

The Sintering Behaviour of Coated Particles

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Abstract

Coatings on powder particles have a great influence on the sintering behaviour depending on the type and the solubility of metallic components which are combined, on the geometrical conditions and the developing structure of core and coat material. The sintering behaviour was studied on sintering models (coil type) as well as on coated powders. In the study the material combinations Cu-Ni (complete solubility) and Cu-Ag (partial solubility) will be discussed in detail. The coatings are produced by electro-deposition. The research is concentrated on the neck growth between wires examined by light microscopy, the shrinkage of coated powders and how the homogenization and interdiffusion affects the sintering process in dependence on coating thickness, sintering temperatures and sintering time.

1. Introduction

For P/M-alloy production, mixed or pre-alloyed powders are used in most cases. However, disadvantageous for mixed powders is the tendency to segregate. In particular if the amount of the alloying element is small. By using pre-alloyed powders homogeneous alloys can be produced; however, at the same time bad compressibility has to be accepted [1, 2, 3, 4]. Advantages in using coated powder particles are [4, 5, 6]: 1) uniform distribution of the alloying elements, 2) easy control of the alloying addition by the coating thickness, 3) good compressibility, 4) large interface between the components and, consequently, rapid homogenization during sintering.

The aim of this investigation is a better understanding of the sintering mechanism in the sintering contact, this mechanism being influenced by the developing structure due to interdiffusion. In order to receive detailed information about sintering effects, investigations on models (wire model and loose-powder sintering) were performed. At first, models of the coil-type consisting of wires with electrodeposited coatings [3, 7] were used for investigating the neck growth, the development of the micro-structure, and the diffusion processes. Furthermore, dilatometer measurements of loose-powders were made to study the shrinkage behaviour of coated powders.

Fritz Thümmel [7] investigated, for particular material combinations, the (defect) activated sintering caused by interdiffusion. Kuhn and Lawley [7] summarized the theoretical knowledge of concentric sphere models, which are used for describing interdiffusion and homogenization in mixed powders. This can also be applied for quantifying the diffusion processes in coated powders.

The material combinations for the investigations are copper-nickel as a system with complete solubility and copper-silver as a system with limited solid solubility. Core- and layer-material were chosen alternately. So, in total, four combinations were studied. The alloying concentration was varied by changing the coating thickness

between 0.2 and 5.9 micrometers. Electrolytic plating was chosen for preparing the coatings [3].

When sintering the system nickel-copper, there is a big difference in the partial (tracer) diffusion coefficients (e.g., at 1000°C $D_{\text{Cu(in NiCu)}} (1 \cdot 10^{-14} \text{ m}^2/\text{s}) > D_{\text{Ni(in CuNi)}} (2 \cdot 10^{-15} \text{ m}^2/\text{s})$ [8]). This leads to the formation of Frenkel-Porosity¹ and Kirkendall-Effect (displacement of contact grain boundary) [9]. Because of the low difference between the (tracer impurity) diffusion coefficients, these effects will play a minor role when sintering the system silver-copper (e.g., at 700°C $D_{\text{Cu(in Ag)}} (5.4 \cdot 10^{-15} \text{ m}^2/\text{s}) > D_{\text{Ag(in Cu)}} (2.2 \cdot 10^{-15} \text{ m}^2/\text{s})$ [10]).

2. Experimental Procedure

The wire-models were prepared by winding coated wires several times onto a coil made of the same material as the wire. Subsequently, this model was sintered. The advantage of the sintered, cut and metallographically prepared model is that it offers many sintering contacts for performing the various analyses [7]. The characteristics of the wires and coats used are listed in detail in [3]. The measurements of the neck widths were carried out on the microscope Nikon FXA. In the second series of tests, spherical powder (gas atomized with N and Ar, respectively) was electro-plated² and sintered in a dilatometer as a loose-powder. Material combinations, alloy contents as well as sintering conditions are equal to those of the wire model. Only in the case of the sintering atmosphere, hydrogen was chosen – instead of a vacuum. The characteristics of the materials used are given in Table 1. The particle size of smaller core-particles is between 90 and 125 µm (in the following signified as “100 µm”) and that of bigger core-particles between 175 and 250µm („200 µm“). The alloy content is defined by the coating thick-

¹ Frenkel-Porosity is also called Kirkendall-Porosity, both terms signifying diffusion porosity

² process has been developed at the Institute of Materials Science, TU-Dresden, electrolytes are commercial

ness of 0.2 to 5.9 micrometers (approximately 0.5 to 16.2 mass%). The amount of the second component (coat) in the system silver-copper (limited solid solubility) was chosen in two different areas of the phase diagram [3]. First, in the area of the homogeneous mixed crystal and, second, in the miscibility gap. The sintering temperatures are in the range of solid-state sintering.

core particle	nickel	copper	silver	copper
Chemical impurity ³ [ppm]	O 30,	O 50, N 10, C 20	O 30, N 10	O 50, N 10
Average grain size [μm]	25.6	23.5	12.6	23.5
coat material	copper	nickel	copper	silver
Chemical impurity [ppm]	O 280, N 40, C 120, S 80	O 2500, N 320	O 1060, N 30, C 290, S 60	O 60, N 10
Average grain size [nm] ⁴	105	30	65	25

Table 1: Characteristics of coated particles used for sintering experiments.

Dilatometer measurements were made with the vertical dilatometer TMA 92-16.18 (Setaram). For this purpose, the coated powder was filled up to 3 mm with tap density into a ceramic crucible (diameter 5 mm). The load of the displacement sensor was 5 g ($\sim 2,5 \times 10^{-3}$ MPa).

3. Results and Discussion

Because of a coat on the powder particles, the mass transport in the particle contact (sintering contact) is superimposed with interdiffusion. The presence as well as the arrangement of the zone of higher defect density is determined by the partial diffusion coefficients of the sintering partners involved [3, 11]. The different vacancy transport in both materials causes excess vacancies whereas the resulting tensions may produce dislocations. [12] The zone of higher defect density develops on the side of the material with the higher diffusion coefficient, which increases the material transport into the contact area. Therefore, sintering activation or sintering inhibition can be expected to occur depending on the selection of core- and coat materials and coating thickness (that is, the distance of the zone of higher defect density from the sintering-neck area)[2].

2.1 Wire-Model

System Nickel-Copper The neck growth measured on the wire-model is shown in Fig. 1 in dependence on temperature, holding time and coating thickness. In addition to neck growth, there is also neck size reduction, which is

caused by the formation of small pores during interdiffusion or structure development [3].

The generally higher sintering activity in the presence of copper-coatings is due to the higher diffusion coefficient of copper compared with nickel. However, the distance of the zone of higher defect density from the sintering neck is also of great importance, which is directly influenced by the coating thickness.

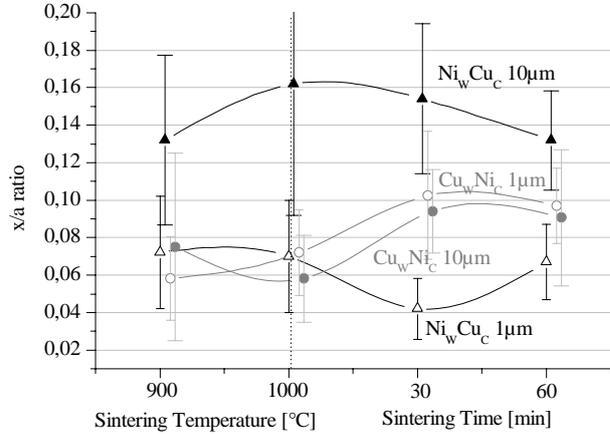


Fig. 1: Neck growth of System Cu_WNi_C and Ni_WCu_C ⁵ in dependence of temperature and holding time. x represents the neck width and a the particle diameter. Vertical bars present standard deviations.

Previous measurements using the Energy Dispersive X-ray method [3] showed that the greatest influence of interdiffusion on the sintering activation occurs in the non-isothermal sintering phase as well as at the beginning of the isothermal phase.

System Silver-Copper The system silver-copper also showed the tendency that, in the presence of a coat on a wire, there is a higher sintering activity compared with sintering without a coat. Decreasing of the neck diameter was also observed in the system Ag_WCu_C , which is due to the healing up of the point defects in the electroplated coat [3].

2.2 Loose-powder Sintering

Fig. 2 demonstrates the shrinkage curves of the material combinations investigated in dependence on temperature, holding time, coating thickness and size of powder particles. Shrinkage curves of the loose-powders without coating are given as well.

In the non-isothermal sintering phase, after the first contact formation, rearrangement processes take place, particle movement being connected with the breaking up of sintering necks.

In this phase, the formation of micro-porosity predominates, which can be measured in the growth of the sample. This is followed by the growth of the sintering contacts connected with simultaneous center-to-center approach, which results in measurable shrinkage of the sample.

³ LECO TC 463 - O, N; LECO CS 400 - C, S; IFAM Dresden

⁴ The measurements were done with X-Ray diffraction. The twin grain boundaries are included in the results.

⁵ Cu_WNi_C : W meaning wire and C coat.

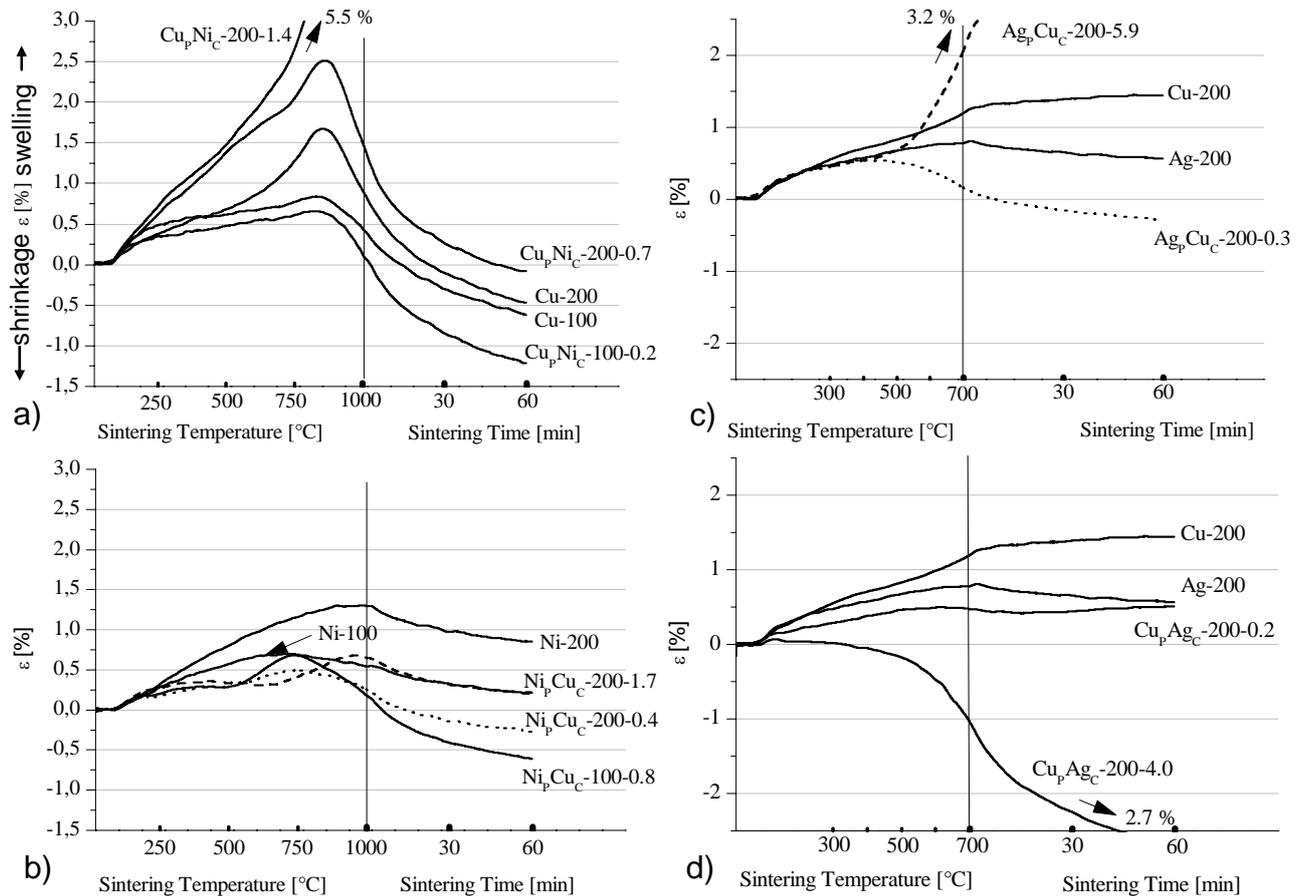


Fig. 2: Shrinkage curves of loose-powder sintering with raw and coated powder particles a) system Cu_pNi_c , b) system Ni_pCu_c , c) system Ag_pCu_c , d) system Cu_pAg_c . First number in sample description denotes particle size, the second one the approximate coating thickness in μm .

System Nickel-Copper The increased sintering activity of copper-powder (Fig. 2a) compared with nickel-powder (each 200 μm in diameter) is a result of the higher homologous temperature. Due to the higher activity of smaller powder particles, the shrinkage curve of the 100 μm copper powder is shifted to higher shrinkage values. The smaller swelling effect compared with that of larger powder particles is caused by the higher sintering activity of the smaller powder particles, which, in addition, affects an earlier shrinkage.

Coating of copper-particles with a very thin layer of nickel (Cu_pNi_c -200-0.7) causes a more intensive swelling effect in the non-isothermal sintering phase (heating-up) compared with pure copper. This is due to the formation of micro-porosity because of the very different diffusion coefficients (Frenkel-Porosity). The zone of higher defect density is not directly located in the sintering contact area and, therefore, has only a small influence on the sintering activity. At the end of the heating-up phase, there is a higher shrinkage rate in contrast to that of copper-powder particles. This activation can be supposed to be caused by the increasing defect density during the formation of a solid solution. The further slope of the curve corresponds to that of the copper curve.

Cu_pNi_c -200-1.4 shows quite a different behaviour. At the beginning, the slope of the curve is analogous to that of system Cu_pNi_c -200-0.7. But at higher temperatures and during the following holding time, a continuous growth of the sample can be observed. Later, in the isothermal sintering phase, the growth becomes smaller and is su-

perimposed by shrinkage processes (center-to-center-approach). The growth of the sample is caused by Frenkel-Pores. The arrangement of the components (copper-particle – nickel-coat) prevents the developed porosity to be dissolved by the transport of the vacancies to the surface. With progressing homogenization, the zone of diffusion porosity spreads into the direction of the particle centre. Then follows coarsening of the pores (Ostwald ripening).

In copper-coated nickel-particles, the situation is quite different (Fig. 2b). In this case, the porosity develops in the copper-coat and can easily be dissolved on the surface. Moreover, the zone of higher defect density is closer to the sintering contact and, therefore, contributes more to the sintering activity than the inverse arrangement of particle- and coat-material. A thinner coat (Ni_pCu_c -200-0.4) results in a higher sintering activation than a thicker one (Ni_pCu_c -200-1.7), because the zone is closer to the sintering neck. Compared with the shrinkage curve of pure nickel particles, the shrinkage in the system Ni_pCu_c -200-0.4 occurs at lower temperatures. Rearrangement processes as well as Frenkel-Porosity cause the initial rising of the shrinkage curve. Because of the higher defect density due to interdiffusion, the initial growth of the sample gradually changes into shrinkage. The thin coatings on smaller powder particles (Cu_pNi_c -100-0.2 and Ni_pCu_c -100-0.8)) always lead to sintering activation. Frenkel-Porosity is in the system Cu_pNi_c -100-0.2 of minor importance, whereas defect activated sintering has a greater influence on the sintering process. In-

vestigations of models and the sintering of loose-powders show similar tendencies with respect to the decreasing neck width and the growth of the sample, the latter starting at lower temperatures. This earlier start may be due to Frenkel-Porosity. Then follows the transport of the vacancies from the surface of the pores to the near neck surface, which results in the decreasing of the neck diameter. Moreover, it can be seen that a distinct sintering activity takes place in the system Ni_pCu_c . This means, if the coating material is that with the higher partial diffusion coefficient, the sintering process can be activated, which results from the close distance of the defect-rich zone to the sintering contact.

System Silver-Copper Thin copper layers on the silver particles ($Ag_pCu_c-200-0.3$) cause strong sintering activation. At the beginning of the heating-up time, the curve (Fig. 2c) shows a similar behaviour (swelling) like that, of pure silver, which may be caused by rearrangement processes. The subsequent sintering activation in the presence of the thin copper layer is caused by the higher defect density in the sintering contact during interdiffusion. Due to the different partial diffusion coefficients during the formation of the solid solution, copper diffuses faster in silver than silver in copper. This causes the zone of higher defect density to be close to the particle contact (sintering neck), which, in turn, leads to sintering activation. The fine grain size of the coat can also effect sintering activation. Furthermore, shrinkage-inhibiting rearrangement processes are less intensive with decreasing grain size [1]. With increasing coating thickness ($Ag_pCu_c-200-5.9$) there is no sintering activation in contrast to pure copper. The stronger rise in the shrinkage curve in $Ag_pCu_c-200-5.9$ than in that of pure copper is caused by porosity, which, in turn, is generated by healing up of the lattice defects of the galvanic plated coatings [3]. In addition, the zone of higher defect density is not directly located in the sintering contact area and, therefore, does not produce the same activation effect as $Ag_pCu_c-200-0.3$.

Considering the system Cu_pAg_c , a rising sintering activation can be seen with increasing coating thickness ($Cu_pAg_c-200-0.2$ and $Cu_pAg_c-200-4.0$). In both cases, the activation is due to the small grain size of the coat and the presence of a zone with high defect density in the contact area. It can be supposed that, in the system with the thin layer the activation is mainly effected by the processes connected with the formation of the solid solution and in systems with the thick layer by the small grain size.

The shrinkage curve of $Cu_pAg_c-200-0.2$ shows, at the beginning of the isothermal sintering phase, a temporary shrinkage due to the formation of the solid solution. The growth after this shrinkage has the same origin as the growth when sintering pure copper particles (rearrangement processes) – however, in this case there is a copper-rich alloy (Cu-Ag) in the sintering contact. If the binary alloy is situated in the miscibility gap of the phase diagram ($Cu_pAg_c-200-4.0$), pure silver is present in the sintering contact during the whole sintering process. The higher homologous sintering temperature causes a stronger shrinkage in contrast to an alloy with complete miscibility ($Cu_pAg_c-200-0.2$).

5. Conclusion

The investigations demonstrated that coatings on powder particles influence the sintering activation in the sintering contact area due to interdiffusion and the structure of the coating (grain size and defect density). The material combinations investigated are nickel-copper and silver-copper. Because of interdiffusion, a defect rich zone is generated. The geometrical arrangement of the materials involved defines the position of this zone through the difference of the partial diffusion coefficients. It has been found that there is higher activation of the sintering process, if the material with the higher partial diffusion coefficient represents the coating material. In this case, the zone of higher defect density is closer to the sintering neck compared with the inverse arrangement of particle- and coat-material.

In addition, vacancies which agglomerate to form pores (Frenkel-Porosity or porosity dependent on structure) especially in Ni_wCu_c und Ag_wCu_c are the reason for “negative” sintering (decreasing of neck diameter and growing of the sample) because atoms have to be taken from the neck surface to fill up these pores.

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