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A Phenomenological Analysis of Sintering Kinetics from the Viewpoint of Activated Volume

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Abstract:

The sintering kinetics of real systems has been viewed as a process of transport of activated volume. Activated volume is a parameter that can be used to describe mass transport during the sintering process. It defines the movement of point defects and dislocations during the sintering process. A phenomenological equation has been defined using this parameter, which can be applied to analyze kinetics of the sintering process. It has been applied to analyze the sintering process of several disperse systems. Values obtained for parameters of the equation have also been analyzed.

Keywords: *Sintering kinetics, phenomenological analysis, mass transport.*

1. Introduction

The basic moving force of the sintering process is free system energy that is reduced when a material is heated and material transport occurs by diffusion mechanisms, vapour transport or plastic flow [1]. Powder sintering at elevated temperatures leads to grain joining, reduction of the surface area and creation of grain boundaries. The driving force for material transport in sintering and grain growth is excess free energy associated with the surface and grain boundary. Excess free energy stored in a system directly activates material transport leading to system changes towards an equilibrium state [2]. From the thermodynamic point of view the analyzed system is not in equilibrium, which is the consequence of the presence of point defects and dislocations. Activated volume is a parameter that can describe mass transport during the sintering process as it defines the movement of point defects and dislocations during the sintering process [3].

A phenomenological approach, based on the behaviour of real materials, enables establishment of a functional connection between parameters characteristic for sintering kinetics.

V. A. Ivensen [4] made one of the first attempts to explain sintering mechanisms. He performed a quantitative analysis of densification kinetics during sintering of porous bodies where he analyzed all processes occurring during sintering as phenomenologically elementary

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processes, defined by an elementary kinetics, which can be analyzed using simple quasi-chemical kinetic and empirical relations. He based his analysis of sintering kinetics on the assumption of a constant relative pore volume reduction during a certain time period independent of the starting compact porosity.

V. V. Skorokhod [5] analyzed the sintering process of real systems from the viewpoint of a rheological theory. He introduced the term effective viscosity and assumed that pore shrinkage is the consequence of dislocation-viscous flow. His theory is based on the phenomenological concept of generalized viscous flow of porous bodies.

M. M. Ristic and S. Jovanovic [6] analyzed the sintering kinetics from the viewpoint of possible application of the general process equation. Their starting assumption was that the process rate constant changed both with the temperature and time of sintering.

Physical principles of sintering kinetics based on the definition of activated volume [7] as a universal parameter of the defect structure of a material have been given in this paper. The results obtained were applied to an analysis of sintering iron powder [8].

2. Sintering as the consequence of transport of activated volume

In [9] activated volume has been defined as:

$$v^+ = -RT\left(\frac{\partial \ln D}{\partial p}\right) \tag{1}$$

where the diffusion coefficient D is defined as:

$$D = \gamma a^2 v \exp\left(-\frac{\Delta G}{RT}\right) \tag{2}$$

and R - is the gas constant, T - sintering temperature, ΔG - the change in free energy, p - pressure, γ - geometric factor, a - crystal lattice constant, v - Debey frequency.

Mass transport during the sintering process can effectively be interpreted as movement of the effective activated volume of the system. At the onset of sintering a system is characterized by a starting effective activated volume - v^0. From the viewpoint of processes occurring during sintering, this process can be described as gravitation of the electronic system towards an equilibrium state, which also contains certain defects. The equilibrium state of a system can be characterized by an equilibrium activated volume v^+. The effective activated volume of a system (v) at any moment during the sintering process is a parameter that with the increase of sintering time gravitates towards the value of equilibrium-activated volume.

From a physical viewpoint the effective activated volume of a system can be defined as:

$$v = \frac{N_0}{N_r}v^+ \tag{3}$$

where: N_0 represents the concentration of all defects at any given moment and N_r - the equilibrium concentration of defects in the analyzed system.

According to [7] reduction of effective activated volume can be defined as:

$$\frac{v}{v^+} = 1 + \left(\frac{v^0}{v^+} - 1\right)\cdot e^{-t/\tau} \tag{4}$$

where τ - is a time constant.

In the most general sense kinetics of the sintering process can be expressed in terms of the dependence of volume shrinkage of a material during isothermal sintering on the sintering temperature and time as [6]:

$$\frac{\Delta V}{V_0} = K^*(st)^n \tag{5}$$

where K^* - the sintering rate constant, which depends on the sintering temperature and time, n - a constant which depends on the process mechanism, s – a time constant, t - sintering time.

The sintering rate constant is then defined as:

$$K^* = K \cdot \varphi(st) \tag{6}$$

where K represents the process rate constant to which the Arrhenius dependence can be applied:

$$K = K_0 \exp\left(-\frac{E}{RT}\right) \tag{7}$$

where K_0 is a constant, R - is the gas constant, E - is the process activation energy and T - sintering temperature.

The parameter $\varphi(st)$ represents a measure of the degree of sintering. If sintering is viewed as the consequence of the transport of activated volume, then the degree of sintering can be defined as the ratio between the equilibrium activated volume and the effective activated volume:

$$\varphi(st) = \frac{v^+}{v} \tag{8}$$

then taking into account eq. (4) we obtain:

$$\varphi(st) = \frac{1}{1 + C\exp(-st)} \tag{9}$$

where $C = \dfrac{v^0}{v^+} - 1$ is a constant defining the ratio between the starting effective activated

volume and the equilibrium activated volume, s $(=1/\tau)$ - a time constant.

Thus, the following equation can be used to describe the sintering kinetics:

$$\frac{\Delta V}{V_0} = \frac{K}{1 + C\exp(-st)} \cdot (st)^n \tag{10}$$

2. Sintering of iron powder

Iron powder was pressed and then sintered in hydrogen atmosphere in the temperature interval of 873-1153 K for 1-116 minutes. The change of relative sample volume was measured and results obtained are given in table I.

Tab. I Relative volume shrinkage of Fe during isothermal sintering [8]

Sintering time (min)	Sintering temperature (K)			
	873	973	1073	1153
1	0.0066	0.0135	0.0420	0.0756
2	0.0081	0.0189	0.0531	0.0900
4	0.0111	0.0246	0.0699	0.1161
7	0.0147	0.0336	0.0885	0.1434
11	0.0195	0.0456	0.1110	0.1683
16	0.0240	0.0564	0.1299	0.1917
26	0.0324	0.0759	0.1596	0.2154
56	0.0480	0.1170	0.2130	0.2751
116	0.0660	0.1500	0.2565	0.3060

A detailed description of this procedure is given elsewhere [8].

3. Discussion

The phenomenological equation defined has been successfully applied to analyze isothermal sintering of iron and the results obtained are given in fig. 1.
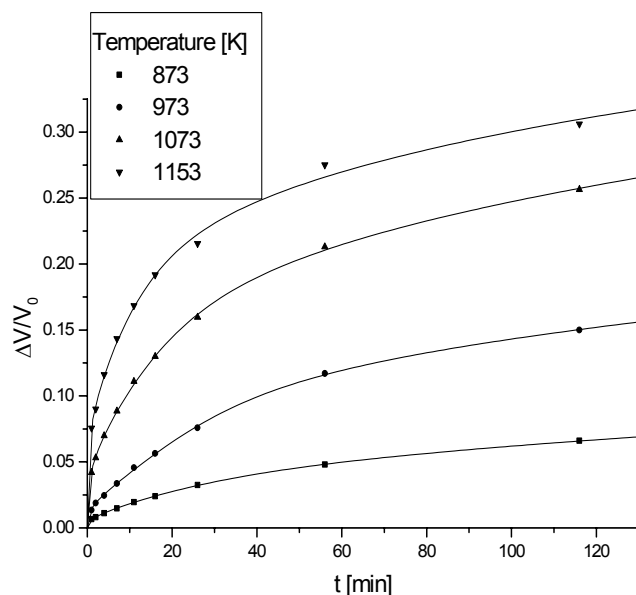

Fig. 1 Dependence of relative volume shrinkage of Fe on time (full lines represent curves fitted using equation (10))

The advantage of the equation applied for the analysis of sintering kinetics of real systems is that starting from the general equation of sintering kinetics it uses activated volume as a parameter defining the degree of sintering. Thermodynamic formulation of activated volume enables definition of mass transport during the sintering process, regardless whether it occurs by diffusion processes or diffusion-viscous flow. As previously stated the dependence of the process rate constant K on the sintering temperature can be expressed using the Arrhenius dependence (eq. (7)) and it is given in fig. 2. Parameter E in eq. 7 represents the activation energy of the responsible mass transport process (movement of activated volume) and in this case it is 39.195 kJ/mol K.

Tab. II Activation energy of iron obtained by different methods

Activation energy [KJ/mol]	Diffusion mechanism	Ref.
60	Isothermal shrinkage, nanometric powder in H_2	[10]
118	Isothermal shrinkage, nanometric powder in vaccum	[10]
239	Lattice diffusion in polycrystalline Fe	[11]
174	Grain boundary diffusion in polycrystalline Fe	[11]
62	Nanopowder, microwave sintering in H_2	[12]
155	Self-diffusion	[13]

It is interesting to compare the value of activation energy for transport of activated volume with other values of activation energy of the responsible mass transport process

obtained by different methods for sintering iron (tab. II). We can see that all literature values are higher than the one obtained in this paper. It is closest to the values obtained for sintering nano-iron powder in H_2 [10, 13]. First iron powder does not behave the same in H_2 and vacuum. In [10] they explain lower activation energy for sintering in H_2 as related to two possible phenomena: the first associated with the chemical ability of hydrogen to reduce oxygen and the second to the physical property that hydrogen acts as a lattice-defect catalyst. Activated volume defines the movement of point defects and dislocations during the sintering process, thus resulting in smaller values of activation energy.
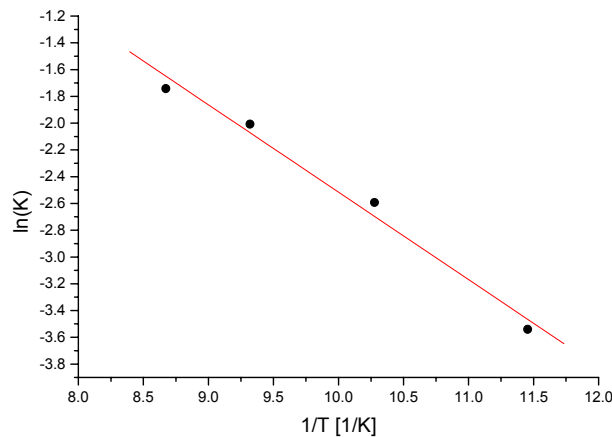

Fig. 2 Dependence of the process rate constant on the sintering temperature of Fe

During the sintering process the analyzed system is not in equilibrium and contains a certain amount of unstable defects. These defects can be removed by heating. The rate of their disappearance is a function of the sintering temperature and time. At higher temperatures the disappearance rate of system defects is higher. An effective activated volume can characterize all these processes.

As previously defined parameter C represents the ratio between the starting effective activated volume and equilibrium activated volume and corresponds to the measure of starting system activity (fig. 3). This parameter increases for sintering temperatures between 873 and 973 K, after which it decreases for the remaining two sintering temperatures.
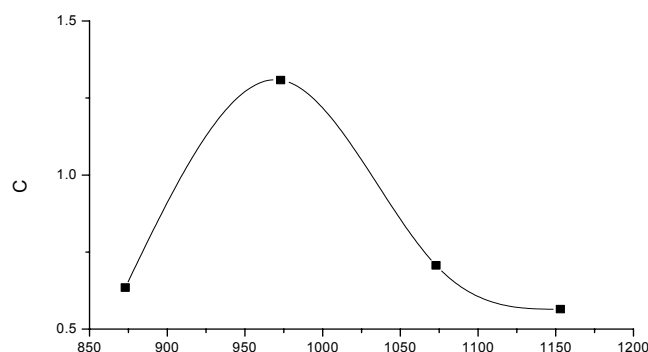

Fig. 3 Dependence of the measure of starting system activity on the sintering temperature of Fe

The ratio between the equilibrium activated volume and effective activated volume at any sintering point describes the degree of system activity at that moment. This dependence

for the analyzed system is given in fig. 4. With the increase in sintering time for all four sintering temperatures the effective activated volume decreases and gravitates towards the equilibrium value, indicating that for longer sintering times the concentration of defects in the crystal lattice has reached its minimum. It is interesting to note that due to higher values of parameter C the sintering degree for the temperature of 973 K is the lowest, but for higher sintering times it reaches equilibrium values.

Conclusion

The sintering kinetics of real systems has been viewed from the viewpoint of activated volume. A phenomenological equation was defined using this parameter and was successfully applied to an analysis of the sintering kinetics of iron. Values obtained for the process rate constant enabled determination of the process activation energy.

Acknowledgement

References

1. H. E. Exner, E. Arzt, Sintering Processes, in Physical Metallurgy, fourth revised and enhanced edition (Eds. R. W. Cahn and P. Haasen), Elsevier Science, 1996
2. H. Tanaka, Shape Changes of Spheroidal and Rectangular Grains Driven by Excess Free Energy, J. of the European Ceramic Soc. 24(2004), 2763-2768
3. N. Nikolic, M. V. Nikolic, S. M. Radic Ristic, M. M. Ristic, Sintering as a Process of Transport of Activated Volume, Sci. Sintering 34(2002), 53-56
4. V. A. Ivensen, Sintering Phenomenology, Metallurgiya, Moskva, 1985 (in Russian)
5. V. V. Skorokhod, Mechanism of Material Flow during Sintering and Superplasticity of Polycrystal Materials, Powder Metallurgy, 5, (1978), 34-40
6. M. M. Ristic, S. Jovanovic, A General Kinetic Definition of Sintering, Poroshkovaya Metallurgiya, 9 (57), (1967), 102-109 (in Russian)
7. C. P. Flynn, Point Defects and Diffusion, Clarendon Press, Oxford Press, Oxford, 1972
8. Z. Nikolic, M. M. Ristic, Mathematical-Physical Analysis of Some Kinetic Sintering Equations, Chemical Industry 34 (1980), 143-146
9. M. M. Ristić, Kinetics of the Sintering Process from the Viewpoint of a Thermodynamic Formulation of Mass Transport, Glas CCXCV, Serbian Academy of Sciences and Arts, Department of Technical Sciences, vol. 11, 1976 (in Serbian)
10. O. Dominguez, J. Bigot, Material Transport Mechanisms and Activation Energy in Nanometric Fe Powders Based on Sintering Experiments, Nanostructured Materials, 6 (1995), 877-880
11. F. B. Swinkells, M. F. Ashby, Acta Metall., A Second Report on Sintering Diagrams, 29 (1981) 259-281
12. D. Juve-Duc, D. Treheux, P. Guiraldenq, Self-diffusion of Iron in an α-γ Interface Compared with Diffusion in Grain Boundaries, Materials Science and Engineering 42 (1980), 281-288

13. L. J. Kecskes, R. H. Woodman, Effect of Powder Characteristics on the Sinterability of a Microwave-Plasma-Synthesized Iron Nanopowder, Scripta Materialia 48(2003), 1041-1046

Резюме: *Кинетику спекания реальных систем наблюдали с точки зрения переноса активированного объема. Активированный объем – это параметр, который используется для описания переноса массы в ходе процесса спекания. Он определяет движение точечных дефектов и дислокаций при спекании. Использованием данного параметра определено феноменологическое уравнение, применимое к анализу кинетики процесса спекания. Это уравнение применено к анализу спекания полидисперных систем. Проведен также анализ значений параметров уравнения.*
Ключевые слова: *Кинетика спекания, феноменологический анализ, перенос массы.*

Садржај: *Кинетика синтеровања реалних система посматрана је са гледишта транспорта активиране запремине. Активирана запремина је параметар који може да се користи за опис транспорта масе за време синтеровања. Она дефинише кретање тачкастих дефеката и дислокација током процеса синтеровања. Коришћењем овог параметра дефинисана је феноменолошка једначина која се може применити на анализу кинетике процеса синтеровања. Она је примењена на анализу синтеровања полидисперзних система. Такође су анализиране вредности добијене за параметре једначине.*
Кључне речи: *Кинетика синтеровања, феноменолошка анализа, транспорт масе.*