JOURNAL OF MATERIALS SCIENCE 10 (1975) 1719–1724

The geometry of sintering wires

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The geometries of various sintering wire compacts are determined for both surface- and bulk-transport controlled processes. The results indicate very little difference in the geometries during the initial stage of sintering. However, significant differences become apparent when the latter stage of sintering is approached. Under the action of a bulk-transport mechanism, compact shrinkage is expected. The present calculations of shrinkage versus neck size are compared favourably with previously published data. As a result, the relation between shrinkage and neck size is modified. Finally, the specific surface area variation with neck growth is determined for both forms of mass transport, indicating this may be an alternative measure of sintering progression.

1. Introduction

Ever since the early work of Kuczynski [1], considerable theoretical effort has been devoted to the kinetic modeling of spherical particle sintering. Conclusions resulting from these efforts have attributed the time dependence of sintering to a particular mass-transport process believed to be dominant under a given set of experimental conditions. Results of numerous experiments have been successfully interpreted along the specified limits of this approach. However, uncertainties in the generated time-dependence results and disagreements concerning their interpretation are quite evident [2].

To simplify the analysis of neck growth, aligned wires have been used instead of sphere-to-sphere or sphere-to-plate geometries. Since it is expected that the neck size remains constant along the sintering region of the wires, use of wire compacts is believed to have the advantage of ease of preparation and measurement of the neck region. Reports on the use of wire compacts as sintering models and discussions concerning difficulties in their use are provided by numerous authors [3–9]. Of these difficulties, that related to the metallographic preparation and neck enlargement is of major concern [9]. Other difficulties, resulting from grain-boundary migration [4, 5], uneven wire contact [9], and plastic deformation [5], have also been reported. Despite these considerations, wire sintering studies are recognized as being an important means of isolating the dominant mass-transport mechanism under a given set of experimental conditions [10]. Accordingly, almost all of the theoretical treatments of sintering have been extended to include the behaviour of wire compacts. Unfortunately, the instantaneous geometrical relations during wire compact sintering are available only for the cases of surface [11] and volume diffusion [12, 13] controlled processes. Relationships for other mass-transport processes [14] (grain-boundary diffusion, evaporation-condensation, and plastic and viscous flow) are not available. Distinguishing only between mechanisms with densification (bulk-transport) and those without densification (surface-transport), we have calculated precise morphologies for the neck region of various wire compact configurations. The results of such calculations provide new insight into wire compact studies by interrelating the significant variables governing the morphological development during the sintering process. Furthermore, the interpretation of wire-wire sintering is now possibly by two additional morphology measurements.

2. Mathematical approach

In two previous papers [15, 16], a model was developed for surface-transport and bulk-transport controlled sintering of spheres. The present approach closely resembles those calculations except for the altered geometry. It is assumed that the wires are of unchanging length and are initially aligned with no neck or deformation. As previously shown [15] a hyperbolic cosine curve can be taken to represent a minimum surface area geometry for the neck region under existing boundary conditions [15, 16]. The morphology of the wire surface beyond the neck is assumed to remain cylindrical in nature.

Growth of the neck region proceeds either by wire diameter shrinkage or by interpenetration, depending on whether the process is controlled by surface-transport or bulk-transport, respectively. Fig. 1a and b show the respective models for these two cases. For the surface-transport mechanism the expression describing the neck surface, y_n, must satisfy the boundary conditions: $y_n\ (z = 0) = x$ (the neck radius in Fig. 1a) and $y_n'\ (z = 0) = 0$. These conditions were found to be satisfied by the following form of a modified catenary:

$$y_n = \cosh(\beta z) + x - 1. \qquad (1)$$

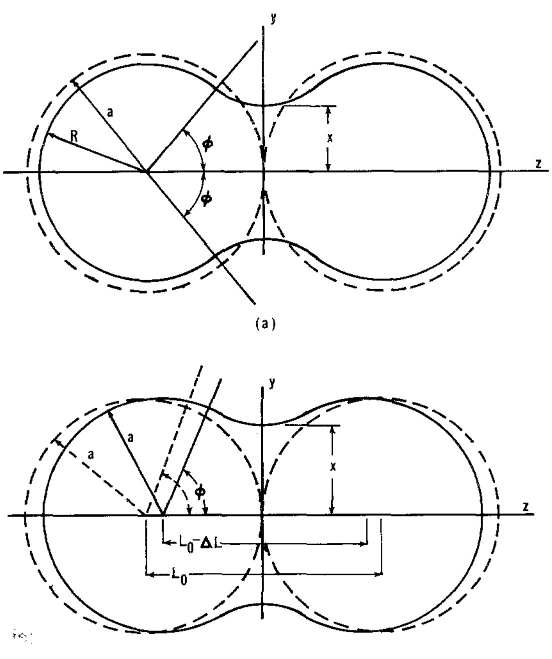

Figure 1 Models for sintering wires controlled by (a) surface-transport and (b) bulk-transport.

For the bulk-transport mechanism, the corresponding boundary conditions, $y_n = x$ and $y_n' = 0$ at $z = a - \Delta L$ are met by the following expression:

$$y_n = \cosh[\beta(z - a + \Delta L)] + x - 1. \qquad (2)$$

Along with continuity requirements (representing a smooth transition between the neck and the adjacent wires), solution of Equations 1 and 2 is accomplished with the additional stipulation of volume conservation. Details of such calculations have been presented previously [15, 16].

The approach presented here differs basically from published models in that it utilizes the concept of minimization of surface area (and hence surface free energy) as the basis for calculation. In the previous models the approach had centred on the concept of localized differences in the chemical potential. As will be shown later, calculations resulting from the model described here are in good agreement with those generated by the previous, more complicated approaches. In spite of the fundamental differences between this and the previous models, agreement between the results is not unexpected. The sintering path, as implied by the present model, proceeds along points of minimum surface area, governed by the prevailing boundary conditions.

In a wire compact, various arrangements of wires are possible. Considering only monosized wires, co-ordinates ranging from one to six can be attained. In this analysis, N_c will represent the co-ordination number for a given wire in a compact. It can then be assumed that during the initial portion of sintering, the effects of neck growth can be isolated to the wire segment inside an angle 2ϕ as shown in Fig. 1a and b. The relation between ϕ and N_c is then expressed as $\phi = \pi/N_c$ and in effect it is assumed that the localized neck formation and growth processes proceed independently from one another. This assumption is valid for the initial stage of sintering.

Since the earlier papers [15, 16] have adequately illustrated the mathematical modelling employed in the solution of similar problems, details of this approach will not be presented in this paper. Solutions to the geometries shown in Fig. 1a and b have been achieved within the limits of the present model with the requirements of minimizing the neck surface area and maintaining continuity in neck region while conserving volume. Wire co-ordination of one through six have been considered for both the surface-transport and bulk-transport cases. An additional assumption which had been implied in the previous papers is that concerning grain-boundary energy. In this and the previous calculations the grain-boundary energy has been assumed to be zero.

3. Results

For the surface-transport controlled sintering of wires, neck growth is accomplished by reduction in the wire diameter. Fig. 2 shows the normalized diameter reduction R/a, where a is the initial wire radius, as a function of the normalized neck size x/a, for $N_c = 1, 2, 3, ..., 6$. In a manner similar to that for the surface-transport controlled sintering

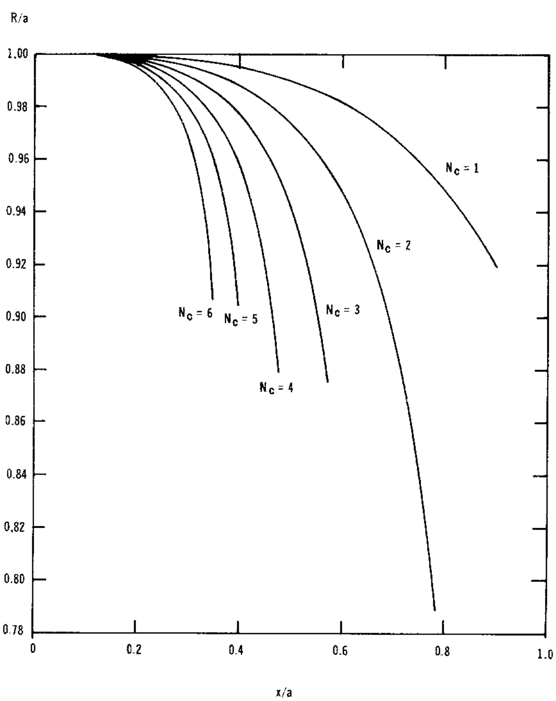

Figure 2 Normalized wire radius versus normalized neck size for surface-transport controlled sintering.

of spheres [15] appreciable neck growth occurs before significant wire diameter reduction. Furthermore, increased wire co-ordination is shown to enhance the rate of diameter reduction with neck growth. The specific surface area variation with increased neck size is shown in Fig. 3 for the six values of N_c. The ratio S/S_0 represents the instantaneous surface area S, divided by the initial surface area S_0. This ratio is equivalent to the ratio of perimeters of a wire compact cross-section since the length is assumed constant.

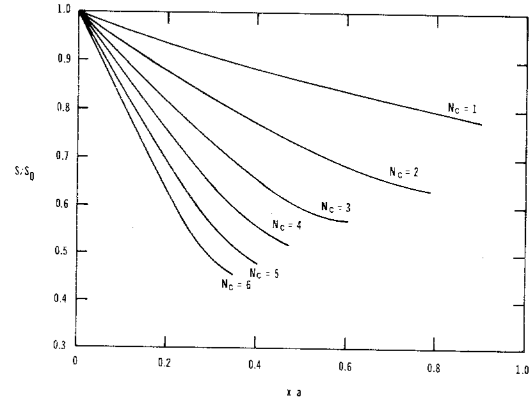

Figure 3 Reduction in specific surface area with neck growth by a surface-transport mechanism for six wire co-ordinations.

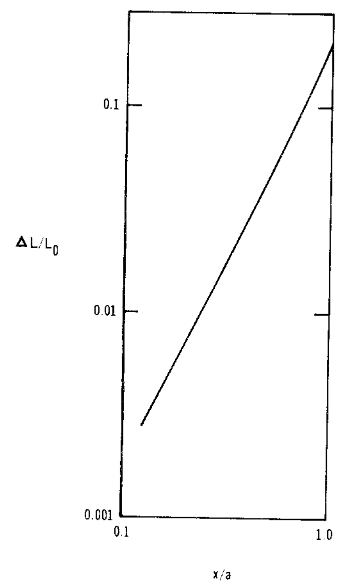

Figure 4 Log–log plot showing wire compact linear shrinkage with neck growth by bulk-transport controlled sintering.

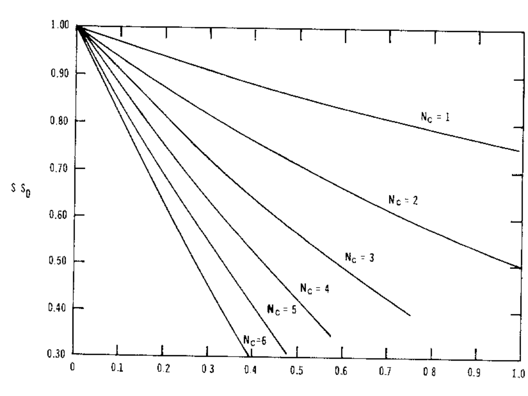

Figure 5 Variation in the specific surface area with inter-wire neck growth by bulk-transport control.

The sintering of wires under the action of a bulk-transport mechanism provides an alternative morphology. In this case, neck growth is accomplished by a shrinkage in the spacing between wire centres. The relation between shrinkage and neck size has been normalized and is presented in Fig. 4. The shrinkage results are independent of wire compact co-ordination, an observation equivalent to that for the sphere-sphere sintering configuration [16]. Shrinkage is expressed as $\Delta L/L_0$, where ΔL represents the change in the initial length L_0, resulting from the formation of a normalized neck size of x/a. In Fig. 5, the specific surface area variation with neck size and wire co-ordination is shown for the bulk-transport controlled sintering case. As expected, increased co-ordination results in a more rapid decrease in S/S_0.

At small neck size ratios ($x/a < 0.2$) the neck morphologies of wires sintered by either mechanism are essentially identical. However, as the sintering process progresses, significant differences in these morphologies develop. The reduction in the total surface area is significantly greater for the case of surface-transport sintering. Associated with the differences of surface area reduction are, of course, corresponding variations in the profiles and morphologies of the neck regions. Regardless of these variations, the morphologies resulting from these mechanisms possess surfaces with curvature differences which are in the correct direction to give the appropriate atomic flux.

4. Discussion

Two simple mathematical checks on the results shown in Figs. 2 to 5 are available. The equilibrium configuration for $N_c = 2$ is a plate. Such a configuration occurs within the limits of these calculations. Under the action of surface-transport controlled sintering, the interwire distance remains unchanged, but the wire diameter reduces. Volume conservation dictates an equilibrium plate height corresponding to $x/a = \pi/4$ or 0.7854. At the terminus of the $N_c = 2$ curve of Fig. 2, $x/a = R/a = \pi/4$, which correlates with the expected equilibrium configuration. Also, the surface area ratio for the terminus of the $N_c = 2$ curve of Fig. 3 is 0.6366, in agreement with the equilibrium value $2/\pi$. For the bulk-transport case, the corresponding equilibrium geometry for $N_c = 2$ is a plate with $x/a = 1.0$. Based on this configuration, volume conservation leads to the result that $\Delta L/L_0 = 0.2146$ and $S/S_0 = 0.5$ at $x/a = 1.0$. Both of these checks correlate with the results of this study.

Data on surface area or perimeter reduction for wire compacts are unavailable. However, simultaneous data on shrinkage versus neck growth for copper wire compacts has been provided by both Alexander and Balluffi [3] and Ichinose and Kuczynski [5]. In both studies it was observed that the initial sintering kinetics followed that predicted for volume diffusion control. Also, it was observed that shrinkage discontinued with the disappearance of grain boundaries from the neck region. Based on the compact geometries, a co-ordination of six is applicable to these studies, thereby limiting the present comparison to x/a values of less than 0.4. Shown in Fig. 6 is a comparison of the results of this study with the published results on copper wires. In spite of the scatter in the experimental data, agreement with the present calculations is quite evident. Mathematically, the relation between neck size and shrinkage can be approximated by the following:

$$\frac{\Delta L}{L_0} \simeq 0.1844\,(x/a)^2. \qquad (3)$$

Equation 3 is valid up to neck sizes of approximately one-half, with an error of less than 1%. At larger neck sizes the constant of Equation 3 increases rapidly with increasing x/a. Ichinose and Kuczynski [5] have previously used a similar expression in which the value of the constant was 0.25. Although the neck size-shrinkage relations differ, the results of the previous studies are relatively unaffected.

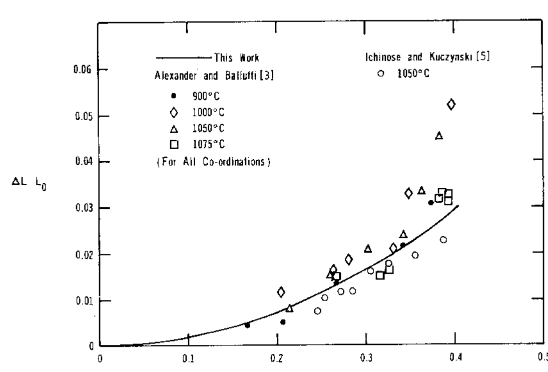

Figure 6 Comparison between the present calculations and experimental shrinkage versus neck size data for sintering copper wires.

The sintering of aligned wires by a surface-diffusion mechanism has previously been analysed by Nichols [11]. Using a computer simulation technique, Nichols was able to generate neck profiles at various stages of sintering for a line of wires while studying the time dependence of neck growth. A slight undercutting was observed in the neck region. Although the present calculations do not provide for undercutting, the validity of the results is not significantly altered. Lack of volume conservations and the nature of the finite difference approach to the problem detracts from Nichols' morphology results. However comparison with the present analysis substantiates our neck shape model. Shown in Fig. 7 is a comparison of sintering wire profiles obtained in this study for a surface-transport mechanism, with those reported by Nichols. Despite differences in assumptions, boundary conditions, and means of derivation, the two sets of results are in good agreement. Unfortunately, a similar comparison with the results of Easterling and Tholen [12, 13] is not possible because of the qualitative nature of their results.

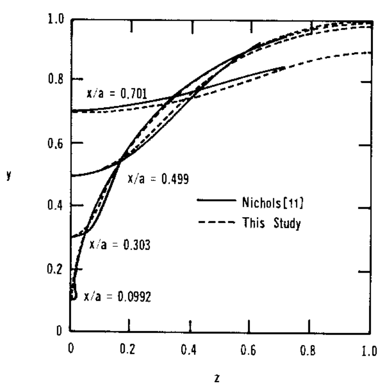

Figure 7 Comparison of neck profiles for surface-transport controlled sintering of a line of wires ($N_c = 2$).

The present calculations involving sintering wires do not explicitly aid in the identification of the dominant mass-transport mechanism. From a morphology standpoint, only a distinction between a surface versus a bulk-transport process is possible. Final isolation of the rate controlling sintering mechanism must be obtained from kinetic studies. However, these results do provide new approaches to the understanding of the sintering process. For the surface-transport sintering of wires, it is shown that both the wire size reduction and surface area change are uniquely defined by neck size for a given co-ordination. Thus, final distinction between surface-diffusion and evaporation-condensation is possible by introducing time dependence into either of these three variables. Alternatively, the scaling laws of Herring [17] can be directly applied in a mannner previously outlined [15]. Similarly, final distinction between the various bulk-transport mechanisms is dependent on kinetics. Relations between neck size or shrinkage and sintering time have been developed by numerous authors for the various bulk-transport mechanisms [2]. Thus, time dependence can be introduced into the present results for $\Delta L/L_0$ and S/S_0 as well as for x/a. Likewise, the scaling laws of Herring [17] can be applied to shrinkage and surface area closure because of the unique dependence on neck size. The present work provides a means of extending the sintering kinetics to other morphology parameters besides neck size. In doing so it enhances the usefulness of the wire compact technique in the efforts aimed at providing a total understanding of the mechanisms of sintering.

5. Conclusions

The present analyses provide a complete definition of sintering wire morphology for both bulk- and surface-transport controlled processes. From the standpoint of quantitative metallography, the sintering variables of neck size, wire diameter, shrinkage, surface area and pore–solid perimeter are now precisely interrelated. Thus, the sintering of wire compacts can be studied by a variety of morphology measures. It is shown that the specific surface area or pore–solid perimeter is an alternative measure of the progress of sintering in a wire compact. The previous estimate for the relation between shrinkage and neck size during bulk-transport controlled sintering has been refined. Finally, the possible uses of these morphology results are outlined, realizing that final identification of the specific rate controlling mechanisms is dependent on introduction of kinetics.

Acknowledgements

Discussion and aid by H. D. Jones and J. E. Smugeresky of Sandia Laboratories are gratefully acknowledged. This work was supported by the United States Atomic Energy Commission under Contract At-(29-1)-789.

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Received 7 February and accepted 26 March 1975.