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Sintering as a Process of Transport of Activated Volume

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(Dedicated to Professor Dr. Drago Kolar in memory of a great scientist and a great man)

Abstract: Starting with the fact that sintering is the consequence of the process of transport of activated volume, it has been shown how the kinetics of the sintering process can be defined. The activated volume was in principle defined as a parameter which describes a system's defectivity on an atomic level.

Keywords: Sintering Theory; Activated Volume; Diffusion.

Резюме: Исходя из того, что спекание является результатом процесса транспорта активированного объема, в данной работе показан способ определения кинетики процесса спекания. При этом учтено, что активированный объем в принципе параметр, определяющий дефектность системы на атомном уровне.

Ключевые слова: Теория спекания; активированный объем; диффузия.

Садржај: Полазећи од чињенице да је синтеровање последица процеса транспорта активираних запремина показано је како се може дефинисати кинетика процеса синтеровања. При том се пошло од чињенице да је активираних запремина у принципу параметар који дефинише дефектност система на атомском нивоу.

Кључне речи: Теорија синтеровања; активираних запремина; дифузија.

Introduction

Starting with atomic concepts of mass transport during the sintering process, modern science sometimes disregards the decisive significance of the electronic composition of a solid. It is the objective cause of the consequential movement of activated volume [1], which is the only thing that can bring about macro changes in the volume of a system being sintered. Diffusion in solid materials depends on the lattice configuration and atomic mass. However, in real systems it is essentially controlled by bond strength and structure. This in other words means, that if, for example, d-elements are analyzed, diffusion depends on the number of d-electrons participating in the formation of bond energy, and on the filling level of different electronic clouds [2]. A change in the electronic distribution in dependence on temperature also leads to changes of values of bond energy and the corresponding activation energy of diffusion, which is connected with deviations from the Arrhenius line (Fig. 1) [3].

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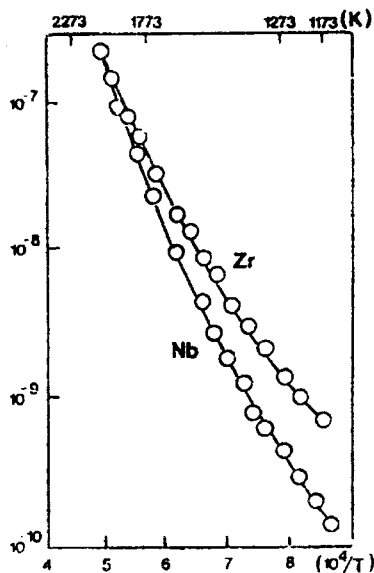


Fig. 1 Dependence of the self-diffusion coefficient of Nb and Zr on temperature.

In accordance with this, when analyzing the essence of the sintering process a connection can be made between different approaches to describing the kinetics and mechanism of sintering, if one starts with activated volume as a general parameter defining system defectivity. If the electronic structure enables a principal unity of matter and movement from the viewpoint of internal harmony of such forms, then at the same time it gives a singular answer to the impossibility of separating the existence of structural defects as statistical characteristics of macro states and movement leading to changes. They are defined by changes of only the crystal structure or sometimes by simply macrostructural evolution.

Changes of the electronic distribution in a system being sintered essentially influence the fact that mass transport during this process can only occur due to consequential movement of effective activated volume of the system [4]. Such an approach, according to our theoretical research, can be of universal significance and can be applied not only to crystal, but also to ultradisperse and amorphous materials.

Let a system at the beginning of sintering be characterized by a starting effective activated volume - v_a^0 and let the activated volume at any moment be v_a ; then its value gravitates towards equilibrium activated volume - v_a^+ when time gravitates towards infinity [1]. In accordance with this the difference

$$\Delta v_a = v_a - v_a^+, \quad (1)$$

defines the concentration of all defects of the crystal lattice at a given moment.

Having in mind the analysis performed by C. R. Flynn [5], reduction of the relative effective activated volume can be defined as:

$$\frac{v_a}{v_a^+} = 1 + \left(\frac{v_a^0}{v_a^+} - 1 \right) \exp\left(-\frac{t}{\tau}\right), \quad (2)$$

where τ - time constant.

The ratio $v_a / v_a^+ = \varepsilon$ represents system activity at a given moment. At the beginning of sintering $v_a^0 > v_a^+$ and $\varepsilon > 1$, while in equilibrium conditions $v_a^0 = v_a^+$, so $\varepsilon = 1$. It follows that the system is more active when ε has a higher value, and sintering will be faster.

If, in accordance with this general analysis, sintering of a system occurs by viscous or diffusion-dislocation flow, then in accordance with [6] the kinetics of this process is defined by the following equation:

$$\theta = \theta_0 \cdot \exp\left(-\frac{8}{9} \frac{\sigma}{\eta R} t\right), \quad (3)$$

where θ and θ_0 – porosity at the beginning and during sintering, R – particle radius, σ – surface tension, t – sintering time and η – viscosity, which according to [7] can be defined by the following equation:

$$\frac{1}{\eta} = \frac{v_s}{v_a^{1/3}} \exp\left(-\frac{E}{kT}\right), \quad (4)$$

where: v_a – the activated volume, E – activation energy of flow, k – Boltzmann's constant, T – temperature, v_s – specific volume of the material

Starting with the definition for activated volume:

$$v_a = v_s \exp\left(\frac{E-U}{kT}\right), \quad (5)$$

where U – effective energy of internal pressure, one can obtain the expression which characterizes the kinetics of the sintering process:

$$\ln \frac{\theta}{\theta_0} = -F \cdot v_a^{2/3} \exp\left(\frac{U-2E}{kT} t\right), \quad (6)$$

where

$$F = \frac{8}{9} \frac{\sigma}{R \sqrt{2\pi m k T}}.$$

It is obvious that sintering kinetics depends on the activated volume of the material being sintered, but also on the effective energy of internal pressure, which is a function of bond energy in the system being sintered, thus – the electronic structure.

A new contribution in the analysis of processes of mass transport in solids, i.e. the sintering process, has been made by stating that quasi-particles such as phonons, excitons, electrons etc. are responsible for these transport processes [8]. The possibility of using such an approach depends on the degree of particle control according to relaxation rates. This degree is determined both by the composition and structure of solid bodies. Thus, an investigation of ionic conductivity (for example electric-resistance sintering) of alkali halogen materials has shown that the movement of atoms and their vacancies in stable configurations of solid bodies can be considered as Fermi lattice excitations, differing from phonon excitations [9].

Understanding sintering as a complex, but essentially unified process, enables to a great degree the obtaining of materials whose properties and structure are defined in advance.

Conclusion

Defectivity of the crystal lattice during the sintering process has been defined as a difference between the effective activation volume during this process and equilibrium activated volume at the end of this process. Based on this, under the assumption that sintering occurs by flowing, a principle defining the sintering kinetics has been described.

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