UNCLASSIFIED

SEP-229

1
METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

FUNDAMENTALS OF SINTERING—I

First Annual Progress Report for June 30, 1955
to June 30, 1956

By
A. Pranatis
L. Seigle

October 5, 1956

Atomic Energy Division
Sylvania Electric Products, Inc.
Bayside, New York

Technical Information Service Extension, Oak Ridge, Tenn.

UNCLASSIFIED

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.

2

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 20 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

SEP-229

FUNDAMENTALS OF SINTERING - I

By

A. Pranatis

L. Seigle

First Annual Progress Report
June 30th, 1955 to June 30th, 1956

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

October 5, 1956

Atomic Energy Division
SYLVANIA ELECTRIC PRODUCTS INC.
Bayside, New York

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	5
I. INTRODUCTION.....	6
II. THE SINTERING OF CUPROUS OXIDE.....	7
III. INERT-MARKER SINTERING STUDIED.....	10
REFERENCES.....	13

ABSTRACT

A study is being made of the mechanism of sintering in pure oxides and metals. In order to ascertain whether the sintering rate of Cu_2O is controlled by the diffusion of copper ions, the effect of oxygen pressure upon the sintering rate was measured. The sintering rate increased with the oxygen pressure as predicted, but the results were not in quantitative agreement with the Wagner theory. Furthermore, the activation energies for sintering were less than one third those for the diffusion of Cu^+ in Cu_2O . Interpretation of the results was complicated by an exaggerated grain and void growth during sintering, which undoubtedly affected these rates.

Further studies of metal wire compacts with embedded inert markers support a diffusional mechanism of sintering, but the marked inhibition of shrinkage by the "inert" markers is not yet understood.

I. INTRODUCTION

It is usually agreed that material transport during sintering may involve the following mechanisms:

- 1) evaporation and condensation
- 2) surface diffusion
- 3) viscous flow
- 4) volume diffusion
- 5) plastic flow

On the basis of theoretical considerations, it would not seem possible for either evaporation and condensation or for surface diffusion to produce densification in a powder compact. Therefore, only volume diffusion and viscous or plastic flow are usually considered as the predominant or exclusive operative mechanisms where shrinkage is involved.

Earlier work at the Sylvania laboratories has established the importance of volume diffusion during sintering and of the role played by grain boundaries.⁽¹⁾ However, plastic flow cannot be excluded as a contributing mechanism to sintering, particularly in the case of oxides and non-metals.^(2,3,4,5)

The work described in this report, which is a continuation of the earlier Sylvania program on the fundamentals of sintering, has had as its object a further clarification of the mechanism of sintering in oxides as well as in metals. An attempt was made to relate the variation of the sintering rate of Cu_2O to the change in the diffusion coefficient of copper induced by changes in the external oxygen pressure. In metals, efforts to observe mass flow directly by examination of wire-wound compacts containing various inert markers were continued.

II. THE SINTERING OF CUPROUS OXIDE

Cuprous oxide was selected for an initial investigation of the sintering of oxides because it sinters at reasonable temperatures, its chemical properties are fairly well known, and its diffusion behavior has been studied previously. The predominant diffusing ion in Cu_2O is Cu^+ . For sintering to occur, it is necessary that both Cu and O be transported; therefore, sintering rates may not be controlled by Cu^+ diffusion solely, as are oxidation rates. Nevertheless, it was considered desirable to check the hypothesis that sintering is controlled by copper ion diffusion. In order to do this, an attempt was made to determine the effect of oxygen pressure on the sintering of Cu_2O .

According to the Wagner theory of oxidation⁽⁶⁾, the diffusion coefficient of copper in Cu_2O is related to the vacancy content and to the external oxygen pressure. Wagner proposes that the reaction between oxygen and copper takes place in the following manner:

where e represents free electrons and (e) and (Cu^+) electron holes and Cu^+ holes, respectively. The equilibrium constant for this reaction is:

$$K = \frac{[\text{h}(\text{e})]^4 [\text{h}(\text{Cu}^+)]^4}{P_{\text{O}_2}}$$

If it is assumed that the concentration of electron holes is equal to the concentration of cuprous ion vacancies, it follows that the concentration of Cu^+ vacancies is proportional to the 1/8th power of the external oxygen pressure.

At low vacancy concentrations, the diffusion coefficient is directly proportional to the vacancy concentration, and therefore the rate of diffusion of Cu should also be a function of the 1/8th power of the oxygen pressure. Although this relationship between the diffusion coefficient and oxygen pressure has not yet been established experimentally, it has been shown that the electrical conductivity and the parabolic rate constant for the oxidation of copper which, according to this picture, are similar functions of oxygen pressure, both increase linearly with the 1/7th power of the pressure,^{7,8}

From the usual equations proposed for a diffusional mechanism of sintering⁹, the sintering rate is directly proportional to the value of the diffusion coefficient; therefore, if sintering in cuprous oxide takes place by means of the migration of copper ions, then the rate of shrinkage should also be directly proportional to the 1/8th power of the external oxygen pressure. This hypothesis was tested by measuring the rate of shrinkage of pressed Cu₂O compacts sintered under various oxygen pressures.

Specimens were prepared from analytical grade Cu₂O by pressing the sized powders to a 1/4" square cross-section in a rectangular die at 10,000 psi. The specimens were placed in the optical dilatometer which was then evacuated to the desired pressure. Pressure was maintained by continuous pumping of either dried air or purified oxygen through a controlled leak. After reaching the desired pressure, the dilatometer was up-quenched in the pre-heated furnace, and initial readings were taken. The specimens were heated to within 10 degrees of the desired temperature in 4 minutes, and temperature equilibrium was attained in 15 minutes. Individual readings were reproducible within 0.00016".

Preliminary tests showed that oxygen pressures could be varied from about 0.04 mm to 2 mm without conversion to copper at the lower limits or to CuO at the upper. The presence of free copper was found to accelerate the rate of sintering greatly. No attempt was made to determine the decomposition limits exactly, as it was believed that

the theoretical 60% change in sintering rate resulting from this 50-fold change in pressure could be easily detected.

Fig. 1 shows the effect of pressure on the rate of shrinkage of -325 mesh powder at 1000°C and is typical of the data for other temperatures. To eliminate the varying effects of the initial heating period, these plots have been normalized to zero shrinkage at 10 minutes time. According to this data, the rate of shrinkage varies as the 1/14th power of the oxygen pressure instead of the 1/7th or 1/8th power predicted by the Wagner theory of oxidation. In general, the effect of oxygen pressure was found to be much less than would be expected if the diffusion coefficient of copper were the only affected variable.

The slopes of the shrinkage versus the logarithm of time plots yield an activation energy of 10,000 cal/mol. These data are illustrated in Fig. 2. No effect of oxygen pressure on activation energy could be detected. The activation energy for the self-diffusion of copper in Cu₂O has been reported by Moore and Selikson⁽¹⁰⁾ as 36,100 cal/mol. Therefore, the data are again not in accord with the idea that diffusion of Cu⁺ is the rate-controlling step.

It was clear from inspection of the microstructures that exaggerated grain growth accompanied sintering. Fig. 3 shows the progressively increasing grain size observed in compacts sintered at 1000°C and 2 mm oxygen pressure for 120, 360, 714 and 5,100 minutes. Moreover, the average pore size increased markedly with time. This unusual coarsening of the structure undoubtedly influenced the sintering rates.

Work on the effect of initial particle size has not been completed but a few preliminary runs seem to indicate that the rates are inversely proportional to the particle size squared, which bears out both the Kuczynski theory and Herring¹² prediction of the effect of particle size on rates of sintering by a diffusional mechanism.

Following the Kuczynski⁽⁹⁾ model of sintering, with the assumption of constant geometry, rates of shrinkage should be directly proportional to the self-diffusion coefficient and inversely proportional to the particle size squared.

$$\frac{dl}{dt} \sim \frac{D_0 \exp \frac{-\Delta H}{RT} t}{d_0^2}^{1/5}$$

In the present work, it is necessary to take into account the variation of the increasing grain size. Theory is not yet capable of explaining satisfactorily grain growth in either non-metals or in metals, but it is usually assumed that the equation for the rate of grain growth is of the form:¹¹

$$\frac{dd}{dt} = \frac{K' \sigma v}{d}$$

where d is the grain diameter, σ the surface tension, v the atomic volume and K' a temperature dependent constant of the form,

$$K' = K_0 \exp \frac{-Q_g}{RT}$$

Integration of this equation leads to an expression for grain size

$$d = \left[K_0 \sigma v t \exp \frac{-Q_g}{RT} \right]^{1/2}$$

If this is substituted in the Kuczynski equation for sintering, the activation energy for sintering becomes equal to $(\Delta H_d - Q_g)$; that is, the observed activation energy for sintering is the difference between the activation energy for diffusion and the activation energy for grain growth. This might explain the observed low value. However, the basic mechanism of sintering of Cu_2O is not yet clear.

III. INERT-MARKER SINTERING STUDIES

As part of the earlier studies at the Sylvania Laboratory

of mass flow during sintering, wire-wound compacts containing fine graphite particles near the outer layers were used by Balluffi¹³; however, results were ambiguous. Sintering was found to be greatly inhibited by the fine particles and the particles themselves gradually disappeared during sintering. To determine whether these results were due to the chemical effects of the carbon particles or to mechanical effects, these experiments were repeated, using other supposedly inert markers; fine WO_3 powder and various sizes of fine tungsten powder.

A mixture of copper and the inert markers was electroplated onto the surface of the copper wires from an agitated copper sulfate bath containing the powders. A layer of pure copper was then electroplated onto that surface. The wires were then drawn through dies to smooth their surfaces and finally annealed for several hours in a vacuum at $1000^{\circ}C$ before being wound into compacts.

The compacts containing the tungsten and tungsten oxide markers behaved similarly to the graphite-marked specimens of Balluffi. Sintering was markedly slowed down and in some cases, completely inhibited. However, the behavior of the markers themselves was somewhat different. Instead of disappearing completely, a few of the markers (or the pores surrounding them) spheroidized and grew at the expense of the others. Fig. 4 and 5 show the sintered necks between wires held at $1000^{\circ}C$ for 90, 270 and 420 minutes. It will be noted that the cross-section of the wires, as delineated by the markers, remains essentially circular and that there is no evidence of distortion such as might be expected if plastic flow were taking place. However, the sintering rate has decreased by various degrees. The width of the necks between the wires in these compacts is only about one third that in similar but unmarked samples. Fig. 6 shows compacts in which sintering has been completely inhibited, even though the wires are obviously in intimate contact.

The cause of this behavior is still obscure. From the similarity of behavior of compacts containing different

types of markers, it may be concluded that effects are not due to the chemical nature of the markers, but rather to their physical effects. The presence of fine discontinuities near the sintered interfaces might be expected both to alter the stress pattern and also to act as preferential sinks for vacancies migrating from the neck between the wires. In view of the equal effect of both large and small particles, the latter effect is probably predominant.

REFERENCES

1. B. H. Alexander, R. W. Balluffi, M. H. Dawson, C. A. Dube, H. P. Kling and F. D. Rosi, "Self-Diffusion of Metals and Associated Phenomena", Interim Technical Report, April 1, 1950 to Oct. 1, 1950, SEP-43.
2. P.W. Clark and J. White, Trans. Brit. Cer. Soc. 49, (1950) p. 305.
3. P. W. Clark, J. H. Cannon and J. White, Trans. Brit. Cer. Soc. 52, (1953) p. 1.
4. C. B. Allison and P. Murray, Acta Met. 2, (1954) p. 487.
5. L. Navias, J. Am. Cer. Soc. 39, (1956) p. 141.
6. C. Wagner, Z. phys. Chem. B 22, (1933) p. 181.
7. H. Dunwald and C. Wagner, Z. phys. Chem. B 22, (1933) p. 212.
8. C. Wagner and K. Grunewald, Z. phys. Chem. B 40, (1938) p. 455.
9. G. C. Kuczynski, J. Metals 187, (1949) p. 169.
10. W. J. Moore and B. Selikson, J. Chem. Phys. 19, (1951) p. 1539. See also W. J. Moore, ibid, 20 (1952) 927.
11. J. E. Burke and D. Turnbull, "Recrystallization and Grain Growth," Progress in Metal Physics vol. III, 1952, Interscience Publishers Inc., New York.
12. C. Herring, J. App. Phys. 21, (1950) p. 301.
13. R. W. Balluffi, F. D. Rosi and L. L. Seigle, Progress Report April 1, 1953 to October 1, 1953, SEP-152.

Fig. 1 - Shrinkage of -325 mesh powder at 1000°C.

Fig. 2 - Variation of shrinkage rate with temperature.

a) 120 minutes Plate No. 14405

b) 360 minutes Plate No. 14387

c) 714 minutes Plate No. 14408

d) 5,100 minutes Plate No. 5003

Fig. 3 - Cu_2O compacts sintered at 1000°C at 2 mm oxygen pressure.
Grain size and pore size have both increased. 250 X

a) 90 minutes Plate No. 14502

b) 90 minutes Plate No. 14501

Fig. 4 - Copper wire compacts sintered at 1000°C for 90 minutes.
Circular cross-section of wires remains undistorted. 500 X

a) 270 minutes Plate No. 14449

b) 420 minutes Plate No. 14448

Fig. 5 - Copper wire compacts sintered at 1000°C for 270 and 420 minutes. Note spheroidization of porosity. 500 X

a) 90 minutes Plate No. 14523

b) 270 minutes Plate No. 14527

c) 420 minutes Plate No. 1452b

Fig. 6 - Copper wire compacts held at 1000°C showing complete inhibition of sintering. 500X

CHIEF ENGINEER

B. HOPELMAN
N. ZAFFI, SECY.