ag nanopowders.

Effect of annealing temperature on the powder size and morphology

Microstructure of powders produced in He atmosphere

Powders produced in a pure 20 mbar helium atmosphere with no additional oxygen were sintered at 100, 150, 200 and 300°C for 60 min and their microstructures were evaluated both as produced and in annealed conditions. Before sintering, the particles were roughly spherical and about 75 nm in size. These particles were found not to be separated from

each other and were generally found to be necked in a chain-like network (Fig. 2a).

It is known that during the synthesis of nanoscaled particles by IGC growing occurs by coalescence when particles collide. Coalescence takes place provided that the temperature is high enough and the surface of the particles is clean. Since pure helium was used in this experiment as the carrier gas, it is believed that no reaction took place between the carrier gas, particles and tungsten evaporator. This resulted in the formation of a very clean particle surface without the surface oxide layer that facilitated the growth of the particle together with sinter necks. EDX analysis also indicated that there was no W in the powders produced in a pure helium atmosphere (Fig. 2b). This kind of sinter neck was found to be good for the electrical conductivity of the silver powders in polymer matrix (Busmann *et al.*, 1999).

After annealing at 100 and 150°C, small amounts of powder necking together with increasing particle size occurred where 150 nm particles were achieved (Fig. 2c). Increasing the sintering temperature to 200°C and 300°C resulted in increasing sinter necks and particle sizes. After annealing at 300°C for 60 minutes, powder size increased to over a micron with the formation of very coarse sinter neck interfaces (Fig. 2d). In some areas, due to the diffusion of Ag atoms, more than two particles combined and became a new and coarse particle. However, the initial particle interfaces were clearly visible in SEM micrographs after this stage. At low magnification, the sintered particles looked like a porous compact material (Fig. 2e).

SEM investigation and BET results indicated that sintering of the particle is negligible up to 200°C since there was almost no difference in the specific surface area of powders. Strong changes occurred after sintering at 200°C and 300°C. Due to the cleaner Ag nanoparticle surface on these particles compared to that of the particle produced in an oxygen containing environment, slightly faster particle coarsening was observed.

Microstructure of Powders Produced in Helium with 10 sccm/min Oxygen Gas Flow

Powders produced in 20 mbar helium with an additional 10 sccm/min oxygen were sintered at 100, 150, 200 and 300°C for 60 minutes and microstructures of as produced and annealed particles were evaluated. The initial particles were more spherical and smaller (44 nm) than those produced in a helium atmosphere without additional oxygen. These small particles were generally found to be separated from each other and agglomerated into chains and tangles, together with small amounts of sinter necks (Figure 3a). Mean particle size was about 30 nm.

The formation of fine spherical particles with small amounts of sinter necks was due to the carrier gas, which contained some oxygen. Oxygen caused the formation of Ag oxides and/or WO_2 (Fig. 3b), both contributing to the particle coating, and thereby reduced surface diffusion (Borg and Dienes, 1998) and sinter neck growth rate. This suppressed the growing behaviour of powders during processing and also changed the surface tension of powders and resulted in the formation of fine spherical particles.

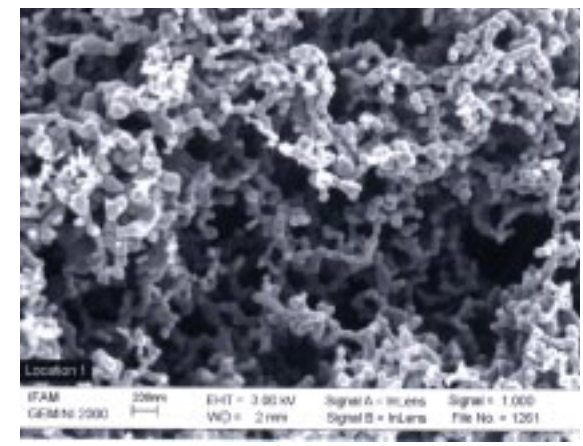
After sintering at 100°C, almost all powders were still perfectly spherical, although there was only a small amount of irregularly shaped particles in some areas (Fig. 3c). The mean powder size was about 60 nm. When increasing the sintering temperature to 300°C, both necking and powder size increased. Finally, a particle size over 500 nm was obtained after sintering at 300°C for 60 min (Fig. 3d). Particles were roughly spherical in most areas and particle sizes varied from place to place. The low magnification micrograph shows (Fig. 3e) that there are still considerable amounts of un sintered particles in the powders.

The difficulty in sintering on these particles is due to the surface oxide layer that formed during processing in an oxygen containing environment. At lower temperatures (100 and 150°C), almost no sintering or particle coarsening occurred. However, when increasing the annealing temperature to 200 and 300°C, both particle coarsening and sinter necking occurred on the powders. But this growing behaviour was still much slower compared to that seen on the powders produced in a pure helium atmosphere.

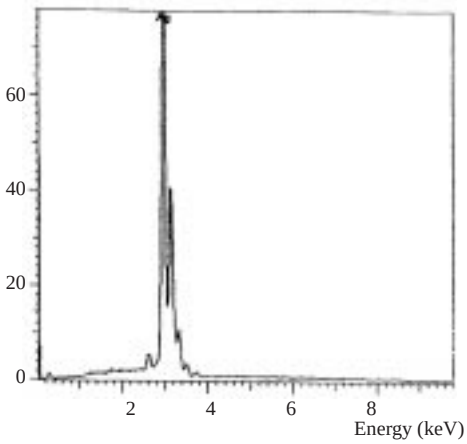
Determination of powder surface area

Effect of oxygen content on the powder specific surface area

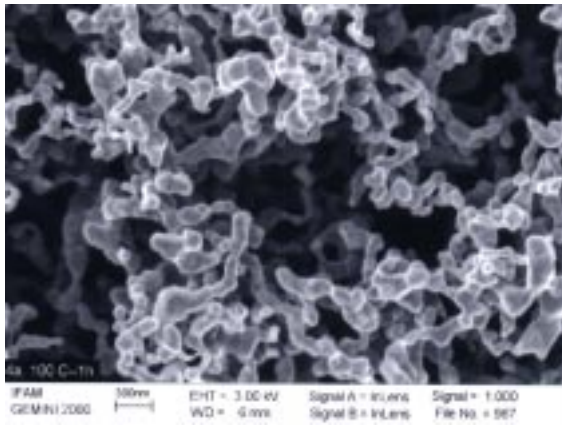
In general, it can be seen from BET results (Fig. 4) that, with increasing amounts of oxygen, the specific surface area of powders increased, i.e., primary particle size decreased. SEM investigation showed that in powders produced without additional oxygen, the average particle size was about 75 nm, whereas the value was about 44 nm when the powders were produced with a 10 sccm/min oxygen flow rate.



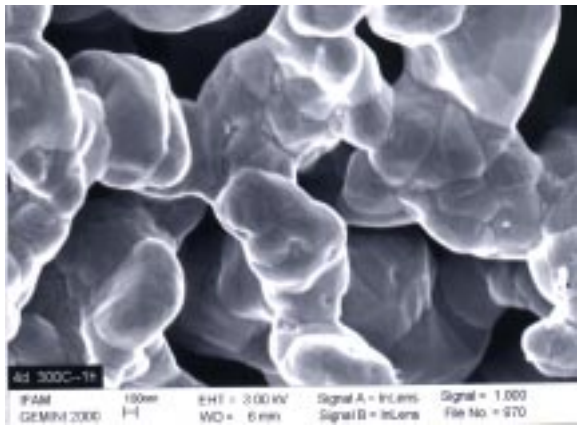
(a)



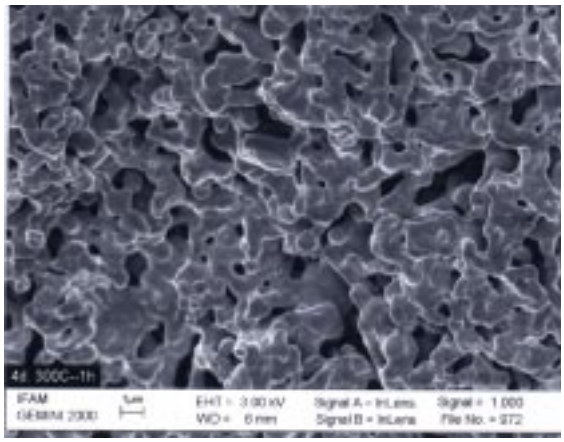
(b)



(c)

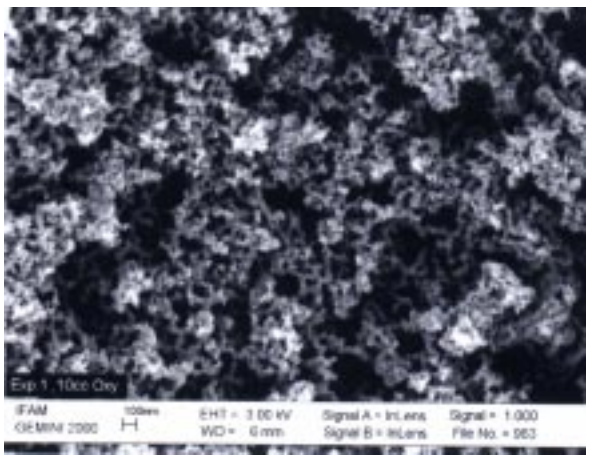


(d)

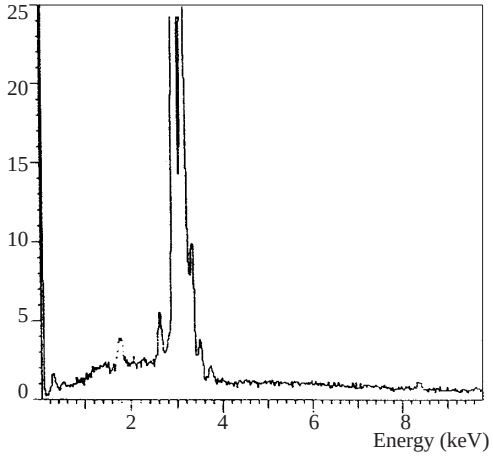


(e)

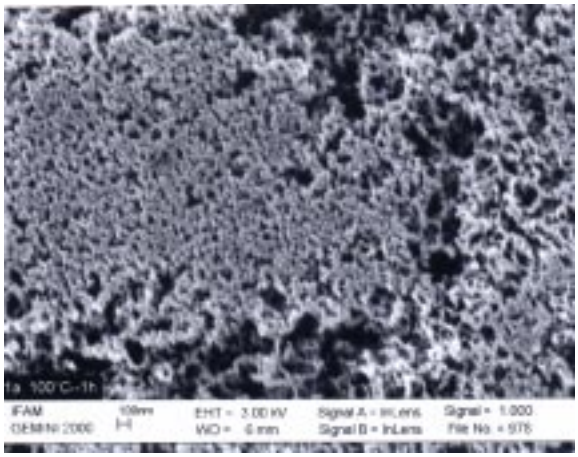
Figure 2. SEM images of powders produced in 20 mbar helium atmosphere: (a) as produced (b) EDX analysis indicates no W in powders (c) small amount of particle coarsening after annealing at 100°C for 60 min, (d) formation of coarse particles together with sinter necks after annealing at 300°C for 60 min, (e) general view of particles annealed at 300°C for 60 min at low magnification.



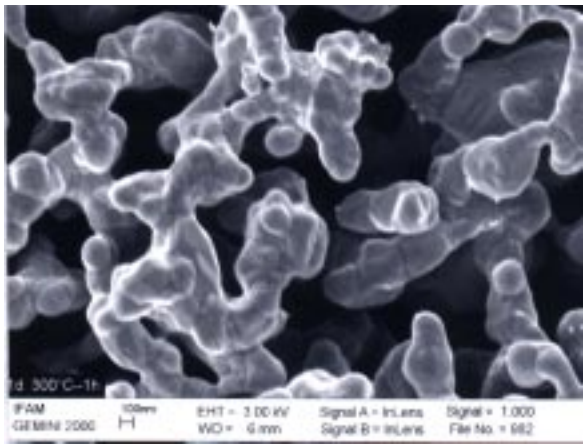
(a)



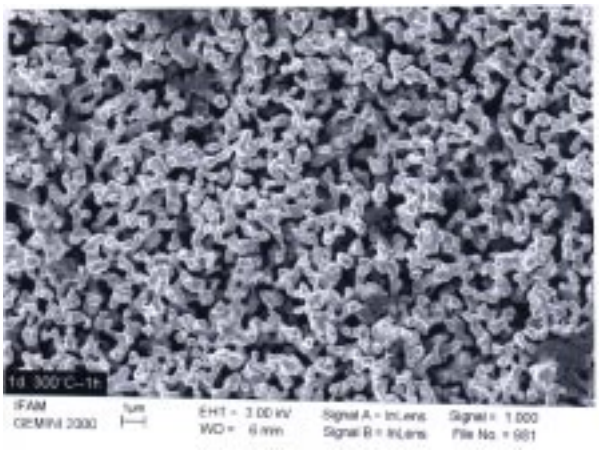
(b)



(c)



(d)



(e)

Figure 3. Microstructures of powders produced in helium with 10 sccm/min oxygen: (a) as produced, (b) EDX analysis indicates a small amount of W in powders, (c) small amount of sinter necks and particle coarsening after annealing at 100°C for 60 min, (d) formation of coarse particles together with sinter necks after annealing at 300°C for 60 min, (e) general view of particles annealed at 300°C for 60 min at low magnification.

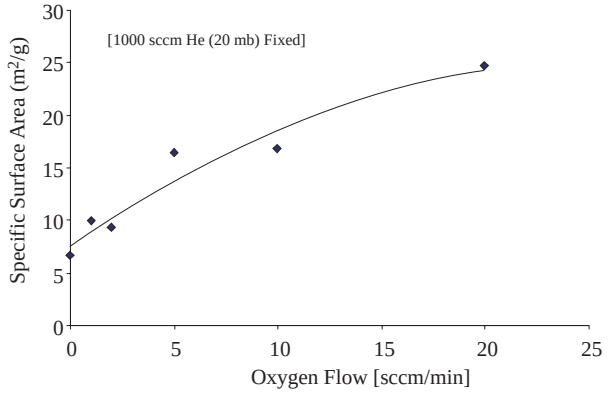


Figure 4. Effect of oxygen content in the helium carrier gas on the specific surface area of Ag nanopowders.

BET results showed that when powders were produced under a pure helium atmosphere, the surface area of the powders was 6.5 m^2/g. When increasing the oxygen content to 20 sccm/min, the specific surface area of particles increased to 24 m^2/g. These results indicated that a higher oxygen content within the carrier gas resulted in a decrease in the primary particle size and a change in the shape of Ag nanopowders.

Effect of sintering temperature and oxygen content on the powder specific surface area

The two powders produced in pure helium or with 10 sccm/min oxygen flow were isothermally annealed at different temperatures of 100, 150, 200 and 300 °C (373, 423, 473 and 573 K) for 60 minutes and specific surface areas were determined by BET. As seen in Figure 5, in both samples (with or without oxygen) small amounts of necking and particle coarsening and consequently a slight decrease in powder specific surface areas were determined after sintering at 100°C and 150°C. However, considerable amounts of sinter necking took place in both types of powder on sintering at 200°C and 300°C. A sharp decrease in the specific surface areas of the particles was observed.

On the other hand, powders produced in a 10 sccm/min oxygen flow rate had a larger initial surface area (16.76 m^2/g) compared to that produced in a pure helium environment. Almost no change occurred in the specific surface areas of the powders after sintering at 100°C or 150°C. However, a sharp reduction occurred in the specific surface areas of the powders after annealing at 200°C or 300°C.

These results indicated that small amounts of grain growth and necking before 200°C were only seen in the particles produced in a helium atmosphere, whereas almost none was seen on the particles produced in an oxygen containing environment. However, in both samples the main particle growth and sinter necking processes took place at temperatures of 200°C or above. This behaviour was more pronounced the powders produced in a helium atmosphere. The SEM investigation also confirmed these results.

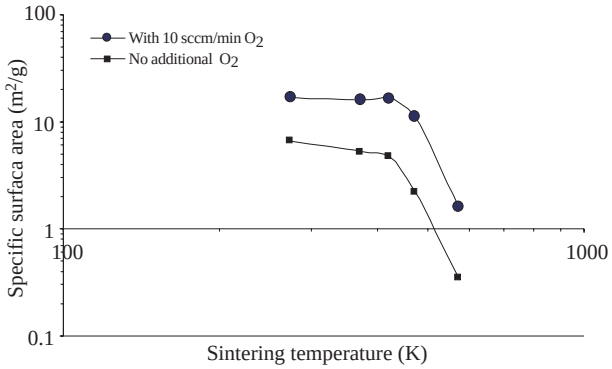


Figure 5. Effect of temperature in 60 minutes sintering on the specific surface area of Ag nanopowders produced at two different oxygen levels in the helium carrier gas.

The difficulty in sintering of the oxygen processed particles at lower annealing temperature (up to 200°C) is presumably due to the formation of a small amount of AgO layer on the surface of the particles. This oxide layer hindered the formation of sintering at lower temperatures. However, at higher temperatures (200 and 300°C) AgO decomposed and enabled better metal-metal contact, which resulted in sintering, particle coarsening and decreasing specific surface areas. Since the particles produced in a pure helium environment did not form a surface oxide layer, these particles could be slightly sintered at the lower temperatures (up to 200°C) and much faster at higher temperatures (200 and 300°C).

Another possible factor that affected the sintering behaviour of these powders was particle shape. In the case of an oxygen containing environment, the particles were almost perfectly spherical compared to those produced in helium. In the case of spherical particles, they came into contact with each other only at one point, which made pressureless sintering difficult. However, in the case of irregular particles, larger contact areas were observed, which made sintering easier.

Conclusions

Ag nanopowders were produced by IGC in a pure helium atmosphere with or without additional oxygen at flow rate of 1, 2, 5, 10 and 20 sccm/min, and the size, morphology, specific surface area and sintering behaviour of the particles were evaluated. The following results were obtained:

- With increasing amounts of oxygen, the specific surface area of particles increased due to the formation of finer spherical silver nanoparticles with less chain-like morphology
- Particles produced in a pure helium atmosphere showed better sintering behaviour with coarser sinter necking compared to those seen on the powders produced in an oxygen containing environment. This is due to the formation of less spherical particles with no surface oxide layer, which facilitated the sintering behaviour of particles. These irregular particle shapes had more than one contact point, making sintering easier.

Acknowledgements

The author would like to thank TÜBİTAK for its financial support of his work carried out in IFAM/Bremen (Germany) with NATO B2 Project during the summer of 2000. Many thanks Prof. B. Günther for his valuable discussions. The author also thanks Prof. Kunze and Dr. F. Petzoldt for giving him the opportunity of using the facilities in IFAM.

References

Borg R.J. and Dienes G.J., An Introduction to Solid State Diffusion, Academic Press Inc., San Diego p 296, 1988

Busmann H.G., Gunther B. and Mayer U., "Polymer Matrix Composite Filled with Nanoporous Metal Powders: Preparation and Electrical Properties", NanoStructured Materials, 12, 531-534, 1999.

Ding J., Miao W.F., Tsuziki T., McCormick P.G. and Street R., Synthesis and Processing of Nanocrystalline Powder, Ed by D.L. Bourell, The Mineral and Material Society, 69-78, 1996.

Einar Kruis F., Fissan H. and Peled A., "Synthesis of Nanoparticles in the Gas Phase for Electronic, Optical and Magnatic Application-A Review", Journal of Aerosol Sci., 29, No.5/6, 511-535, 1988.

Gunther B.H., "Metal Nanopowders for Electrical Conductive Materials", The International Journal of Powders Metallurgy, 35, 53-58, 1999.

Heimenz P.C., Principles of Colloid and Surface Chemistry, Marcel Dekker, New York, 1986.

Nieman G.W., Weertman J.R. and Siegel R.W., "Mechanical Behaviour of Nanocrystalline Cu, Pd and Ag Samples", Microcomposite and Nanophase Materials, The Mineral and Materials Society, Ed. By D.C. Van Aken *et al.*, 15-25 1991.

Siegel R.W., Nanophase Materials Assembled from Atom Clusters" Material Sci and Eng., B19, 33-43, 1993.