UNITED STATES ATOMIC ENERGY COMMISSION

FUNDAMENTALS OF SINTERING—III

Third Annual Progress Report for June 30, 1957
to June 30, 1958

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June 30, 1958

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Department of Commerce, Washington 25, D. C.

SEP-250

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**Contract AT(30-1)2102
AEC Division of Research
Project No. 1852**

Issued: June 30, 1958

Sylvania Research Laboratories

A Division of

**Sylvania Electric Products Inc.
Bayside, N.Y.**

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	5
I. INTRODUCTION	6
II. NECK GROWTH VS. DENSIFICATION	6
III. EXPERIMENTAL METHOD	7
IV. RESULTS	8
V. DISCUSSION	9
VI. CONCLUSIONS	11
VII. FUTURE WORK	12
REFERENCES	13

ABSTRACT

The influence of the presence of grain boundaries on the rates of sintering of nickel, copper and iron wire wound compacts was studied. In iron compacts sintered in the alpha range, surface diffusion appears predominant and no grain boundary effect is therefore expected or evident. On the other hand, sintering of copper and of nickel compacts at temperatures close to their respective melting points apparently occurs by volume diffusion but with varying grain boundary effects. Neck growth in both materials appears entirely unaffected by the presence or absence of grain boundaries. Void shrinkage was found to be sharply inhibited in nickel samples from which grain boundaries had been deliberately eliminated, but no definite effect was noticed in copper, in apparent contradiction to previous results.

I. INTRODUCTION

According to the Herring-Nabarro theory^(1,2), grain boundaries play an important role in the sintering of a crystalline powder mass at elevated temperatures. However, the only direct evidence for the action of grain boundaries on the sintering rate of metals is that of Alexander and Balluffi⁽³⁾ for copper. This evidence confirms the Herring-Nabarro picture and suggests that, in the absence of grain boundaries, the rate of densification of a mass of crystalline powder is negligibly low.

Since the grain boundary effect is of such fundamental significance in the sintering process, it was felt desirable to obtain additional confirmation of the phenomenon, preferably in a metal other than copper. Therefore, investigations were begun some time ago of the sintering of compacts of fine nickel wire, using the technique applied by Alexander and Balluffi. Nickel wire compacts sintered more slowly near the melting point than copper, however, and insufficient densification was obtained to verify the grain boundary action.

In the present report period, experiments with wire compacts of nickel and other metals were continued with the aim of testing the Herring-Nabarro theory. In addition, further consideration has been given to the delineation of the diffusion path during sintering, and the significance of this for neck growth and densification.

II. NECK GROWTH VS. DENSIFICATION

Various relationships expressing rates of neck growth and in some cases rates of volume shrinkage as a function of time, temperature and particle size have been proposed by various authors including Kuczynski⁽⁴⁾, Cabrera⁽⁵⁾, Clark and White⁽⁶⁾, Rhines, Birchenall and Hughes⁽⁷⁾, Kingery and Berg⁽⁸⁾, and Herring⁽¹⁾. These have been discussed at length in a previous report⁽⁹⁾. Data for nickel and gold obtained earlier in this investigation agreed in almost all respects with the predictions of the Kuczynski⁽⁴⁾ diffusion equation:

$$\frac{x^5}{R^5} = \frac{80 \pi}{3} \frac{\delta^3 \gamma}{R^3 k T} D t \quad (1)$$

Here, x is the half-width of the sintered neck, R the radius of the wire, δ the atomic diameter, γ the specific surface energy, k is Boltzman's constant, T the absolute temperature, D the self-diffusion coefficient and t the time of sintering.

The Kuczynski diffusion equation makes no specification of vacancy sinks but implies that diffusion occurs inward uniformly from the surface of the sintered neck. This equation applies specifically to neck growth and does

not attempt to predict the rate of void elimination. It can easily be demonstrated on the basis of simple geometrical arguments that the rates of volume or linear shrinkage are not uniquely related to the rates of neck growth, the only parameter calculable from the Kuczynski equation, but depend markedly on the diffusion path. This is illustrated in Figs. 1, 2 and 3. In these simplified models, with material transported from the horizontally to the vertically shaded areas, it is assumed that the radius of curvature of the surface of the neck is approximately equal to the height of the neck and that a minimum surface configuration of the wires and neck can be attained by the transport of only a negligible amount of material, i.e., that smoothing of the sharply cusped necks does not affect the rates of either neck growth or of void shrinkage. In these models, R is the original wire radius, L the center-to-center distance of the wires (which before sintering is equal to $2R$, but not necessarily so after sintering), x the half neck width and ρ both the height of the neck and the radius of curvature of the neck. It will be noted that the relation between neck growth and void shrinkage depends upon the details of mass transport. The significance of this result will become clear in subsequent discussion of the experimental data.

III. EXPERIMENTAL METHOD

Wire compacts were prepared according to the techniques developed by Alexander⁽¹⁰⁾, Kuczynski⁽⁴⁾ and others^(11,12) by winding wire in a close-packed array on 1/4" spools. Three different materials were studied: vacuum-cast iron, vacuum-cast nickel and OFHC copper.

To study the effect of grain boundaries on sintering rates, grain boundaries were deliberately eliminated in some of the specimens, at times much earlier than would occur normally during the course of sintering. In the copper and nickel specimens this was achieved by pre-sintering the compacts until initial wire-to-wire bonds were obtained and then straining the specimens about 5% in axial compression. On reheating to the sintering temperature, recrystallization resulted in the elimination of about 50% to 75% of the cross-neck grain boundaries. In the iron compacts, a similar result was obtained by taking advantage of a transformation phenomena reported by Cizeron and Lacombe⁽¹³⁾. The specimens were pre-sintered at 895°C below the alpha-gamma transformation temperature to obtain wire-to-wire bonding and then homogenized for a short time at 920°C above the transformation temperature. Cooling to 895°C, the final sintering temperature, resulted in considerable grain coarsening and elimination of about 50% of the cross-neck boundaries. Typical results of these various treatments are shown in Figs. 4, 5 and 6.

Standard metallographic techniques were employed for examination of the sintered compacts. Neck widths were picked off photomicrographs with dividers, and void areas were measured planimetrically. Averages of two to six photographs were used to obtain each of the points of the sintering plots, and each point represents the average of 30 to 60 measurements.

IV. RESULTS

Initial neck growth up to times at which the necks were approximately equal to $1/3$ the wire diameter in both the copper and nickel samples occurred at a rate proportional to the one-fifth root of time, confirming earlier work^(3,4,9) and in agreement with the predictions of the Kuczynski equation for volume diffusion. No difference in rates of growth was found for necks crossed by a grain boundary and those in which grain boundaries had been eliminated by recrystallization. In the iron samples, however, sintered at temperatures both relatively and absolutely much lower than either the copper or the nickel, neck growth proceeded at rates nearly proportional to the one-seventh root of time. This, according to the Kuczynski equations, would indicate neck growth by surface diffusion, which should be favored at lower temperatures. Neck growth data are presented in Figs. 7, 8 and 9.

Void shrinkage data were unavoidably subject to greater uncertainty of measurement than neck growth; at short sintering times from the error in initial void areas introduced by even the slightest mismatching of the wires, and at very long times from the non-uniform shrinking of the long thin pores. This erratic closure of the pores shown in Fig. 10 is principally responsible for wide variations in pore size at the longer times shown in Figs. 12 and 13. Hence there is a considerable scatter in the shrinkage data.

In the nickel compacts, void shrinkage appeared to be dependent upon the presence of grain boundaries, since noticeably less shrinkage occurred in those compacts from which grain boundaries had been partially eliminated. The copper compacts, on the other hand, from which grain boundaries had been partially eliminated by strain annealing, appeared to shrink as rapidly as those with a full quota of grain boundaries.

The void shrinkage data from compacts sintered for a very long time are, as already mentioned, difficult to interpret because of the wide variation in void sizes which developed upon extended annealing. Even with many separate measurements of void areas, the 95% confidence limits on the means are uncomfortably wide. Nevertheless, it appears as if void shrinkage occurred in these compacts after the elimination of grain boundaries by exaggerated grain growth. This result is not in agreement with that obtained by Alexander and Balluffi⁽³⁾ and is being checked by further tests.

Consistent with the surface diffusion mechanism indicated by the dependence of neck growth in iron compacts on the one-seventh root of time, the shrinkage in the iron compacts was much less than either copper or nickel at corresponding stages of neck growth and too small to show any grain boundary effect. Fig. 14 shows the comparable shrinkage of the voids in copper and nickel compacts containing the normal number of grain boundaries as a function of neck width and the insignificant shrinkage of iron voids.

Attempts to measure changes in external dimensions were unsuccessful, and it seemed that linear shrinkage in these compacts was small. To determine whether the slowness of linear shrinkage was due in any measure to the restraints exercised by bonding to the base and to other wires, sintering

in several specimens was interrupted and the compacts cut longitudinally in several places, thus freeing them from at least tangential restrictions. Further, linear shrinkage in specimens prepared from single wires (as in Fig. 15) treated in the same way was also found to be below the limits of measurement error.

V. DISCUSSION

A. Neck Growth

The diameter of the necks in nickel and copper wire compacts increased with the one-fifth root of time, indicating, in agreement with Kuczynski's equations, mass transport by volume diffusion. This result has now been confirmed on copper, gold, nickel, silver and thorium wires and spheres sintered near the melting point^(4,9,14).

It is very interesting that the neck diameters in iron wire compacts sintered at 895°C, 65% of the absolute melting temperature, increased with the one-seventh root of time, which, according to Kuczynski's equations, indicates mass transport by surface diffusion. Since surface diffusion might be expected to predominate over volume diffusion at sufficiently low temperature, this result seems to support Kuczynski's analysis over that of Cabrera and Schwed^(5,15). The appearance of the compacts of Fig. 4 also support this conclusion, since neck growth by surface diffusion would be expected to result in elongated necks, as shown by the simplified model of Fig. 1.

In none of the metals was neck growth noticeably affected by the presence or absence of grain boundaries. This result had actually been predicted by Herring⁽¹⁶⁾ some time ago, who calculated that neck growth would not be appreciably accelerated by the presence of a grain boundary, even if this were necessary for densification. Since it is reasonably certain that the necks in the nickel and copper compacts are growing by a volume diffusion process, it seems clear that the diffusion path for neck growth does not involve the grain boundary. Neck growth for a significant part of the sintering process seems to be primarily connected with void spheroidization, which can occur by diffusion between adjoining or neighboring surfaces of differing curvature.

If it is true that neck growth in the iron wire compacts occurs by surface diffusion, then the grain boundary would not be expected to make a contribution, since the expected diffusion path would lie along the free surface of the void.

B. Void Shrinkage

Voids in the nickel and copper wire compacts shrank noticeably with time, but very little shrinkage occurred in the iron wire compacts, as would be expected if sintering were occurring mainly by surface diffusion in iron at 895°C. The relationship between void shrinkage and neck growth is compared for these metals in Fig. 14, which clearly illustrates the relative

lack of shrinkage of the iron compacts. In the nickel compacts, void shrinkage appears to be dependent upon the presence of grain boundaries and occurs at greatly diminished rates in those specimens whose grain boundaries have been partially removed by recrystallization. Spontaneous grain boundary elimination resulting from pore spheroidization occurs at such late stages of sintering that inhibition of shrinkage from this cause could not be detected in nickel, as has been shown by Alexander and Balluffi⁽³⁾ for copper. Nevertheless, the data obtained support the concept of densification by the transfer of atoms into the void from a nearby grain boundary.

In contrast to the behavior of nickel from the onset of sintering, void shrinkage in the copper compacts both with and without boundaries occurs at comparable rates. Furthermore, it seems that in the compacts sintered at times longer than about 100 hours, which compacts' grain boundaries had migrated as a result of pore spheroidization, shrinkage continued at a noticeable rate. Because of the scatter of data, this cannot be taken as a firm conclusion. However, the results of Alexander and Balluffi do not seem to have been confirmed.

Although it did not appear in the shrinkage data, some definite association of pore disappearance and the presence of grain boundaries was noticed in the microstructure. This is shown in Fig. 16. The disappearance of pores within certain areas of the sample seems to be related to the grain boundaries passing through them, particularly along the base of the windings where the initial void areas are approximately three times as great as those within the body of the compact. However, as is shown in Figs. 17(a) and 17(b), the disappearance of voids is not always connected with the presence of a grain boundary. In Fig. 16, some association of void disappearance and grain boundaries still exists, but to an extent much less than in Fig. 17(a), and in Fig. 17(b) void disappearance appears to be completely random.

It might be argued that the void disappearance in Figs. 17(a) and 17(b) is nevertheless associated with the few remaining grain boundaries which have migrated from their original sites as soon as pore spheroidization permitted their movement. However, the disappearance of single pores in Figs. 16 and 17 in a fashion completely isolated both from grain boundaries and other areas of pore disappearance, suggest the operation of vacancy sinks other than grain boundaries.

Vacancy migration between pores and to dislocations within the wires may be considered as alternative diffusion paths. Closure of the pores during sintering of the type shown in Fig. 10 results in the formation of surfaces of different curvature, with correspondingly different vacancy concentrations beneath the surface. This vacancy gradient would result in migration from pores of a low radius of curvature to those of high and increasingly rapid shrinkage of the smaller pores. Such migration has been reported by Rhines, Birchenall and Hughes⁽⁷⁾. It will be noted in Figs. 12 and 13 that the variation in pore sizes increases as sintering times are increased and

that upper limits of the one sigma variations are higher at the longer times than at the shorter, possibly indicating this type of behavior.

A reconsideration of the data of Fig. 13 lends weight to this argument. These data, as plotted, represent actually the shrinkage of the compact since the averages include pores of zero volume. If only actual pore volume is plotted, it is evident that although average pore size decreases, it does so only slowly and with a marked increase in the size of some of the pores.

The foregoing process is essentially one of spheroidization, and could not account for a continuing shrinkage of the total void volume in the absence of grain boundaries, if this is actually occurring. For the compact to shrink, according to the volume diffusion mechanism, lattice vacancies must somehow be eliminated, not merely transferred from one void to another. In the absence of grain boundary sinks, this could conceivably occur by the transfer of vacancies to the outer surface of the compact, or absorption at edge type dislocations within the body of the specimen. As shown by Pines⁽¹⁷⁾, shrinkage by transfer to an external surface is a very slow process, and most interest centers in the second possibility.

If only the region of the neck is considered, dislocation density is probably too low to provide the number of jogs necessary to accomodate all the vacancies migrating from the curved surface of the neck. However, if the entire population of suitable dislocations within the wires -- edge and Frank partials -- can act as sites for vacancy annihilation, this mechanism appears more probable. Possibly even more important than the migration of vacancies to jogs on edge and Frank partial dislocations is the operation of dislocation mills of the type whose role in crystal growth processes has been demonstrated, since theoretically the operation of one such mill could result in the erosion of an entire grain by a process of atom-vacancy interchange.

One factor in the above picture that remains unclear is the role of stress interactions among dislocations, which could inhibit the absorption of vacancies by dislocation climb. Herring's preliminary treatment suggested that the vacancy potential generated by the usual curved surfaces would not be high enough to move dislocations out of a stable network. It is felt, however, that his treatment is not detailed enough to eliminate this possibility decisively. In aluminum, dislocation motion is detected at extremely low stresses.

VI. CONCLUSIONS

- (1) Rates of neck growth in copper and in nickel wire-wound compacts are in agreement with those predicted theoretically for a volume diffusion mechanism.
- (2) In iron compacts sintered at low temperatures, both rates of neck growth and of void shrinkage are consistent with those to be expected from surface diffusion.

- (3) Void shrinkage in nickel is markedly dependent upon the presence of grain boundaries in the compacts.
- (4) Void shrinkage in copper compacts appears unaffected by the removal of grain boundaries.
- (5) In view of these observations, a unique equation relating neck growth, void shrinkage and linear shrinkage does not appear attainable without a specification of mechanism.

VII. FUTURE WORK

A key question that still requires a decisive experimental answer is whether or not void shrinkage actually stops when grain boundaries are eliminated from a porous metal compact during sintering. In other words, can dislocations function as effective vacancy sinks during sintering, as they seem to during diffusion? Initial attention will be given to settling this question by continuing studies of the sintering of metal wire compacts. A second technique is to study void shrinkage in porous copper prepared by de-zincifying brass. A porous single crystal, or coarse-grained polycrystal, can be prepared in which the behavior of voids isolated from grain boundaries and free surfaces may be examined.

Following the above, it is intended to resume investigation of the sintering of oxides, and metal-oxide mixtures in order to ascertain the rate controlling processes and effect of microstructure.

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SURFACE DIFFUSION

$$\rho = \frac{x^2}{2R}$$

$$\Delta L = 0$$

$$\Delta A_v = 0$$

Fig. 1. Wire sintering by a pure surface diffusion mechanism. It is assumed that material is removed uniformly from the surface and deposited at the cusp. Both void areas and center-to-center distances remain unchanged.

GRAIN BOUNDARY DIFFUSION OR
VOLUME DIFFUSION TO CROSS-NECK
GRAIN BOUNDARY

$$\rho = \sim \frac{x^2}{4R}$$

$$\Delta L = \sim \frac{x^2}{2R}$$

Fig. 2. Wire sintering by diffusion of vacancies to the cross-neck grain boundary. Both void areas and center-to-center distances decrease.

VOLUME DIFFUSION TO DISLOCATIONS

$$\rho = \frac{x^2}{2R} = \sim \Delta R$$

$$\Delta L = \sim \frac{6}{64} \frac{x^3}{R^2}$$

$$\Delta A_v = \frac{3x^3}{R}$$

Fig. 3.

Wire sintering by volume diffusion of vacancies from the cusped neck to dislocations within the particles. The wire shrink uniformly with material deposited at the necks.

(a) Sintered for 7 1/2 hours at 895°C.

Plate #18827

(Spec. IC-22)

750X

(b) Sintered for 6 1/2 hours at 895°C, held at 920°C for 1/2 hour; cooled to 895°C and held for 65 hours.

Plate #18831

(Spec. IC-23)

750X

Fig. 4. Grain boundary elimination in .003" Ferrovac iron wire compacts by alpha-gamma-alpha transformation.

(a) Sintered for 156 hours at 1400°C .
Plate #21454 (Spec. NC-169)

250X

(b) Sintered 6 hours at 1400°C . Strained about 5% at room temperature. Resintered for 150 hours.

Plate #21452

(Spec. NC-168)

250X

Fig. 5. Grain boundary elimination in .005" nickel compacts by strain annealing.

(a) Sintered 16 hours at 1060°C .
Plate #21341 (Spec. Cu-14)

300X

(b) Sintered 1 hour at 1060°C . Strained in compression 5%.
Resintered for 15 hours at 1060°C .
Plate #21376 (Spec. Cu-3)

300X

Fig. 6. Grain boundary elimination in copper specimens.

Fig. 7. Neck growth in .003" Ferrovac wire wound compacts. Dashed line is drawn with the slope of $1/7$ indicative of a surface diffusion mechanism.

Fig. 8. Neck growth in .005" nickel wire wound compacts. The dashed line is drawn with a slope of 1/5, appropriate to a volume diffusion mechanism.

Fig. 9. Neck growth in .004" OFHC copper wire wound specimens. The dashed line is drawn with a slope of 1/5, appropriate to a volume diffusion mechanism.

Fig. 10. Longitudinal section of .005" nickel wire-wound compact sintered for 800 hours at 1400°C.

Plate #20126

(Spec. NC-161 A)

75X

Fig. 11. Void shrinkage in .003" Ferrovac iron compacts sintered at 895°C.

Fig. 12. Void shrinkage in .005" nickel wire-wound compacts sintered at 1400°C.

Fig.13. Void shrinkage in .004" OFHC copper wire-wound specimens sintered at 1060°C.

Fig. 14. Void shrinkage as a function of neck width in iron, nickel and copper wire-round compacts.

Fig. 15. Sintering of single wires, free from tangential and longitudinal restraint.

Plate #21530

300X

Fig. 16. Pore elimination in .004" OFHC copper wire-wound compact sintered at 1060°C for 351 hours, showing association of the grain boundaries with the zone of pore elimination.

Plate #21191

(Spec. Cu-5 A)

100X

(a) Plate #21194

(Spec. Cu-10)

100X

(b) Plate #21197

(Spec. Cu-11)

100X

Fig. 17. Random pore elimination in OFHC copper compacts sintered for 400 hours at 1060°C.