研究

Macrokinetics of the Sintering of α -Nb₂O₅

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The authors have studied the sintering kinetics of α -Nb₂O₅ by means of a comparative analysis under isothermal and non-isothermal conditions. It was demonstrated that there exists non-linear dependence between the effective diffusion coefficients and the reciprocal temperature value.

The change in the relative linear shrinkage rate

$$\frac{\partial \left(\frac{4L}{L_0} \right)_T}{\partial \sqrt{\tau}}$$

follows the law of distribution, very close to the normal distribution, the maximum of which is the result of the change in the material structure state due to the change in the disperse system "activity". As the point defect concentration is the function of the oxygen partial pressure and temperature, characterized by both the ever-decreasing and increasing functions, it has been demonstrated that the abrupt increase of the relative linear shrinkage rate is the result of the existence of some other structure defects.

The qualitative analysis of the sintering process carried out from aspect of the subatom electronic configuration theory indicates that the high temperature of the sintering of α -Nb₂O₅ is the result of the great statistic weight of the atoms with stable configuration of niobium.

(Received September 11, 1972)

Introduction

In the greatest number of papers on the physics of sintering particular attention has been given both to the considerations on models and to the idealized considerations based on the assumption that a definite mass transfer mechanism is in action. However, those considerations, regardless of their definite advantages, do not make it possible for us to estimate the significance of the basic processes occurring during the sintering of real disperse systems, the densification of which is the result of the simultaneous action of a series of the atomic mechanisms, which are difficult to be identified under real conditions. A specific case, to which considerable attention has been given, is the sintering of the compounds of variable composition. The intensification of the mass transfer process during the sintering of non-stoichiometric compounds, in relation to the stoichiometric disperse systems, is the result either of the trend to the decrease of the non-stoichiometric ratio or the increase of the diffusion components mobility or the increase of the activity of those compounds, e.g. in the homogeneity area, where the activity increases with the decreasing content of one component i.e. with the increasing degree of defection in the corresponding sub-lattice¹⁾.

The nature of the non-stoichiometry α -Nb₂O₅ has been the subject of numerous studies²⁻¹¹⁾.

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It was established, by measuring the electric conductivity^{2,3,5,8)}, that the conductivity increased with the decrease of the partial oxygen pressure at a constant temperature, indicating that Nb_2O_5 becomes an n -type semiconductor possessing oxygen vacancies or niobium interstitials. The experimental results³⁻⁹⁾, were interpreted on the basis of the existence of single and double ionized oxygen vacancies.

Greener et al.^{3,8)} and Kofstad⁵⁾ have shown that the isothermal conductivity of sintered samples is proportional to $p\text{O}_2^{-1/4}$ within the oxygen pressure of 10^{-3} —1 atm and the temperature ranges of 700–1350°C. On the other hand, Kofstad and Anderson⁴⁾ have demonstrated, on the basis of thermogravimetric examinations, that the weight change was proportional to $p\text{O}_2^{-1/6}$ at a constant temperature in the range on the oxygen partial pressure of 10^{-7} — 10^{-18} atm and in the temperature range of 900–1400°C. Based on the oxygen vacancy model, the results obtained by Greener and Kofstad were interpreted as an indication that the single ionized oxygen vacancies were the predominant defects in non-stoichiometric α - Nb_2O_5 in the examined oxygen partial pressure and temperature ranges, while the results given in Kofstad and Anderson's paper⁴⁾ indicated the existence of double ionized oxygen vacancies as being the predominant defects of α - Nb_2O_5 in the examined interval of variables.

Chen and Swalin¹¹⁾ also studied the electrical conductivity of Nb_2O_5 in the oxygen partial pressure range of 10^{-6} —1 atm and in the temperature range of 600–1350°C. They concluded that the single ionized oxygen vacancies were the predominant defects in the α -range, since the electric conductivity was directly proportional to $p\text{O}_2^{-1/4 \pm 0.3}$. However, in the low-temperature range, the value of the exponent was not constant and in some cases it amounted to 1/12. Out of the electrical conductivity temperature dependance, two apparent activation energies were determined, the high-temperature activation energy of 1,4 eV, corresponding to a half of the oxygen vacancy formation enthalpy, and the low-temperature activation energy of 0,4 eV connected with the surface reactions. It was found that the activation energy of the oxygen vacancies mobility was 1,2 eV. Since the oxygen vacancy formation enthalpy was 2,8 eV, the activation energy of the oxygen ion self-diffusion in α - Nb_2O_5 must evidently be $2,6 \text{ eV} \left(\frac{2,8}{2} + 1,2 \right)$.

Our study includes the analysis of the sintering kinetics for Nb_2O_5 . Our wish was, above all, to direct attention to the correlation between the role of the point defects, caused by the non-stoichiometry and the other structure defects, existing in one powder disperse system, but which affect the mass transfer during the sintering. With the purpose to generalize the considerations, the analysis of the sintering process, from the aspects of the subatomic theory of the electronic configuration, was carried out¹²⁾.

Experimental work

The Nb_2O_5 powder used for the experiments, was supplied by Fluka AG Buchs SG; it was of high purity with the content of Nb_2O_5 over 99,9%. As Nb_2O_5 is characterized by a great number of modifications, the starting powder was annealed at 1000°C, for 10 hours in the oxygen current in order to be converted into the stable α -form. In order to increase the powder activity, the grinding was done in the ball mill, lasting 48 hours. The mean agglomerate size, determined by the sedimentation method, was $\sim 10.0 \mu\text{m}$. The mean particle size, determined by the electronic-microscopic method, amounted up to $1,5 \mu\text{m}$, but the powder specific surface $1,54 \text{ m}^2/\text{g}$,

established by AREAMETR. The samples used for the study of the sintering kinetics were pressed under 1 t/cm^2 ; their porosity was $\sim 50.0\%$.

The analysis of the sintering process proceeding under the isothermal conditions was carried out in the temperature range $1100\text{--}1450^\circ\text{C}$, and in intervals of $15\text{--}240$ minutes. The sintering was carried out in the oxygen flowing current with the partial oxygen pressure of $\sim 10^{-2}$ atm. The compacts were directly pushed into the hot furnace and at the fixed time taken out. The density dependence on the isothermal sintering temperature and time is shown in Fig. 1, where the abrupt transition into the range of $\sim 1250^\circ\text{C}$ can be seen.

The sintering kinetics under non-isothermal conditions was examined by the dilatometric method on the "GEBRUDER NETSCH" Type 402 E, with an automatic recording of the changes of the sample sizes, temperature and time. The examinations started from 1100°C , i.e. from the temperature at which the shrinkage began first. The experiments were carried out in the stationary oxygen atmosphere with the gas partial pressure of 5.10^{-1} atm. The heating rate was

Fig. 1 Density dependence of the sintered samples of the isothermal sintering temperature and time.

Fig. 2 Relative linear shrinkage dependence on the isothermal heating temperature and time under the step-wise heating conditions.

100°/min. The temperature steps in all the tests were approximately of the equal value of $\sim 50^\circ$, while the isothermal heating time was 10, 25 and 60 minutes. The characteristic diagram of the relative linear shrinkage dependence on the isothermal heating temperature and time under the conditions of a step-wise heating technique is shown in Fig. 2.

Discussion

Bearing in mind the specificity of the sintering of real disperse systems, at which the considerations reached on models cannot be applied, we used V. Gropjanov's considerations for the analysis of the sintering kinetics for $\alpha\text{-Nb}_2\text{O}_5$, as they were given for real systems.

V. Gropjanov¹³⁾ has looked upon the sintering process as a kinetics process characterized by the second order equation, because in each elementary act there take part the atoms of the two contacting surfaces which tend, as a result of their interaction, to the diminishing of the volume of the sintered material. The free energy of such an interaction is equal to the energy that is released due to the disappearance of the surface during the atom transition process. According to V. Gropjanov, the kinetics of the sintering process may be adequately described by the equation:

$$L = L_\infty \frac{Ct}{1 + Ct} \quad (1)$$

or because of the easier mathematical procedure

$$\frac{1}{L} = \frac{1}{L_\infty} + \frac{1}{L_\infty Ct} \quad (2)$$

where

L —degree of densification

L_∞ —boundary densification degree for $t \rightarrow \infty$

C —the sintering rate constant

The physical sense of the sintering rate constant C is given in the following relation

$$C = \frac{\sigma \Omega (S \cdot d_T)^3 D}{K_B T} \quad (3)$$

where

σ —specific surface energy on the boundary of the solid body with vacuum or with its own vapour (erg/cm²)

$\Omega = \frac{M}{A d_T}$ —molecule volume

M —molecule weight

d_T —material theoretical density (g/cm³)

A —the Avogadro number

D —diffusion coefficient

$(S \cdot d_T)^3 = N$ —particles concentration (cm⁻³)

K_B —the Boltzmann constant

T —absolute temperature

In that way it is possible to determine the effective diffusion coefficient which conditions the mass transport during the sintering process, and which has some definite importance, regardless to the fact that it is not sensitive to time. The L^{-1} dependence on t^{-1} for the temperature range ex-

amined is shown in Fig. 3. The values of the sintering rate constant C were determined by the least-square method, but on the basis of those values and the corresponding data

$$d_T = 4,564 \text{ g/cm}^3$$

$$A = 6,023 \cdot 10^{23}$$

$$S = 1,54 \text{ m}^2/\text{g}$$

$$N = 7,028 \cdot 10^{10}$$

$$M = 255,81$$

$$K_B = 1,38 \cdot 10^{-16}$$

$$\Omega = 9,661 \cdot 10^{-23}$$

$$\sigma = 10^3 \text{ erg/cm}^2$$

The values of the effective diffusion coefficient D were also determined, shown in Fig. 4, in the temperature function and there can be observed the non-linear dependence of the effective diffusion

Fig. 3 Dependence of $1/L$ on $1/t$

Fig. 4 Diffusion effective coefficient dependence on temperature

coefficient on the reciprocal temperature value.

The examination of the kinetics of the sintering process under isothermal conditions do not correspond to the strictly isothermal conditions, as the shrinkage occurs in the period needed to reach the examination temperature, but which is not identical for all the temperatures; further, because the disperse system undergoes considerable changes in that period. That is the reason why one takes to the study of the sintering kinetics under non-isothermal conditions, either by means of the step-wise heating technique or by the constant heating rates¹⁴⁾.

The phenomenology analysis of the sintering process under the step-wise heating conditions shows that the sintering kinetics can be described with the empirical relation in the form:

$$\frac{\Delta L}{L_0} = m + n\sqrt{\tau} \quad (4)$$

where

$\Delta L/L_0$ —relative linear shrinkage

m —the process constant, corresponding to the relative linear shrinkage for $\tau=0$

n —isothermal shrinkage rate

τ —time of the isothermal sintering at one temperature

The values m and n are the functions of temperature and time of the isothermal heating, and the value m increases with the temperature, while the parameter n dependence on temperature takes the form of the distribution function with the maximum dependant on the investigation conditions, and which indicates the temperature range where the greatest qualitative changes of the system state occur.

The characteristic experimental result is shown in Fig. 5 in the form of relation (4). From such experimental results we determined the value of the parameter n in the function of temperature and time of the isothermal heating by means of the least-square method (Fig. 6). As we knew that

Fig. 5 Relative linear shrinkage dependence on the sintering temperature and time

Fig. 6 Change in the relative linear shrinkage rate due to the sintering temperature and time

Fig. 7 Change in the relative linear shrinkage due to temperature and initial porosity ($\tau=25$ min).

the parameter n represents the shrinkage rate on one isotherm

$$\frac{\partial \left(\frac{\Delta L}{L_0} \right)_T}{\partial \sqrt{\tau}}$$

we can say that the maximum on the distribution curve $n=f(T, \tau)$ may be either the result of the changed material structure state connected with the annihilation of the greatest part of defects, or the result of the changed porosity. That the maximum on the curve $n=f(T, \tau)$ is exclusively the result of the change in the material structure state is shown in Fig. 7, where identical temperature interval, within which the maximum change in the shrinkage rate took place, was recorded in samples pressed under 1 t/cm² and 3 t/cm², under the identical experimental conditions.

The constant m , according to the considerations of B. Ja. Pines and Ja. E. Geguzin¹⁵⁾, represents the sintering constant which can be given in the form

$$m = B \exp \left(-\frac{E}{RT} \right) \quad (5)$$

where

B —the preexponential multiplier

E —activation energy

R —universal gas constant

The constant m dependence on $1/T$ is shown in Fig. 8, and it can be noticed that it is completely analogous with Fig. 4. Further, the existence of the three parts of the curve, that may be

studied individually, can also be seen, exactly as in Fig. 4. The part *A* which corresponds to the range where a very slow increase in the shrinkage rate takes place, the range *B* where the shrinkage rate is exceptionally great due to the annihilation of most of defects that exist in the material, and the range *C* where the shrinkage rate decreases due to the disappearance of the greatest quantity of defects in the range *B*. In that way due to the existence of the temperature intervals within which the annihilation of various quantities, and perhaps even of various kinds of defects occurs, the indicated intervals are characterized by different values of the effective activation energy, as it is shown in Fig. 8, which is in accordance with some of our earlier considerations¹⁶⁾.

In the similar way, starting from the densification kinetics general equation that defines the shrinkage rate¹⁷⁾:

$$\frac{1}{V_0} \cdot \frac{dV}{dt} = -\lambda D_{eff} \quad (6)$$

where

$dV = V_0 \dots V_s \dots$ volume changes

λ —the constant of the material sintered

D_{eff} —The effective diffusion coefficient, defined by the relation $D_{eff} = D_{kv} + \Delta D e^{-qt}$

D_{kv} —the quasi-equilibrium diffusion coefficient

ΔD —constant

q —defect annihilation rate

it is easy to show that the ratio of the effective diffusion coefficient, that characterizes every successive and every previous isotherm, D_{i+1}/D_i is proportional to the shrinkage rates under the step-wise heating conditions¹⁴⁾

$$\frac{D_{i+1}}{D_i} = \frac{\dot{V}_{i+1}}{\dot{V}_i} \quad (7)$$

where

$\dot{V}_i$ —the shrinkage rate after certain isothermal heating at the temperature T_i

$\dot{V}_{i+1}$ —the shrinkage rate after the transition from T_i to T_{i+1}

Our results are given in Fig. 9. On the other hand, as in the literature available there are no data on the self-diffusion of the both elementary kinds in α -Nb₂O₅, we have assumed that the activation

Fig. 8 The process constant dependence *m* on temperature

Fig. 9 Ration dependence of the diffusion effective coefficients D_{i+1}/D_i under the step wise heating conditions on the sintering temperature:

energy does not surpass 4 eV, which corresponds to the activation energy of the Nb self-diffusion¹⁸⁾, basing our assumption on the activation energy dependence on the statistic weight of atoms with the stable configuration¹²⁾. Anyway, even without giving any quantitative significance to the data obtained (Fig. 9, curve 1), it is evident that the theoretical dependence of $\frac{D_{i+1}}{D_i} = f(T)$ must submit itself to the analogous laws.

With the purpose to estimate the defect structure role in the sintering process, we have studied the following ideal case. Let's assume that in the material there are only point defects, the concentration of which is the function of the oxygen partial pressure and temperature:

$$C_1 = f(p\text{O}_2, T) \quad (8)$$

As we already know that $\alpha\text{-Nb}_2\text{O}_5$ is a non-stoichiometric compound deficient in oxygen, which is the result of the existence of a definite oxygen vacancy concentration, the sintering in oxygen atmosphere causes the vacancy concentration to decrease because the oxygen is setting into the $\text{Nb}_2\text{O}_{5-x}$ lattice²⁻¹¹⁾. On the other hand, with the increasing temperature the vacancy concentration increases according to the Boltzmann factor

$$C_2 \sim \exp\left(-\frac{E}{K_B T}\right) \quad (9)$$

However, it is quite certain that the change in the point defect concentration in the function of the oxygen partial pressure and temperature is described in each case both by the ever decreasing and increasing functions, so that the abrupt increase in the relative linear shrinkage rate values as well as in the effective diffusion coefficient ratio (Fig. 9) cannot be explained in that way. In another words, the equation (8) is not complete, so it must be written in the form

$$C' = (p\text{O}_2, T, D_T) \quad (10)$$

Here D_T is the total quantity of the non-equilibrium structure defects existing in a polydisperse system, and which are mostly responsible for the abrupt increase of the shrinkage rate, i.e. the increase of the effective diffusion coefficient.

If we bear in mind the character of the $\alpha\text{-Nb}_2\text{O}_5$ sintering process (little shrinkage up to very high temperatures), then high temperature defects are here certainly in question, as the temperature of the intensive proceeding of sintering is $\sim 0.8 T_m$. According to some general considerations related to the field of the physics of the solid state, they are, first of all, dislocations

and other macroscopic defects of the structure element interboundary type, although their origin and character have not been defined unequivocally up to now.

In order to general study the problems of the sintering kinetics of α -Nb₂O₅, it is absolutely necessary to examine its electronic structure¹²⁾. Even more so, because there are considerable disagreements regarding the explanation of the atomic mass transfer mechanism occurring during the sintering process, but a great number of papers, that pretend to the generalization, studies only some part of this very complicated process¹⁹⁾.

Starting from the basic postulates put forward in the sintering electronic theory, the fact is that in some oxides, owing to the presence of a great part of the atom metals and oxygen with stable electronic configurations (high SWASC), dissociation of these configurations is possible only at high temperatures, close to the melting point. Knowing that Nb has a high degree of the localization of d^5 electrons (76%), it is logical to expect that the dissociation of these configurations will proceed only at high temperatures, which is clearly expressed in our case, as the temperature of the intensive proceeding of the sintering is $\sim 0.8 T_m$. At the same time, the activation of the sintering process by means of the sintering in the atmosphere where certain super-equilibrium of the vacancy concentration is maintained (Fig. 10) is the result of the intensive dissociation of the stable electronic configurations, which leads to the decrease of the statistic weight of the stable configuration atoms (SWASC), i.e. to the intensification of the sintering process. Namely, besides the existence of d^5 configuration of Nb atoms, there exists also s^2p^4 configuration of oxygen atoms. With the increasing α -Nb₂O₅ structure defection, due to the existence of oxygen vacancies, the activation energy decreases due to the ever looser bonds between Nb-O and Nb-Nb, and that's why the mass transport occurring during the sintering process is getting intensified.

Conclusion

The sintering kinetics of α -Nb₂O₅ was studied by means of a comparative analysis carried out under both isothermal and non-isothermal conditions. On the basis of our considerations it may be concluded:

Fig. 10 Relative linear shrinkage dependence on the sintering temperature and oxygen partial pressure ($dT/dt=5^\circ\text{C}/\text{min}$).

The effective diffusion coefficients, obtained on the basis of Gropjanov's considerations put forward for real systems, point to the non-linear dependence of the diffusion coefficient on the reciprocal temperature values, and there exists full analogy with the $m=f(1/T)$ dependence, obtained under non-isothermal conditions.

The change in the relative linear shrinkage rate follows the law of distribution, which is very close to normal distribution. The maximum on the distribution curve

$$\frac{\partial \left(\frac{\Delta L}{L_0} \right)_T}{\partial \sqrt{\tau}}$$

is the result of the change in the material structure state, due to the change in the powder "activity". Bearing in mind the fact that the point defect concentration is the function of the partial oxygen pressure and temperature, characterized by both the ever decreasing and increasing functions, the abrupt increase in the relative linear shrinkage rate can not be the result of the existence of point defects exclusively. It is evident that some other structure defects must effect this. The sintering character of the examined α -Nb₂O₅ is the evident proof that high temperature defects really exist.

The qualitative analysis of the sintering process from the aspect of the subatomic electronic configuration theory indicates that the high temperature of the intensive sintering of α -Nb₂O₅ is the result of the high localization part of d^5 niobium atoms.

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