AFOSR TN 59-481
ASTIA AD 215 734

THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING
Department of Chemical and Metallurgical Engineering

SINTERING OF VANADIUM PENTOXIDE

G. Parravano V. J. Lee

UMRI Project 2832

under contract with:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
AIR RESEARCH AND DEVELOPMENT COMMAND
CONTRACT NO. AF 49(638)-493
PROJECT NO. 9762, TASK NO. 37621
WASHINGTON, D. C.

administered by:

THE UNIVERSITY OF MICHIGAN RESEARCH INSTITUTE ANN ARBOR

June 1959

ABSTRACT

The sintering of vanadium pentoxide microspheres has been studied in the temperature range of from 560 to 650°C in air and with spheres of diameters varying from 0.2 to 0.9 mm.

Rate data have been interpreted in terms of a sintering mechanism involving migration of vacancies along the surface and grain boundaries of the spheres. The role of whisker growth on sintering is discussed. The overall sintering process is shown to be the result of several steps; the initial stage of the kinetic sequence is the growth of oxide whiskers.

INTRODUCTION

The role played by chemical processes on the sintering of zinc oxide has recently been investigated.[1] These studies have shown that zinc oxide, whose initial composition differs from the composition corresponding to the thermodynamic redox conditions prevailing during sintering, undergoes sintering at relatively low temperatures. In this instance, the driving force for the process is supplied by the oxidation reaction of the stoichiometric excess of zinc. Conversely, oxide samples, which are "equilibrated" with the surrounding atmosphere prior to sintering, cannot be welded together even at high temperatures, and the oxide disintegrates without sintering appreciably.

To compare this sintering process (chemical sintering) with a sintering operation not controlled by a chemical process (physical sintering), efforts have been made to find a metal oxide which would undergo sintering under conditions of compositional equilibrium with the surrounding atmosphere. Preliminary runs have shown that vanadium pentoxide fulfilled this requirement. We have, therefore, investigated in some detail the kinetics of the welding together of vanadium pentoxide microspheres at temperatures below their melting point.

The results of these studies are reported here, as is information on the effect on sintering of sphere size and temperature.

EXPERIMENTAL

Vanadium pentoxide microspheres were produced by directing a blast of purified air against a falling mass of molten vanadium pentoxide (C.P. grade).[2] The resulting spheres, sized by means of a series of standard sieves, were subjected to an air annealing treatment to relieve stresses and amorphous regions. A string of spheres of similar size was placed in a platinum boat and heated at constant temperature in a well type of furnace under a slow stream of air. An indication of the extent of sintering was obtained by measuring the width of the neck formed between the spheres as a function of time. These measurements were carried out by means of a creep test microscope, directly placed above the platinum boat. Each value reported for the neck width represents the average of five to six contacts growing under similar conditions. No appreciable bonding was formed between sintering microspheres and the platinum container, which was slightly tilted horizontally to assure the initial contact between microspheres.

The results thus obtained were quite reproducible. Sintering characteristics of nonannealed spheres, however, were erratic and poorly reproducible.

RESULTS

Typical sintering data are summarized in Fig. 1, where the logarithm of the half-width of the neck connecting the spheres is plotted against the logarithm of time, for different temperatures and constant radius (0.73 mm). All runs were performed in air except for one run conducted in one atmosphere of steam. The average inverse slope, computed from the straight lines drawn through the experimental point of Fig. 1, is ~ 4. Data obtained at constant temperature on microspheres with different diameters, 2r (0.2 to 0.9 mm), have been used to investigate the effect of the size of the spheres on the rate of sintering. These experiments showed that the relationship between x, r, and time t, is of the type $x^4/r^2 \alpha t$. The effect of temperature on the rate of sintering has been obtained by noting the time required to obtain a constant value of x at different temperatures. From these data, a value of 32 ± 5 kcal/mole was calculated for the activation energy of the sintering process.

DISCUSSION

Since the composition of the surrounding atmosphere in the course of the reported sintering experiments was similar to composition of the atmosphere prevailing during the preparation of the vanadium pentoxide microspheres, it can be assumed that the chemical composition of the oxide did not vary significantly in the course of sintering. In the present case, therefore, no major contribution to sintering from a chemical process can be expected. Sintering becomes a physical process, whose driving force is provided by the decrease in surface free energy of the system. Supporting evidence for this conclusion can be obtained from the fact that the relationship between x and time was found to be constant throughout the whole range of sintering investigated. This situation does not prevail when a chemical reaction controls the sintering operation.[1] The reported relationship, $(x^4/r^2)\alpha$ time, can then be taken as an indication that sintering of vanadium pentoxide is controlled by a diffusional process, involving migration of vacancies along the surface and grain boundaries, which act as vacancy sink.[3] In view of the polycrystalline nature of the vanadium pentoxide used, grain-boundary processes are likely to be kinetically pronounced. A difference in concentration of vacancies between the surface of the spheres (neck) and the bulk can result from several factors: frozen equilibria during preparation, shape, and stresses. The relatively low value of the activation energy supports the view of diffusion along grain boundaries. The presence of water vapor in the surrounding atmosphere during

sintering did not noticeably alter the rate of the process (Fig. 1). This implies that no large composition changes were produced by the presence of water vapor, possibly due to a large ($\lesssim 54$ kcal/mole) positive free-energy change for the reaction:

$$H_2O + V_2O_5 \rightarrow O_{\text{adsorbed on } V_2O_5} + H_2 \quad .$$

In the course of this work, growth of whiskers on the microsphere surface was observed.[4] To study the role played by whisker on sintering, several runs were performed by placing the vanadium pentoxide microspheres at some distance apart (~ 0.1 mm) in the platinum vessel and observing whisker growth in the space between the spheres at constant temperature. As soon as whiskers, growing at constant cross section, contacted the adjacent sphere, a rapid radial growth of the whisker ensued. Observations of this effect, recorded at 649°C, are schematically represented in Fig. 2.

Morphological changes on the initial whisker were clearly discernible after contact was established. In particular, crystallization around the neck area was quite apparent, since the neck became surrounded by rod-like crystals after 150 min (Fig. 2). Possibly, they were oriented with their main direction parallel to the c-axis, since this is the direction of most rapid crystal growth in V_2O_5.

Kinetically, different growth equations were found to apply to the steps shown in Fig. 2. Therefore we may conclude that sintering of vanadium pentoxide involves several stages, which can be quantitatively characterized by the following relationships in chronological sequence:[4]

1. Whisker growth at constant cross section up to time t_c, when contact with an adjacent microsphere is attained: $x = x_o$;
2. Radial growth of whisker connecting two adjacent spheres: $x = x_o \exp k_1(t-t_c)$, k = constant;
3. Radial linear growth: $x \cong \text{const} + k_2(t-t_c)$;
4. Growth of width of connecting bridge: $x = \text{const} + k_3(t-t_c)^{1/n}$, where $n \sim 4$.

It is worth pointing out that, since whiskers grow generally by a dislocation process at the expense of the local vacancy concentration, it is plausible that a whisker-bridge mechanism of sintering should be controlled by grain-boundary vacancy diffusion.

CONCLUSION

The mechanism of sintering of vanadium pentoxide, deduced from the reported experiments, is the result of a physical process (physical sintering). This is in contrast with sintering controlled by a chemical reaction (chemical sintering).[1] Therefore two general mechanisms for sintering seem to be available, depending on the chemical nature of the sintering materials and experimental conditions. Furthermore, it has been shown that in the case of vanadium pentoxide several stages are followed by the sintering process, whisker growth providing the initial phase of the process. It is possible that a similar, stepwise mechanism is also followed by other metal oxides.

REFERENCES

1. Lee, V. J., and Parravano, G., AFOSR Report No. 58-811.

2. Rollman, W. F., U. S. Patent 2,489,347.

3. Coble, R. L., Journ. Amer. Ceram. Soc., 41, 55 (1958).

4. Lee, V. J., and Parravano, G., AFOSR Report No. TN 59-184.

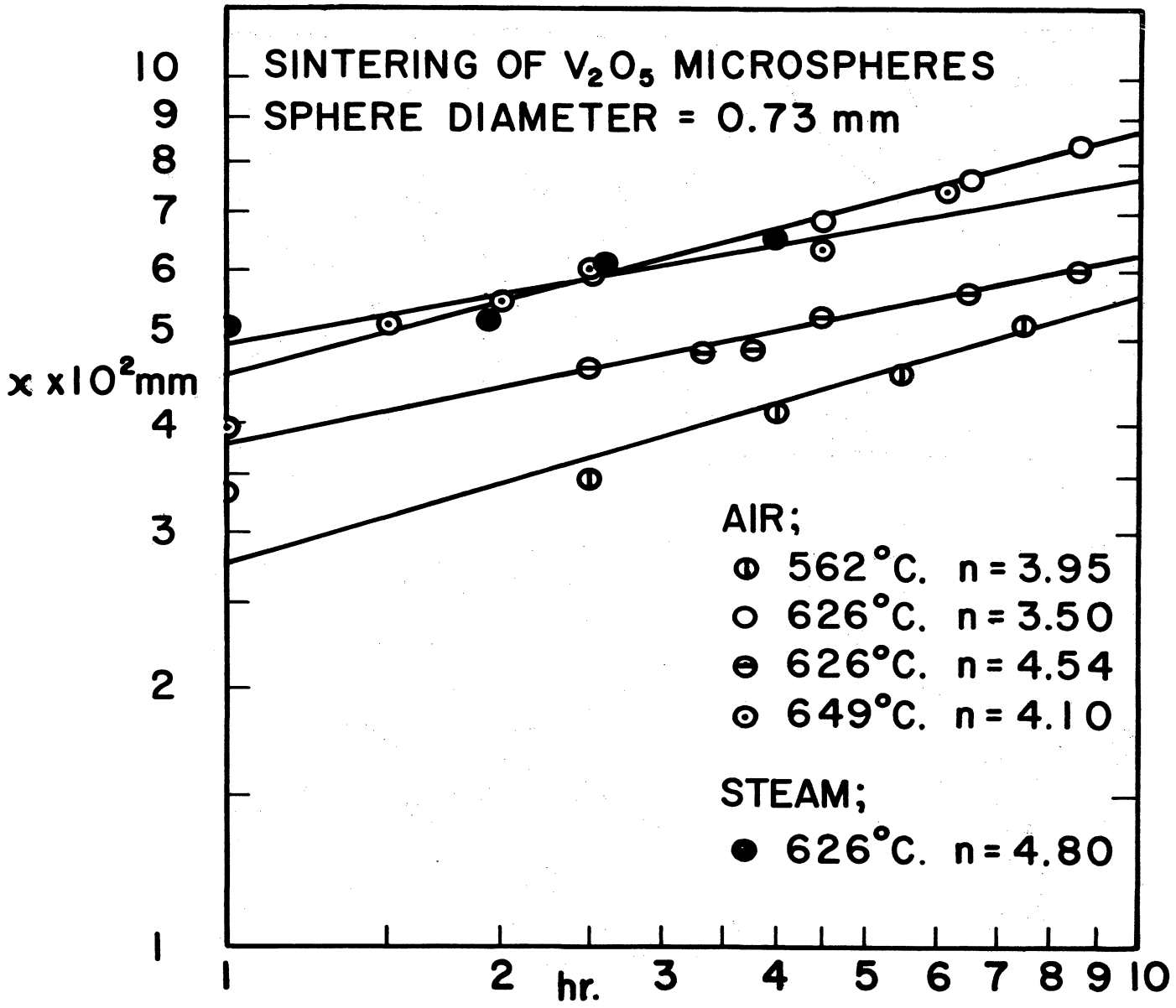

Fig. 1. Sintering of V_2O_5 microspheres; relationship between width of bridge connecting spheres, x, and time of sintering.

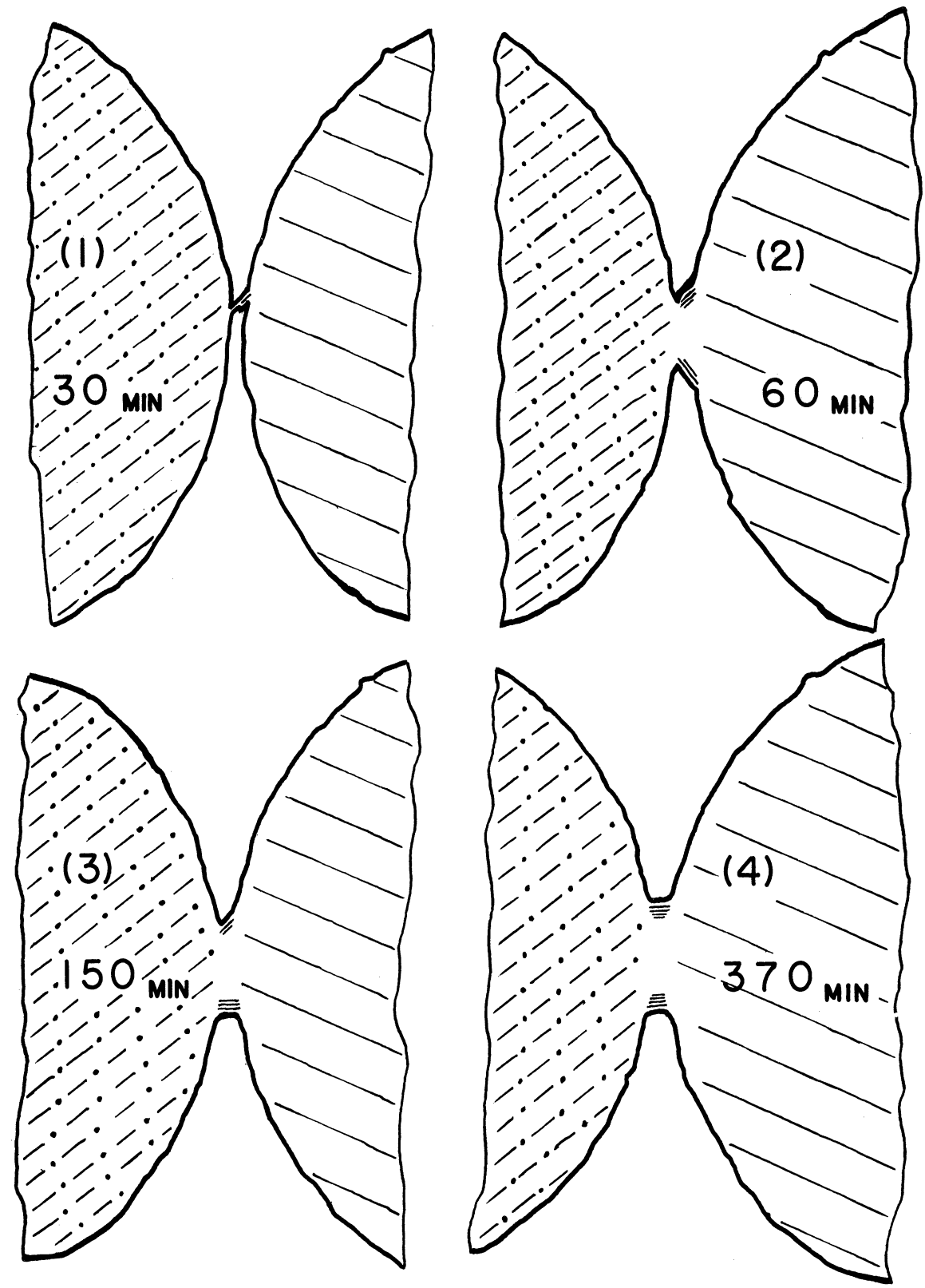

Fig. 2. Schematic representation of observed stages of neck growth in V_2O_5.

DISTRIBUTION LIST

Agency	No. of Copies
Commander, Headquarters AF Office of Scientific Research Washington 25, D. C. Attn: SRQB	5
Commander Wright Air Development Center Wright-Patterson AF Base, Ohio Attn: WCRRH Attn: WCRRL Attn: WCRTL Attn: WCRTM-1	4
Commander AF Cambridge Research Center L. G. Hanscom Field Bedford, Massachusetts Attn: Technical Library Attn: CRRF	2
Commander Rome Air Development Center Griffiss Air Force Base Rome, New York Attn: Technical Library	1
Director Office for Advanced Studies AF Office of Scientific Research P. O. Box 2035 Pasadena 2, California	1
Superintendent Diplomatic Pouch Rooms Department of State Washington 25, D. C. For Transmittal to: Commander European Office, ARDC c/o American Embassy Brussels, Belgium	1
Commander Armed Services Technical Information Agency Arlington Hall Station Arlington 12, Virginia Attn: TIPDR	10
Director Research and Development Hq., U. S. Air Force Washington 25, D. C. Attn: AFDRD-RE-3	1
Department of the Navy Office of Naval Research Washington 25, D. C. Attn: Code 423 Attn: Code 421	2
Officer in Charge Office of Naval Research FPO No. 100 New York, New York	1
Commanding Officer Naval Radiological Defense Lab. San Francisco Naval Shipyard San Francisco 24, California	1
Director Research and Development Division General Staff Department of the Army Washington 25, D. C.	1
Division of Research U. S. Atomic Energy Commission Division Office Washington 25, D. C.	1
Oak Ridge National Laboratory P. O. Box P Oak Ridge, Tennessee Attn: Central Files	1

DISTRIBUTION LIST (Concluded)

Agency	No. of Copies
U. S. Atomic Energy Commission Library Branch Technical Information Division ORE, P. O. Box E Oak Ridge, Tennessee	1
Brookhaven National Laboratory Upton, Long Island, New York Attn: Research Library	1
Argonne National Laboratory P. O. Box 299 Lemont, Illinois Attn: Librarian	1
Ames Laboratory Iowa State College P. O. Box 14A, Station A Ames, Iowa	1
Knolls Atomic Power Laboratory P. O. Box 1072 Schenectady, New York Attn: Document Librarian	1
National Bureau of Standards Room 203, Northwest Building Washington 25, D. C. Attn: Library	1
National Science Foundation 1901 Constitution Avenue, N.W. Washington 25, D. C.	1
Director Office of Ordnance Research Box CM, Duke Station Durham, North Carolina	1
Commander Western Development Division P. O. Box 262 Inglewood, California Attn: WDSIT	1
Office of Technical Services Department of Commerce Washington 25, D. C.	1
Document Custodian Los Alamos Scientific Laboratory P. O. Box 1663 Los Alamos, New Mexico	1
Arnold Engineering Development Center P. O. Box 162 Tullahoma, Tennessee Attn: Technical Library	1
Commanding Officer Ordnance Materials Research Office Watertown Arsenal Watertown 72, Massachusetts	1
Commanding Officer Watertown Arsenal Watertown 72, Massachusetts Attn: Tech. Reports Section, WAL	1
NACA 1512 H Street, N.W. Washington 25, D. C.	1
Commander Air Technical Intelligence Center Wright-Patterson Air Force Base, Ohio Attn: Deputy for Documentation	1
Commander, Headquarters AF Office of Scientific Research Washington 25, D. C. Attn: Technical Library, SREC	2
Commandant AF Institute of Technology Wright-Patterson Air Force Base, Ohio Attn: Technical Library, MCLI	1
Commander Wright Air Development Center Wright-Patterson Air Force Base, Ohio Attn: Mr. R. Besamson, WCLTY-3	1