UNITED STATES ATOMIC ENERGY COMMISSION

FUNDAMENTALS OF SINTERING—II

Second Annual Progress Report, June 30, 1956
to June 30, 1957

By
A. L. Pranatis
L. S. Castleman
L. Seigle

February 15, 1958

Research Laboratories
Sylvania Electric Products, Inc.
Bayside, New York

Technical Information Service Extension, Oak Ridge, Tenn.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA. Price \$1.00. Available from the Office of Technical Services,
Department of Commerce, Washington 25, D. C.

SEP-247

FUNDAMENTALS OF SINTERING - II

A. L. Pranatis
L. S. Castleman
L. Seigle

Second Annual Progress Report
June 30, 1956 to June 30, 1957

Project No. 1852

Prime Contract AT-30-1 GEN 366
AEC Division of Research

Issued: February 15, 1958

This work was performed by the Research Laboratories of Sylvania Electric Products Inc. under sub-contract to Sylvania-Corning Nuclear Corporation.

Metallurgical Research Laboratory
Sylvania Electric Products Inc.
Bayside, N.Y.

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	5
I. INTRODUCTION	6
II. LITERATURE REVIEW	6
III. EXPERIMENTAL METHOD	9
IV. RESULTS	10
A. Sintering Rates	10
B. The Coefficient of Self-Diffusion	10
C. Scale Effects	11
D. Rates of Void Shrinkage	11
E. The Sintering of Gold Wire Compacts	12
V. DISCUSSION	12
VI. FUTURE WORK	16
REFERENCES	18

ABSTRACT

Rates of spheroidization and densification of gold and of nickel wire compacts were measured as a function of time, temperature and wire size. The necks joining the sintered particles were found to grow proportionally to the one-fifth root of time. The value of the coefficient of self-diffusion calculated from the sintering rate is of the same order of magnitude as that obtained by ordinary tracer techniques but with a somewhat higher activation energy. These results are entirely consistent with those predicted by the Kuczynski diffusional theory of sintering, as is the effect of wire size on sintering rate.

The experiments did not reveal a clear effect of grain boundaries on sintering rates. This may be due to a relatively slow densification of the nickel wire compacts at even 0.98 of the absolute melting point, which obscured the effect of grain growth on sintering rate.

I. INTRODUCTION

The sintering of powder compacts at high temperatures obviously requires the transport of large amounts of material. An increasing body of evidence suggests that the principal transport mechanism in non-volatile metals and oxides is self-diffusion. According to the Herring-Nabarro^(1,2) theory of stress-induced diffusion, grain boundaries play an important role in the densification process.

Direct evidence for the action of grain boundaries during sintering is quite meager. Alexander and co-workers⁽⁷⁾ observed retardation of the densification of copper wire compacts upon the occurrence of grain growth. In coarse-grained compacts, voids seemed to be preferentially eliminated in the vicinity of grain boundaries. Recently Burke⁽¹²⁾ presented evidence of a similar grain boundary effect in sintered aluminum oxide powder. In neither aforementioned study was a comprehensive investigation of the grain boundary effect reported, and additional experimental confirmation of this phenomenon would be desirable. The details of mass transport during the sintering of oxides also require further clarification.

The present investigation was started two years ago to confirm the existence of a grain boundary effect in crystalline oxides as well as metals and to clarify the mechanism⁽²⁰⁾ of the sintering of oxides. As mentioned in a previous progress report, a detailed study of the sintering of Cu_2O was made in order to clarify the underlying mass transport mechanisms and also search for the existence of the grain boundary effect. Interpretation of the results obtained using normal powder compacts was complicated by an exaggerated grain and void growth during sintering. Therefore, at the end of this period it was decided to suspend investigations of the sintering of oxides until more definitive experiments could be designed, and to concentrate on obtaining a confirmation of the grain boundary effect in metals other than copper. It was decided that the wire-wound compact was best suited for this purpose and therefore an intensive study was begun of the sintering of fine nickel, silver and gold wire compacts. The use of such compacts also presented the opportunity to test Herring's⁽¹¹⁾ theory of the size effect and obtain additional data on the sintering mechanism of non-volatile metals.

II. LITERATURE REVIEW

Much recent work on the fundamentals of sintering stems from the Kuczynski-Pines^(3,4) model. Kuczynski postulates that the vacancy concentration beneath a curved surface can be expressed by the same Kelvin equation that relates vapor pressure and curvature:

$$\Delta C = \left(\frac{s^3 \gamma}{kT \rho} \right) C_0$$

Here, ΔC is the excess vacancy concentration, δ the atomic diameter, γ the surface tension of the metal, k Boltzman's constant, ρ the radius of curvature (at the sintered neck joining two sintered particles) and C_0 the equilibrium vacancy concentration. This excess concentration of vacancies causes the diffusion of atoms from the inner parts of the system to the neck. The above equation can be combined with an equation expressing the rate of flow of vacancies by diffusion,

$$A \frac{\partial \Delta C}{\partial r} D' = \frac{dv}{dt}$$

and the solution of the Laplacian, $\nabla^2 C = 0$ for the particular geometry involved. Here, A is the area of the surface through which vacancies enter the system, $\frac{\partial \Delta C}{\partial r}$ the gradient of vacancy concentration, D' the coefficient of diffusion for vacancies, v the volume of material transported, and t is the time. Making the necessary assumptions of geometry and diffusion path, Kuczynski obtains the following equation for growth of the neck between two wires or between a wire and a plate:

$$\frac{x^5}{a^2} = \left(\frac{80 \pi}{3} \right) \left(\frac{\delta^3 \gamma}{kT} \right) Dt$$

Here, x is the half-width of the sintered neck, a the radius of the wire and D the coefficient of self-diffusion of the metal. Similar equations have been derived by Cabrere⁽⁵⁾ and by Kingery and Berg⁽⁶⁾.

Using similar assumptions of geometry, Kuczynski has also derived equations of neck growth for the mechanisms of surface diffusion and evaporation-condensation and shown that the width of the neck between two sintered particles is related to the time of sintering in the following way for each of the possible modes of material transport:

Plastic Flow	$w^2 \sim t$
Evaporation and Condensation	$w^3 \sim t$
Volume Diffusion	$w^5 \sim t$
Surface Diffusion	$w^7 \sim t$

Thus the rate of growth of the neck can be used as a criterion of mechanism.

These relationships have been tested experimentally only in a limited number of systems. The fifth power relationship appropriate to a diffusional mechanism has been observed in the sintering of silver by Kuczynski⁽⁴⁾, of copper by Alexander and Balluffi⁽⁷⁾, and most recently of thorium by Meehan⁽⁸⁾. In non-metals, it would appear that other processes might be operative. Kingery and Berg⁽⁶⁾ found neck growth in sodium chloride proportional to the cube root of time, corresponding to

an evaporation-condensation mechanism together with physical changes in the specimens consistent with this conclusion. Glasses, on the other hand, have been found to sinter at a rate proportional to the square root of time, that is, by viscous flow^(6, 9, 10).

A further criterion for distinguishing mechanisms of mass transport has been developed by Herring⁽¹¹⁾, who has derived simple relationships between the time required to attain a given geometry in compacts which are geometrically identical except for scale. For a cluster of wires, the relationship between Δt_1 and Δt_2 , the times required to attain identical geometry, are:

Viscous Flow	$\Delta t_2 = \lambda \Delta t_1$
Evaporation and Condensation	$\Delta t_2 = \lambda^2 \Delta t_1$
Volume Diffusion	$\Delta t_2 = \lambda^3 \Delta t_1$
Surface Diffusion	$\Delta t_2 = \lambda^4 \Delta t_1$

Here λ is the ratio of the wire radii, a_2/a_1 .

It will be noted that the above equations relate only to neck growth and make no predictions about the rate of shrinkage of the compacts. The possible implication that shrinkage and neck growth are independent stems from the absence of any assumptions about diffusion path in the derivation of the equations. It is obvious that material transport by either surface diffusion or evaporation and condensation would result in neck growth and spheroidization without shrinkage. However, the relationship between shrinkage and neck growth in the case of volume diffusion is less clear-cut, since the rate and mode of shrinkage is affected by the diffusion path and the location of the sinks at which vacancies are dissipated. For instance, the discharge of vacancies at the void surfaces would result in spheroidization only, while migration of vacancies to and annihilation at grain boundaries within the system would result in both spheroidization and densification.

Some evidence exists to suggest that grain boundaries are the principal sites of vacancy annihilation. Alexander and Balluffi⁽⁷⁾ found that the Kuczynski relationship for volume diffusion was obeyed only so long as the sintered necks joining sintered copper wires contained a transverse grain boundary, but that after about 90 hours of sintering, when the grain boundaries disappeared, the pores between wires would cease shrinking and merely spheroidize.

Further evidence of the important role of grain boundaries in the sintering process has been presented by Burke⁽¹²⁾ who noted that porosity in sintered alumina compacts had disappeared near grain boundaries after recrystallization had occurred, but persisted within the grains at distances far removed from the boundaries. Further, compacts in which recrystallization

and grain growth were inhibited for some reason could be sintered to almost 100% density, while recrystallized compacts with extremely large grains would attain no more than 95% of theoretical density.

Likewise, Cizeron and Lacombe⁽¹³⁾ found that the sintering rate of iron powder in the alpha region was much reduced if the compacts were heated to above the alpha-gamma transformation temperature for a short time. Cooling again to the alpha region resulted in pronounced grain growth in the compact with isolation of many of the voids within the grains, as contrasted with compacts held entirely within the alpha region in which pores and grain boundaries formed an inter-connected network. Unfortunately, the same treatment caused pronounced changes in the size and number of the voids. It is therefore impossible to attribute the decrease in sintering rates of these compacts solely to the change in grain size or to conclude that densification is possible only in the presence of grain boundaries.

Though the evidence now at hand is strongly indicative that volume diffusion is the principal mechanism operating in the sintering of metals, extension to other systems involved seems necessary to identify both mechanism and diffusion path and to verify both the Kuczynski and the Herring criterion of mechanism. In particular, the effect of changes in grain size on rates of void shrinkage requires further confirmation.

The work described here was undertaken not only to identify the mechanism of mass transport in the sintering of nickel and gold, but to elucidate if possible the path of the mobile ions. Confirmation of the role of grain boundaries as possible sites for vacancy annihilation was a particular goal of the investigation. Comparison of roles of neck growth and void shrinkage in wire-wound compacts in which ultimate grain size could be controlled by varying sintering temperature appeared a feasible approach and was the principal technique employed in this phase of the investigation.

III. EXPERIMENTAL METHOD

With minor modifications, the wire and spool technique developed by Kuczynski^(3,4) and others^(14,15) was used throughout the work. Nickel wires of various sizes were wound in a close-packed array on nickel spools and these idealized compacts were sintered for various times and then sectioned for metallographic examination. Nickel of 0.9999 purity was used to prepare both the wire and the spools. A few runs were made with commercial nickel wire of unknown purity, but these were unusable because of variations in wire diameter and a high impurity content which caused partial melting at the higher temperatures. Likewise, specimens prepared from Mond carbonyl nickel were discarded, since a high inclusion count prevented grain growth. A few specimens were also prepared from commercially-pure gold wire.

The compacts were sintered in Globar-heated furnaces in high-purity

alumina muffles. No other furnace tubes employed were able to withstand the long times and high temperatures used in this work. Most of the samples were sintered under dry hydrogen, though a few were sintered under vacuum with no detectable change in rates. On completion of the runs, the compacts were cooled in hydrogen. Total times of heating and cooling amounted to less than one and a half hours.

Standard metallographic techniques were employed for examination of the sintered compacts, although unusual care was necessary to prevent loss of accuracy through either smearing or over-etching. A combination of mechanical and electrolytic polishing was found to give the most reproducible results. Neck widths were picked off 250X photomicrographs with dividers, and void areas were measured planimetrically. Averages of about a half-dozen photographs were used to obtain each point on the plots of neck width and void area. Typical photomicrographs are shown in Figs. 1 and 2.

IV. RESULTS

A. Sintering Rates

The parameter $\frac{x}{a}$, where x is the half neck width and a the radius, has been used as a measure of the degree of sintering, since this permits direct comparison of sintering rates of wires of various sizes. In Figs. 5, 6 and 7 the logarithm of this quantity is plotted as a function of the logarithm of time of sintering in hours. The straight lines have been fitted to the data by least squares. Table I presents the equations for the least squares lines for the log-log plot of $\frac{x}{a}$ vs. time in hours for each of the temperatures and wire sizes employed.

It will be noted that the values of the exponent are generally somewhat lower than $1/5$. It is not believed, however, that this slight difference is significant, in that none of the values approach either $1/3$, which would denote evaporation-condensation, or $1/7$ which Kuczynski has proposed as the exponent accompanying surface diffusion.

B. The Coefficient of Self-Diffusion

The value of the self-diffusion coefficient of nickel may be calculated from the coefficients of the equations in Table I, since these correspond to the quantity $\left(\frac{80 \pi}{3} \frac{\delta^3}{k} \frac{\gamma}{T} \frac{D}{a^3} \right)$

in the Kuczynski equation for the sintering of wires to a plate (or cylinder). Table II presents the values for D calculated from shrinkage rates for different wire sizes and temperatures using the value 1000 ergs/cm^2 for γ and 2.5×10^{-8} for δ . Values for the diffusion coefficient based on the equation of Hoffman⁽¹⁶⁾,

$D = 1.27 \exp \frac{-66,800}{RT}$ are presented for comparison. The same data are presented in Fig. 8.

Though the absolute values of D obtained from sintering rate correspond well with those of Hoffman, the activation energies are in poor agreement -- 80,000 cal/mol from sintering rates compared to 66,800 cal/mol from tracer measurements. On the basis of the absolute melting point of nickel and comparison with the self-diffusion coefficients, the latter value seems reasonable. The large discrepancy is due not only to the narrow temperature range used in the sintering experiments (only about 100°C), but also to experimental error in the calculation of the coefficients of the Kuczynski equation.

C. Scale Effects

Comparison of sintering rates of the three different size wires employed here can be used to test the Herring criterion of the sintering mechanism. According to Herring, the times to attain similar changes in geometry, if a diffusional process is operating, are related in the following way:

$$t_1 = \lambda^3 t_2$$

Here, λ is the ratio of the wire radii, a_1/a_2 .

The values of the exponent of λ presented in Table III are averages based on the times required to attain three separate values of $\frac{x}{a}$. Agreement with the theoretical value for a diffusional mechanism is good.

D. Rates of Void Shrinkage

Planimetric measurements of the areas of the inter-wire voids were made on the same photomicrographs used to determine rates of neck growth. It was believed that the rates of void shrinkage would furnish a more reliable criterion of the effect of grain boundaries than would rates of neck growth, since diffusion could continue by migration of vacancies to the surface even after grain boundaries had been eliminated, which process would be reflected in the cessation of void shrinkage. The data (plotted in Figs. 9, 10 and 11 on a semi-log scale for convenience, and not because an exponential rate was expected) are somewhat anomalous in two respects: (1) in the lack of any simple parabolic relationship between shrinkage rates and time, and (2) because of the unexpectedly slow initial rates of shrinkage. This second phenomenon is discussed at greater length in the following section. Although it has been reported that the rate at which voids disappear decreases when the grain boundaries

disappear, we observed that the rate of void disappearance was unchanged. In the .0063" wire, grain boundaries began migrating from the specimen at between 100 and 200 hours at 1425°C, and observations were continued up to 400 hours during which time the voids continued to shrink.

E. The Sintering of Gold Wire Compacts

A few compacts similar to the nickel, prepared from .006" gold wire, were sintered in nitrogen for various times at 1050, 1020 and 990°C. In general, results obtained from measuring neck widths substantiate those obtained from the nickel samples. A one-fifth power relationship between neck width and time was observed in these compacts as in the nickel, while the values of the self-diffusion coefficient calculated from the rate of neck growth is higher by a factor of about 3 than that reported in the literature⁽¹²⁾. The activation energy of self-diffusion obtained in this manner is approximately 60,000 cal/mol compared to 53,000 cal/mol from the conventional technique. However, the former value was calculated using only one value of the rate of neck growth at 990°C and is undoubtedly subject to considerable error.

Grain growth in the gold samples is much less pronounced than in nickel, and grain boundaries persist both in the wires and across the necks even at late stages of sintering where they have completely disappeared in comparative nickel samples. For this reason no observations could be made on the effect of grain boundaries.

An anomaly not observed in either nickel or copper specimens was apparent in the gold compacts — porosity located within the necks joining the sintered wires, similar in some respects to that observed in dezincified brass and in high temperature creep specimens⁽¹⁸⁾. This porosity is shown in Fig. 8. At each temperature the secondary pores seemed to grow to a maximum size — in some cases to a size as large as that of the primary pores located between the wires — and then to shrink and disappear. At all temperatures the largest pores were noted at intermediate times, though too few specimens were prepared to permit detailed observations of the pore history.

V. DISCUSSION

Though the value of the coefficients in the equations prepared by Kuczynski⁽⁴⁾ and others^(5, 6) to express the relationship between neck width and time of sintering may be changed slightly by varying the initial assumptions of geometry and diffusion path, the value of the exponent of the time term does seem to be a reliable indication of mechanism. The one-fifth power relationship obtained by previous workers with other metals was also observed here in both the nickel

and gold compacts. The consistency of these results strongly indicates that the same mechanism is operative in all these metals. The conclusion that this mechanism is diffusion is supported by consideration of the exponents obtained in the sintering of non-metals in which diffusion might be considered negligible. In these materials, exponents consistent with viscous flow or evaporation-condensation were observed.

Application of the Herring size criterion also lends support to the view that sintering in metals occurs by a diffusional mechanism. Both in the present work and in that of Meechan⁽⁸⁾, reported since the initiation of the present program, the following relationship was obtained:

$$\Delta t_1 = \left(\frac{a_1}{a_2} \right)^3 \Delta t_2$$

where as before Δt_1 and Δt_2 are the times required to reach identical geometries in compacts made up of wires of radii a_1 and a_2 .

The good agreement obtained between the absolute values of the coefficients of self-diffusion of nickel and of gold calculated from the rates of sintering and by conventional tracer techniques is also strongly indicative that volume diffusion is operative. The lack of agreement in the activation energies may be due to experimental error stemming from the narrow temperature range (about 100°C) used in the sintering work.

To the extent, then, that the predictions of theory are borne out, it would appear justifiable to conclude that sintering in metals results from the diffusion of atoms under a surface tension-induced potential gradient. However, the unexpectedly slow rate of void shrinkage compared to the rapid growth of the necks warrants a re-examination of possible diffusion paths and of other modes of spheroidization.

Mass transport solely by evaporation from the convex wire surfaces and evaporation at the neck would appear inadequate to account for observed rates of neck growth. The maximum rate of evaporation from a convex surface and condensation at a neighboring concave surface can be calculated by the Langmuir equation

$$\Delta G = a \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}} \Delta P$$

where a is an accommodation coefficient whose maximum value is 1, M the molecular weight and ΔP the difference in the vapor pressures at the two sites, which is of course easily calculated by the Kelvin equation. Following Kuczynski and substituting for the particular wire geometry employed leads to the following relationship:

$$\left(\frac{x}{a}\right)^3 = \left(\frac{8}{3}\right) \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} \left(\frac{2\gamma M}{d^2 RT}\right) P_0 t$$

Here, d is the density and P_0 the equilibrium vapor pressure. Substitution in this equation shows that even at 1420°C with .006" wire, neck growth by this process becomes negligibly small after about one hour.

Though a similar equation can be derived for neck growth by surface diffusion,

$$\left(\frac{x}{a}\right)^7 = \frac{16}{3} \frac{\gamma \delta^4}{KT} \frac{D_s t}{a^4}$$

rate calculations are impossible due to a lack of information about the coefficient of self-diffusion, D_s . However, calculation of the value of the coefficient of self-diffusion necessary to account for the observed spheroidization leads to a value, $D_s = \sim 10^{19}$ at 1400°C , an impossibly high value.

The above calculations confirm the hypothesis that bonding occurs by volume diffusion, and therefore it is necessary to consider possible diffusion paths in order to explain neck growth without shrinkage. Close examination of photomicrographs used in the measurement of neck growth and void shrinkage reveals shallow grooves in the wire surfaces near the sintered necks. Such grooves are discernable in Fig. 3, and are even more clearly evident on visual examination at high magnification. Hence it appears that neck growth has occurred primarily by diffusion between portions of the free surface of the void possessing opposite curvatures. Since initial shrinkage is negligible, it also seems that grain boundaries are not acting as sinks for vacancies in the early stages of sintering.

At later stages, when densification is more pronounced, vacancy migration is obviously directed to the interior of the system, where grain boundaries and dislocations are possible sites of vacancy annihilation. The observations of Alexander and Balluffi that voids ceased shrinkage after the elimination of grain boundaries from the compacts, suggests that grain boundaries are the principal loci of vacancy migration and dissipation. However, even in the later stages of sintering, the grain boundary effect could not be confirmed in the present work. As can be seen in Fig. 9, the onset of grain growth and grain boundary elimination in the specimens sintered at about 1430°C occurred after about 90 hours of sintering. Though sintering was continued to about 400 hours, shrinkage in these compacts with grain boundaries partially or totally eliminated proceeded without noticeable diminution in rate. Much of the porosity in the specimens sintered at long times and at high temperatures has disappeared completely even though few or no grain boundaries were present.

Although these observations do not confirm the work of Alexander and

Balluffi⁽⁷⁾, it is difficult to eliminate grain boundaries as the most likely sink for vacancy dissipation, since dislocation climb alone could not account for all the total observed shrinkage. The Kuczynski equation states that vacancy elimination occurs almost completely within a distance ρ from the sintered neck. Simple calculations based on a dislocation density of $10^8/\text{cm}^2$ reveal that the number of dislocations within this distance are completely inadequate to account for the volume changes observed. Hence at the present time it is felt that the behavior of the nickel wire compacts is not completely understood.

The appearance of porosity at the transverse grain boundaries in the necks of the sintered gold wires (Fig. 8) is an interesting phenomenon. The possibility has been considered that vacancies originating at the surface of the void are eliminated by the formation of secondary porosity at these points. However, the nucleation and growth of these pores within the necks would seem to require a mechanism other than the migration of vacancies down a concentration gradient and a driving force in addition to the surface tension of the metal. At 1000°C , and with a neck radius of one micron, the ratio of vacancy concentration beneath the surface to that of the bulk calculated on the basis of Thomson's equation is less than 1.001. Even if this level of supersaturation extends to the center of the neck, it is much lower than that calculated by Balluffi⁽¹⁹⁾ to be necessary for the nucleation of porosity in dezincified brass. Further, the radius of curvature of the just-formed pores is much less than that of the neck. Therefore, the continued growth of the pores would require migration of the vacancies up their own concentration gradient, a process possible only with an additional and opposite potential gradient. Two possible sources of this additional energy are a supersaturation of gases in the metal, and the tensile forces caused by the mechanical restraints exerted by the solid metal core of the compacts which tend to prevent longitudinal shrinkage.

Similar porosity was previously observed in silver wire compacts where it seemed reasonable to attribute its presence to the high solubility of gases in silver. A like explanation for the porosity in gold seems less justifiable. A rough calculation of the volume of the gases required to fill the pores at room pressure would indicate a gas content in the gold wires prior to sintering of about 0.1 w/o, an unreasonably high value in view of the fact that the common gases are usually considered to be completely insoluble in gold.

The complex geometry of the compacts makes difficult an exact calculation of the longitudinal stresses in the compact due to the opposition to shrinkage caused by the solid metal core. However, consideration of the increase in surface area caused by the formation of the secondary porosity compared to the decrease caused by shrinkage of the compact makes it unlikely that this restraint alone is solely responsible for the appearance of the additional porosity.

At present no satisfactory explanation of this phenomenon can be advanced. Its appearance is probably not restricted to wire-wound compacts, but is probably inherent even in pressed-powder compacts where its presence is masked by irregular geometry.

VI. FUTURE WORK

Present interest is centered on the still unconfirmed role of grain boundaries in the sintering process, the diffusion path of the atoms migrating from the sintered neck, the mechanism of the formation of the secondary voids observed in the sintering of silver and gold, and in the mechanism of sintering of oxides and non-metallic crystalline solids.

The principal source of uncertainty of the effects of grain boundaries in the present work has been the inhibition of grain boundary migration by the regularly-arrayed inter-wire voids. The resulting delay in grain boundary elimination has prevented comparison of sintering rates of compacts with and without grain boundaries, except in the final stages of densification where rates are extremely slow. The observations of Cizeron and Lacombe⁽¹³⁾ that a brief passage of alpha iron powder compacts into the gamma region resulted in a greatly enlarged grain size and the isolation of the majority of the pores within the grains suggests the application of similar techniques to wire-wound compacts. Should similar grain growth occur in wire-wound compacts, the marked changes in pore size and distribution accompanying phase transformation in ordinary powder compacts would not be expected to occur. In order to minimize the inhibition of grain growth by inclusion and impurities, vacuum-cast Ferrovac pure iron will be used in these experiments.

Attempts to accelerate grain growth in the early stages of sintering are also being made by straining partially sintered wire compacts in compression before reheating to the sintering temperature. It is hoped that this compression will provide sufficient strain energy to induce grain growth without causing excessive distortion of the compact geometry.

Compacts prepared from gold wire purified and degassed by horizontal and vertical zone melting are being prepared for comparison with the original compacts which showed secondary porosity within the sintered necks. Appearance of this type of porosity in purified metal compacts would be evidence that its formation is truly concomitant to the basic sintering mechanism, and as such might be the source of the anomalous decrease in density of metal powder compacts occasionally reported in the literature. Its non-appearance would indicate that the porosity is associated with impurities in the metal, most likely dissolved gases.

At present the only studies of the sintering mechanism in oxides and ionic crystals, those of Kingery and Berg⁽⁶⁾, suggest evaporation-condensation or plastic flow as possible transport processes in NaCl,

AgCl and NaNO_3 and plastic flow in fluorides, while the evidence for oxides is ambiguous but tends to favor diffusion. In view of this scanty information, further clarifying evidence of the mechanisms of sintering in oxides would seem necessary. Though the present technique of wire-wound compacts is inapplicable to oxides, the preparation of simplified compacts of spheres or rods may be possible. Rate studies of such compacts as a function of time, temperature and vacancy concentration are planned.

REFERENCES

1. C. Herring, J. Applied Physics, 21 (1950) 437.
2. F. R. N. Nabarro, "Report of a Conference on the Strength of Solids", Physical Society, London (1948) 75.
3. G. C. Kuczynski, J. Inst. Metals, (Feb. 1949) 75.
4. G. C. Kuczynski, J. Applied Physics, 21 (1950) 632.
5. N. Cabrera, Trans. AIME, 188 (1950) 667.
6. W. D. Kingery and M. Berg, J. Applied Physics, 26 (1955) 1205.
7. B. H. Alexander and R. Balluffi, J. Metals, 188 (1950) 1219.
8. C. J. Meechan, "Self-Diffusion in Thorium", Paper #57-NESC-7, presented at the 2nd Nuclear Engineering and Science Conference, American Soc. of Mechanical Engineers.
9. G. C. Kuczynski, J. Applied Physics, 20 (1949) 1160.
10. G. C. Kuczynski and I. Zablatynskyj, J. Amer. Ceramic Soc., 39 (1956) 349.
11. C. Herring, J. Applied Physics, 21 (1950) 301.
12. J. E. Burke, J. Amer. Ceramic Soc., 40 (1957) 80.
13. G. Cizeron and P. Lacombe, Rev. de Met., 53 (1956) 819.
14. G. A. Geach and F. D. Jones, Research, 2 (1949) 493.
15. J. H. Dedrick and A. Gerds, J. Applied Physics, 20 (1949) 1042.
16. R. E. Hoffman, Trans. AIME, to be published, quoted by R. A. Swalin and A. Martin, Trans. AIME, 206 (1956) 567.
17. H. A. C. McKay, Trans. Far. Soc., 34 (1938) 845.
18. R. Resnick and L. Seigle, Trans. AIME, 209 (1957) 87.
19. R. W. Balluffi, Acta Met., 2 (1954) 194.
20. A. Pranatis and L. Seigle, "Fundamentals of Sintering - I" (SEP-229) October 5, 1956.

TABLE I

<u>Wire Size</u>	<u>T E M P E R A T U R E</u>		
	<u>1320°C</u>	<u>1400°C</u>	<u>1425°C</u>
.0063	$\frac{x}{a} = .119t^{.17}$	$\frac{x}{a} = .152t^{.18}$	$\frac{x}{a} = .160t^{.19}$
.009	$\frac{x}{a} = .099t^{.18}$	$\frac{x}{a} = .114t^{.19}$	$\frac{x}{a} = .127t^{.19}$
.0126	$\frac{x}{a} = .080t^{.17}$	$\frac{x}{a} = .093t^{.20}$	$\frac{x}{a} = .090t^{.22}$

Table I. Least squares equations for the plots of $\log \frac{x}{a}$ vs. $\log t$ (hour).

TABLE II

<u>Wire Size</u>	<u>T E M P E R A T U R E</u>		
	<u>1320°C</u>	<u>1400°C</u>	<u>1425°C</u>
.0063	3.78×10^{-10}	1.31×10^{-9}	2.15×10^{-9}
.009	3.98×10^{-10}	1.35×10^{-9}	2.11×10^{-9}
.0126	3.88×10^{-10}	1.36×10^{-9}	2.11×10^{-9}
Hoffman	10.1×10^{-10}	2.78×10^{-9}	3.59×10^{-9}

Table II. The self-diffusion coefficient calculated from sintering rates of .0063, .009 and .0126" wire, compared with that of Hoffman⁽¹⁶⁾.

TABLE III

<u>$\lambda = a_1/a_2$</u>	<u>T E M P E R A T U R E</u>		
	<u>1320°C</u>	<u>1400°C</u>	<u>1425°C</u>
<u>.009</u> <u>.0063</u>	3.12	2.90	3.08
<u>.0126</u> <u>.0063</u>	3.08	2.92	3.18
<u>.0126</u> <u>.009</u>	3.10	2.94	3.15

Table III. The value of the exponent of λ in the Herring⁽¹¹⁾ equation relating sintering rates as a function of wire size, $t_1 = \lambda^n t_2$.

10 Hours

1425°C

100X

90 Hours

1425°C

100X

Fig. 1 .0063" Ni wire sintered at 1425°C for 10 and 90 hours. Grain boundaries have migrated from a few of the sintered necks at 90 hours.

Fig. 2. .0063" Ni wire compacts sintered at 1425°C for 217 and 400 hours. Grain boundaries have migrated from about a third of the necks at 217 hours and are almost completely gone at 400 hours.

Fig. 3. .0063" Ni wire compacts sintered at 1400°C for 16 hours. Shallow grooves are evident near most of the sintered necks.

Fig. 4. .006" gold wire compacts sintered at 1055°C for 67 hours.

Fig. 5. The ratio, neck width/wire diameter for nickel wire compacts sintered at 1320°C.

Fig. 6. The ratio, neck width/wire diameter for nickel wire compacts sintered at 1400°C.

Fig. 7. The ratio, neck width/wire diameter for nickel wire compacts sintered at 1430°C.

Fig. 8. The coefficient of self-diffusion of nickel. The dotted line is from the present work based on the rate of sintering. The solid line is that of Hoffman using conventional tracer techniques.

Fig. 9. Void shrinkage in .0126" nickel wire compacts.

Fig. 10. Void shrinkage in .009" nickel wire compacts.

Fig. 11. Void shrinkage in .0063" nickel wire compacts.