Sintering Behaviour of Coated Particles Investigated by a Sintering Model

Kati Flemmig, Klaus-Peter Wieters, Bernd Kieback

Technische Universität Dresden, Institut für Werkstoffwissenschaft IfWW, Helmholtzstraße 7, 01062 Dresden, Germany

Abstract

Coatings on powder particles influence the sintering behaviour in different manner depending on the combination of metallic components, structure of core/coat material and the geometrical conditions. To examine the effects, basic investigations have been carried out with sintering models of the coil-type using wires with electro-deposited coatings. Cu-Ni (complete solubility) and Cu-Ag (partial solubility) systems were investigated. Neck growth between wires, homogenization and interdiffusion are studied by light microscopy, scanning electron microscopy (SEM) - energy dispersive spectrometry (EDX) and discussed in relation to coating thickness, sintering temperature and time.

Introduction

In PM-part production either powder mixes or pre-alloyed powders are used to obtain the alloy composition needed. Difficulties with mixed powders include demixing and insufficient homogeneous alloy formation if small concentrations should be introduced. The homogeneous distribution of all elements can be obtained by the utilization of the pre-alloyed powders which, however, show a poor compaction and sintering behaviour. /1-2/ If coated powders are used the advantages are: easy control of the alloy content (coating thickness), regular distribution of the alloying elements, a good compaction behaviour and the close contact between the components favouring sintering and homogenization. /1, 3-5/

To understand the sintering behaviour of coated powders, wire models were investigated. Similar experiments by F. Thümmler /6/ showed that sintering (neck growth) was activated by interdiffusion of the components. To describe the interdiffusion during sintering concentric sphere model was discussed in H. A. Kuhn, A. Lawley, R. W. Heckel and F. V. Lenel /7-9/. It is the aim of the present work to deeper understand the interaction between the interdiffusion effects and sintering behaviour (neck growth) in the model system. Electrolytic plating was chosen to prepare the coated particles. Two systems one with complete solubility (Cu-Ni) and the other with limited solubility (Ag-Cu) were chosen. Coating thickness was varied between one and ten micrometer.

Experimental Procedure

Wire models were prepared for the investigation of sintering. The advantage of this model is the two dimensional geometry, which allows access to a lot of information from one sample by a metallographic preparation of the cross section (many contacts in one area) /6/. The characteristics of the wires used and of the coats prepared by electrolytic plating are given in Table 1.
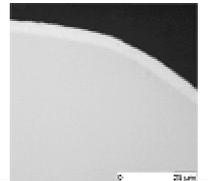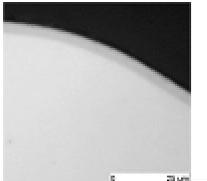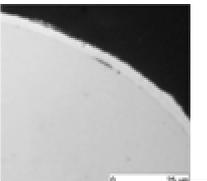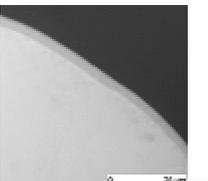
Core	Nickel	Copper	Silver	Copper
Chemical characterization[1]	99,98%	99,9992%	99,9985%	99,9992%
Average grain size	9 µm	17 µm	14 µm	17 µm
Coat	**Cu onto Ni**	**Ni onto Cu**	**Cu onto Ag**	**Ag onto Cu**
Chemical characterization[2, 3] [ppm]	310 O, nd[4] N, nd C, nd S, 79 H	nd O, nd N, 460 C, 41 S, 103 H	179 O, nd N, 145 C, nd S, 121 H	nd O, 166 N, 385 C, nd S, 83 H
Average grain size[5]	12-45 nm	80-150 nm	30 nm	450 nm
Cross microstructure				

Table 1: Characteristics of the coated wires used for sintering experiments.

The wire model dimensions are: ~3000 m coil diameter, 250 µm wire-diameter and three different coatings with the thickness of approximately 1, 5 and 10 µm. The cleaned wires were coated by a galvanic process in a special apparatus[6]. The coated wires were wound three times on a coil of the same material as the wire. The coating thicknesses and temperatures were chosen taking into account the phase diagrams (Figure 1).
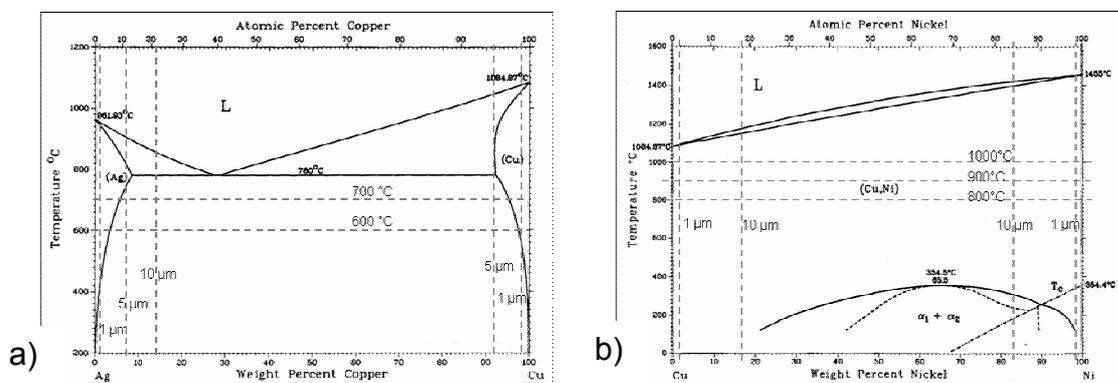

a)   b)

Figure 1: Phase Diagrams of the investigated materials with plotted sintering parameters a) System Ag_wCu_c / Cu_wAg_c[7] and b) Cu_wNi_c / Ni_wCu_c /10/. The dotted vertical lines show the overall composition of the wires for the given thickness of the coat.
In the System AgCu it was aspired to create two different diffusion-profiles: the first one in the region of solubility and the second one in the two-phase region. The measurements of the

---

[1] Specification from supplier AlfaAesar
[2] IFW Horiba Hydrogen Analyser EMGA-621W
[3] LECO TC 463 - O, N; LECO CS 400 - C, S; IFAM Dresden
[4] nd – not detectable
[5] X-Ray diffraction: Siemens D 500 using different fit functions, IfWW
[6] Made by IfWW; Ag and Cu electrolyte: Thome Oberflächentechnik, Ni electrolyte: Krause /11/
[7] Cu_wAg_c, indices: w-wire, c-coat

diffusion profiles were measures by EDX system with a theoretical spatial resolution of 0,4 m /12/.

The tracer diffusion coefficients of the system Ni-Cu at 1000°C ($D_{Cu(in\ NiCu)}$ ($1*10^{-14}$ m²/s) > $D_{Ni(in\ CuNi)}$ ($2*10^{-15}$ m²/s) /13/) show that the copper diffusion into the NiCu-solid solution is faster than approximately one order of magnitude than the diffusion of nickel into the same solid solution (causes Frenkel-Porosity[1] and Kirkendall-Effect[2] /2/). The copper diffusion into silver is only approximately 2 times faster than the diffusion from silver into copper (tracer impurity diffusion coefficient at 700°C: $D_{Cu(in\ Ag)}$ ($5,4*10^{-15}$ m²/s) > $D_{Ag(in\ Cu)}$ ($2,2*10^{-15}$ m²/s) /14/). Small or no Frenkel-Porosity and Kirkendall-Effect are expected.

Results and Discussion

The main driving force for sintering correlates with the neck-radius in the contact zone, while the very high concentration gradient in the interface wire-coat as well as the microstructure of coat and core are expected to interfere with the diffusion mechanisms of sintering.

Figure 2 shows the average x/a values of uncoated and coated wire models, where x is the neck radius and a the radius of the coated wire. The coated sintering partners show an increased x/a ratio in comparison to uncoated ones. Two reasons for the activation of sintering may be considered: a) the higher defect density and smaller grain size of the coat and b) the high defect density due to the high concentration gradient and the hetero diffusion (different diffusion coefficients) at the interface core-coat. In the case of the same material of core and coat the influence of the microstructure of the coat on the sintering behaviour is relatively small except for copper coatings as it was shown in earlier experiments /6/. Our experiments show the same tendency.
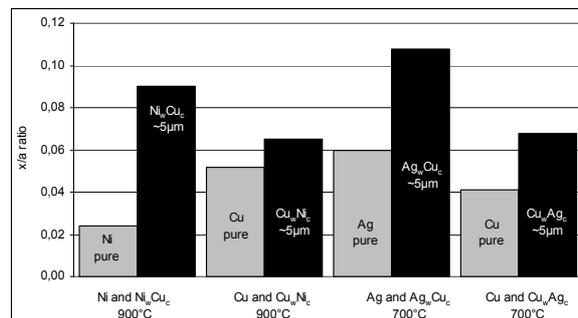

Figure 2: Comparison of x/a-ratio of pure and coated wire models. (Sintering parameters: 0 min holding time in vacuum)

In all experiments porosity was observed in the copper coats after thermal treatment. Copper coats separated from wires after annealing at the same temperature showed porosity too without any interdiffusion happened. Dissolved gases may not be the reason for the porosity because the concentration of the gas is too low (see Table 1). The formation of inner surfaces (pores) is expected to occur by healing up of the lattice defects (vacancies), density of which depends on the plating current density. In the case of more than $5-10x10^3$ A/m² higher porosity could be seen /15/. The investigated copper coats were plated at more than $10x10^3$ A/m² to get a smooth surface and a suitable deposition rate.

---

[1] also named Kirkendall-Porosity
[2] shifting of the initial contact grain boundary because differences in self diffusion coefficients

The diffusion between core and coating during non-isothermal and isothermal sintering is governed by the different partial diffusion coefficients. A significant influence on the neck growth between the coated particles is expected from the chemical diffusion and the resulting vacancy transport.

On the side of the material with the higher diffusion coefficient a zone of higher defect density will develop, which can support the mass transport into the contact zone. The thickness of the coat influences the position of this zone in relation to the contact area. The different diffusion coefficients in the system nickel-copper cause the Kirkendall-Effect and Frenkel-Porosity /2/. Porosity appears within the coat when nickel is copper-coated and below the coat, when copper is nickel-coated (see Fig. 3).
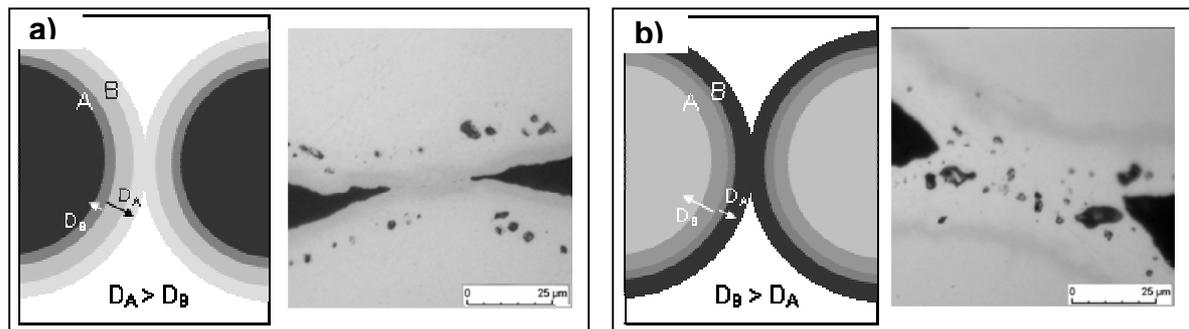

Figure 3: Supposed and observed diffusion behaviour in the particle contact zone: a) System Cu_wNi_c b) System Ni_wCu_c.

The neck growth for the system Cu_wNi_c during heating up to sintering temperature (1000°C) and isothermal sintering for up to 60 minutes is shown in Fig. 4a for two different thicknesses of the coat.
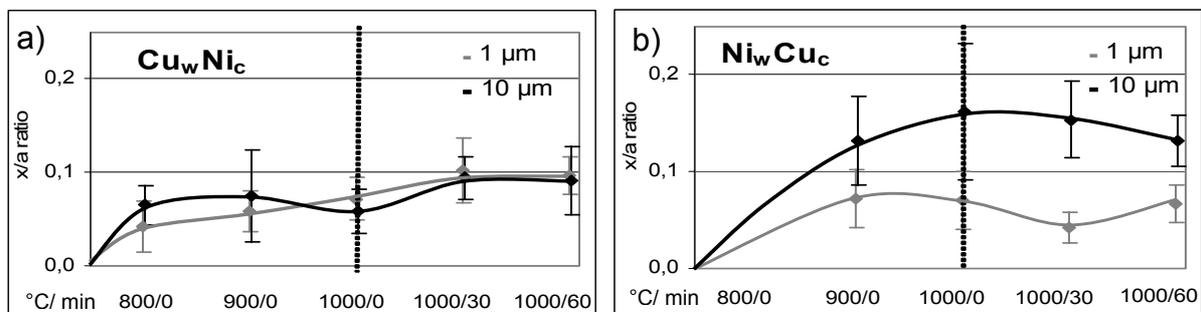

Figure 4: Neck growth for the systems a) System Cu_wNi_c and b) System Ni_wCu_c (atmosphere: vacuum). Vertical bars present the standard deviations.

While with the 1 µm coat the necks grow continuously, with the 10 µm coat a decrease of the x/a ratio was observed at 1000°C. An explanation for the "negative sintering" could be that the small pores formed during the chemical diffusion act as sources for vacancies that anneal at the neck surface.

If copper is used as the material of the coat (Ni_wCu_c) generally higher x/a ratios occur (Fig. 4b). The reason for the increased sintering activity is the higher coefficient of self-diffusion of copper compared with nickel. In addition the different partial diffusion coefficients produce a high defect concentration (vacancies) close to the contact zone thus increasing the effective coefficient of self-diffusion in the region where the mass transport contribute to neck growth. As discussed before in the case of Cu_wNi_c the defect rich zone is located at a certain distance from the contact zone and can not influence the sintering behaviour. (Fig. 3a and 3b)

Furthermore, the "negative sintering" is more intensive than in the system Cu_wNi_c, because Frenkel-Pores, an additional porosity due to healing up of lattice defects, occur in the diffusion zone.

In Figure 5a and 5b qualitative concentration profiles are given, which show the effect of the diffusion coefficients on the interdiffusion. At the higher temperature and 60 minutes isothermal sintering the concentration-gradient decreases significantly and most of the homogenization has already taken place. Therefore processes that activate the sintering during solid solution formation can be expected mainly during the heating period and in the early stage of isothermal sintering. After a longer sintering the neck growth is equivalent to pre-alloyed (homogeneous) partners.
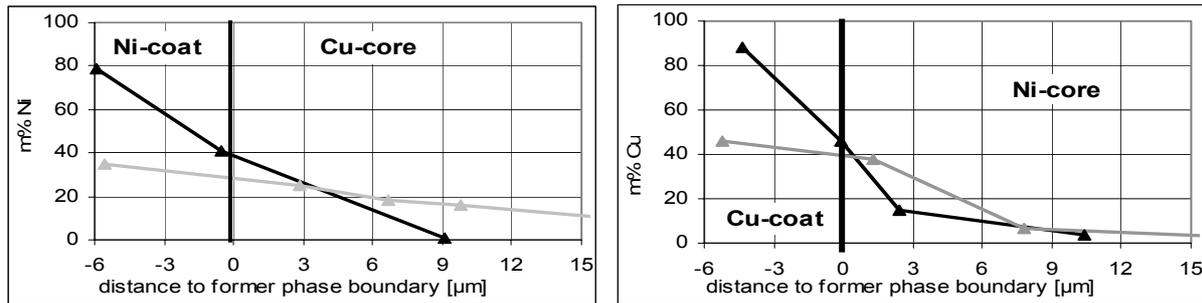

Figure 5: Concentration profiles obtained by EDX. Sintering parameters: 800°C/0 min (black) and 1000°C/60 min (grey); vacuum a) Cu_wNi_c ~5 m, and b) Ni_wCu_c ~5 m.

The Systems Silver-Copper and Copper-Silver

The system AgCu is characterized by a limited solubility of the components. In both cases (Ag_wCu_c and Cu_wAg_c) the coated models (Figure 6) show faster neck growth than the pure silver or copper wires (see Fig. 2).
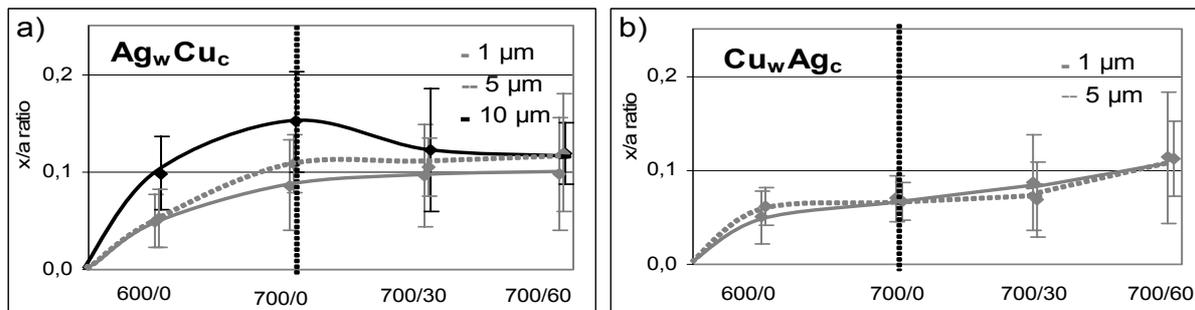

Figure 6: Neck growth for the systems a) System Ag_wCu_c and b) System Cu_wAg_c. (atmosphere: vacuum) Vertical bars present the standard deviations.

In the system Ag_wCu_c generally a thicker coat causes faster neck growth. As discussed already for the system Ni_wCu_c a "negative sintering" is also observed for Ag_wCu_c with the 10 μm coat (see Figure 6a). The reason for the porosity formed in the copper coat was discussed earlier. The system Cu_wAg_c shows no effect of the coating thickness on neck growth for 1 μm and 5 μm coatings. Due to high stresses in the electroplated coat it was impossible to produce models with 10 m coatings for this system.

It should be pointed out that Frenkel-Porosity caused by the different partial diffusion coefficients would occur both in the coat and in the wire depending on which combination was used. Since the porosity was found only in the copper coat the annealing of lattice defects and not chemical diffusion caused the pore formation.

Conclusion

Electroplated coatings on particles surfaces influence the sintering activity through the formation of the solid solution in the interface region, a smaller grain size and a higher defect density. As a model for the development of contacts between powder particles, coated wires were used in the systems Ni_wCu_c/Cu_wNi_c and Ag_wCu_c/Cu_wAg_c. The geometrical arrangement of the components defines the position of the defect rich zone caused by the difference of the partial diffusion coefficients. If the component with the faster diffusion coefficient forms the coat, the defect rich zone at the interface is close to the neck region and the growth rate of sintering contacts is higher than in the opposite case. In addition to the Frenkel-Pores, pores were found in the combinations nickel-copper (Ni_wCu_c) as well as silver-copper (Ag_wCu_c) which have their origin in the galvanic plating process. The small pores in the contact zone can act as sources for vacancies that are responsible for transient "negative sintering". Further investigations with coated powder particles will be performed to transfer the results of model experiments into the fabrication of sintered materials.

References
/1/ E. Friedrich, K.-P. Wieters, O. Chehade: „Sintering Behaviour of Coated Powders", Advances in Powder Metallurgy & Particulate Materials - 1992, San Francisco, USA, Vol. 3, pp. 85-98
/2/ W. Schatt: „Sintervorgänge/Grundlagen", VDI-Verlag, Düsseldorf, Germany, 1992, pp.138-141
/3/ K.-P. Wieters, W. Zeiger, B. Kieback: „Sintering Effects by Particle Coating of Metal Powders", Advances in Powder Metallurgy & Particulate Materials - 2000, Kyoto, Japan
/4/ K.-P. Wieters, B. Kieback: "Coated Metal Powder, Sintering Behaviour and Application in alternative Forming Processes", 15th International Plansee Seminar 2001, Reutte, Germany, Vol. 3, 2001, pp (GT2) 1-15
/5/ K. S. Hwang, M. Y. Shiau: "Effects of Nickel on the Sintering Behaviour of Fe-Ni Compacts Made from Composite and Elemental Powders" Metall. and Mat. Transact. B, Vol. 27B, 1996
/6/ F. Thümmler: „Zur Theorie der Sintervorgänge metallischer Systeme", Habilitationsschrift, TU-Dresden, Dresden, Germany, 1957, pp. 32-37 and 66-76
/7/ H. A. Kuhn, A. Lawley: „Powder Metallurgy Processing - New Techniques and Analyses", Academic Press, New York San Francisco London, 1978, pp. 61-71
/8/ R. W. Heckel: "An Analysis of Homogenization in Powder Compacts Using the Concentric-Sphere Diffusion Model", Trans. of the ASM, Metals Park, Ohio, Vol. 57, 1964, pp. 443-463
/9/ F. V. Lenel: "Powder Metallurgy – Principles and Applications", Metal Powder Industries Federation, New Jersey, USA, 1980, pp. 269-284
/10/ ASM International: "Binary Alloy Phase Diagrams", Vol. 2, Version 1.0, Ohio, ASM International, 1996
/11/ A. Krause: "Bildung und Struktur nanokristalliner Funktionsschichten", Diplomarbeit, TU-Dresden, Dresden, Germany, 2000, pp. 28-29
/12/ O. Brümmer: „Mikroanalyse mit Elektronen- und Ionensonden", Deutscher Verlag für Grundstoffindustrie Leipzig, 2. Auflage, Leipzig, Germany, 1977, pp. 45-49
/13/ T. Heumann: „Diffusion in Metallen - Grundlagen, Theorie, Vorgänge in Reinmetallen und Legierungen", Springer Verlag, Germany, 1992, pp. 171-183
/14/ E. A. Brandes, G. B. Brook: "Smithells Metals Reference Book", Butterworth-Heinemann-Verlag, Oxford, UK, 1992, pp. 13/1-40
/15/ J. E. Geguzin: „Physik des Sinterns", Deutscher Verlag für Grundstoffindustrie, Leipzig, Germany, 1973, pp. 221-224