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ON THE FEATURES OF THE KINETICS OF THE POLYMORPHIC TRANSFORMATION OF ZIRCONIUM DIOXIDE DURING COOLING

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It is generally accepted (^{1,2}) that diffusionless (martensitic) transformations proceed either with athermal or with isothermal kinetics. The present work was carried out in order to show that, at least in the case of the phase transition of zirconium dioxide, there is no fundamental distinction between these two types of transformations.

The diffusionless character of the polymorphic transformation of ZrO_2 is confirmed by the following experimental data.

1. During the thermal decomposition of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), aggregates of the metastable tetragonal modification of ZrO_2 (β'-phase) are formed, resembling in shape the original oxychloride crystal, with a strictly parallel orientation of the crystallites. (When observed in a polarizing microscope, all crystallites composing the aggregate go extinct simultaneously.)

It is important to note that this strict parallelism of orientation is retained after a threefold cycle: heating to 1200°C –cooling to room temperature. This would be unlikely if the polymorphic transformation proceeded by a diffusion mechanism.

Since already after the first cycle, as a result of which the transitions $\beta' \to \alpha$—$\beta \to \alpha \to \alpha$ occur –the low-temperature monoclinic modification, β being the high-temperature tetragonal one –a preparation is obtained that does not differ in any way from "ordinary" zirconium dioxide, the $\alpha \rightleftarrows \beta$ transformation of ZrO_2 should be regarded as diffusionless.

2. In the case of zirconium dioxide, the criterion indicated by G. V. Kurdyumov (^{3}) for the realization of a martensitic transformation is fulfilled: the transformation temperature (T_0) is lower than the temperature at which recrystallization begins (T_p). The latter, according to microscopic observations carried out at our request by N. V. Gulko and M. E. Drizheruk,

Fig. 1. Kinetics of the isothermal $\beta \to \alpha$ transition of ZrO_2 at different temperatures

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is $\sim 1200^\circ$, which is 100–200° higher than the temperature of the $\alpha \rightleftarrows \beta$ transitions of ZrO_2.

3. In accordance with (4), evidence in favor of the diffusionless character of the polymorphic transformation of zirconium dioxide is provided by the limited nature of the isothermal $\alpha \to \beta$ transition and by the already noted in (6) similarity of its kinetics to the kinetics of the isothermal transformation of austenite into martensite (5). Investigations carried out by us on specimens of especially pure zirconium dioxide (content of $ZrO_2 > 99.7\%$) by the method described in (6) showed that the kinetics of the initial stage of the $\beta \to \alpha$ transition is also described by the expression

$$\frac{C(t) - C_\infty}{C_0 - C_\infty} = e^{-qt}. \tag{1}$$

As follows from Fig. 1, the rate of transformation (the slope q of the straight line in the figure) decreases as the temperature of isothermal holding is lowered. Taking for q an exponential dependence on temperature (5)

$$q = A \exp(-U/kT),$$

where U is the activation energy of the transition process, one can, from a graph plotted in the coordinates $\lg q$—$1/T$ (Fig. 2), find the value of U. It proved to be ~ 125 kcal/mol.

However, at a certain supercooling ($\Delta T \sim 100$–200°), the magnitude of which depends on the thermal prehistory of the specimen, the transformation rate increases sharply, and the transformation becomes athermal.

Thus, in the $\beta \to \alpha$ transition of zirconium dioxide, a change in the kinetics of a diffusionless transformation is observed: isothermal kinetics at a certain supercooling is replaced by athermal kinetics.

Fig. 1. Kinetics of the isothermal $\beta \to \alpha$ transition of ZrO_2 at different temperatures

A more detailed study of this phenomenon proved convenient to carry out on specimens of the β'-phase of ZrO_2 obtained by thermal decomposition of zirconium oxychloride. The chemical composition after calcination at 200° was (in wt.%): SiO_2 0.20; Al_2O_3 0.33; Fe_2O_3 0.09; CaO 0.10; TiO_2 and MgO–traces; $Cl_2 + H_2O$ 16.7; HfO_2 1.0; ZrO_2 81.58.

Fig. 2. Dependence of q on temperature

Figure 2: Fig. 2. Dependence of q on temperature

Heating the specimens in the diffractometer furnace leads to the appearance, at $\sim 400^\circ$, of the β'-phase, which agrees with the results of works (7-9). Beginning at 800°, lines of the stable α-modification appear.

It was found that the $\beta' \to \alpha$ transformation occurs not only on heating, as was noted in works (7-9), but also on cooling, provided only that the specimen had previously been heated to temperatures exceeding 600—650°. At the same time, even prolonged (for several hours) heating at temperatures below 600° does not lead to a subsequent $\beta' \to \alpha$ transition on cooling, irrespective of the cooling rate.

To clarify the effect of the duration of heating at temperatures exceeding 600—650° on the kinetics of the $\beta' \to \alpha$ transition on cooling, two series of experiments were carried out.

In the first series, specimens heated in a hardening furnace at 550° were introduced into a zone with a temperature of 650—680°. One of the specimens was immediately quenched in liquid nitrogen, while the others were quenched successively after 1, 3, 7, 17, and 60 min. X-ray examination at the temperature of liquid nitrogen showed that only in the last specimen had the $\beta' \to \alpha$ transformation been completed during quenching. In the remaining specimens the β'-phase was fully retained.

Subsequent 24-hour holding at room temperature did not produce noticeable changes in the first specimen (quenched from 650—680° without holding), ensured the appearance of $\sim 50\%$ α-ZrO_2 in the specimen whose heating had lasted 1 min, and led to a complete $\beta' \to \alpha$ transition in the specimen calcined for 17 min. In specimens heated for 3 and 7 min, the β'-phase was completely retained after 24 hours in liquid nitrogen.

Fig. 2. Dependence of q on temperature

In the second series of experiments, the isothermal $\beta' \to \alpha$ transformation at room temperature was studied in specimens quenched in water after heating at 670° for from 0 to 300 min. The results of these experiments, shown in Fig. 3, indicate that the kinetics of the $\beta' \to \alpha$ transition is described-

is expressed by (1), and the rate of the transition depends strongly on the duration of heating.

The results of the experiments described indicate that, at temperatures exceeding 600-650°, certain processes develop in β'-ZrO_2 that substantially affect the kinetics of the subsequent $\beta' \to \alpha$ transformation. To clarify these processes, the integral and maximum intensity of the (111) line of β'-ZrO_2 was measured during its heating (Fig. 4).

Fig. 3

Figure 3: Fig. 3

The increase in integral intensity during the first 50 min of holding at 430° is evidently associated with the completion of crystallization of the β' phase. The further increase in the height of the line, with unchanged integral intensity, can be due only to an "improvement" of the β'-ZrO_2 lattice, to annealing of defects, since, according to petrographic analysis, the crystallite sizes (1-2 μ) do not change during heating.

Fig. 3. Kinetics of the $\beta' \to \alpha$ transition of ZrO_2 at room temperature as a function of the duration of the preliminary firing: **1** –0; **2** –3; **3** –10; **4** –100; **5** –300 min.

On the curve of the change in maximum intensity there is a break at a temperature of $\sim 630°$. Acceleration of the growth of the maximum intensity in the temperature interval 600-650° is observed in all similar experiments (Fig. 4, curves **b**, **v**), regardless of the heating rate and the duration of the preliminary holdings. This makes it possible to assume that at temperatures of 600-650° the defects responsible for retarding the $\beta' \to \alpha$ transition during cooling begin to anneal out.

It is generally accepted that martensitic transformations proceed by the displacement of dislocations[10,11]. Regardless of the particular dislocation mechanism of the transformation, the presence of isothermal kinetics can be explained by the existence of structural defects that hinder this displacement. Such obstacles may be, for example, dislocations intersecting the slip plane of the transformation dislocations, sessile dislocations of the Lomer-Cottrell barrier type, Cottrell atmospheres, etc. Regardless of the nature of the obstacles, they are overcome by certain thermally activated processes or as a result of "breakthrough." The latter, apparently, is the reason for the change in the kinetics of the $\beta' \to \alpha$ and $\beta \to \alpha$ transitions of ZrO_2 at large supercoolings.

With a large number of defect-obstacles, the rate of displacement of the transformation dislocations may be close to zero even at considerable supercooling. In this case the transformation does not occur, as is the case in ZrO_2 specimens obtained from zirconium oxychloride at temperatures not exceeding 600°, or else a diffusion mechanism of transformation is realized if $T_p < T_0$ (for example, during slow cooling of Mn_3Si[12]).

By changing the number of obstacles and, possibly, their character (i.e., the activation energy for overcoming them), it is possible to regulate the rate of the isothermal transformation over wide limits. In the case of β'-ZrO_2, by appropriate heat treatment one can even ensure a transition to athermal kinetics at sufficiently large supercooling.

Thus, in the case of ZrO_2, isothermal and athermal transformations are not due

Fig. 4

Figure 4: Fig. 4

to fundamentally different mechanisms. Isothermic-

kinetics is the result of the influence of defects that hinder the motion of the transformation dislocations. If the number of obstacles is small, or if conditions are provided for their breakthrough, athermal kinetics is realized.

Fig. 4. Change in the maximum intensity of the (111) line of the β' phase of ZrO_2 on heating; **b, c**—change in $I_{\max}$ in two other experiments

It may be assumed that this, to a certain extent, also applies to other martensitic transformations.

It is easy to show that obstacle defects lead to kinetics described by expression (1), obtained in (6) from phenomenological considerations. Indeed, the probability of a process whose activation energy U is proportional to $\exp(-U/kT)$. The number of obstacles overcome in time Δt is

$$N = A\exp(-U/kT)\Delta t. \tag{3}$$

If n is the number of obstacles in the path of the transformation dislocations, and l is the size of a crystal of the initial phase along the path of dislocation motion, then the change in the size of this crystal is

$$\Delta l = -\frac{l}{n}A\exp(-U/kT)\Delta t. \tag{4}$$

Since $\Delta l/l \sim \Delta V/V$ (V is the volume of the crystal), then

$$\frac{\Delta V}{V} = -\frac{B}{n}\exp(-U/kT)\Delta t. \tag{5}$$

Integrating (4) and taking into account the amount of phase that does not transform at the given temperature, after passing to concentrations we obtain formula (1), in which

$$q = \frac{B}{n}\exp(-U/kT). \tag{6}$$

This expression coincides with dependence (2), used to determine the activation energy of the $\beta \to \alpha$ transformation of ZrO_2.

The transformation-rate parameter q decreases as the number of obstacle defects and the activation energy for overcoming them increase. If, by analogy with

$U = U(\sigma)$ (σ is the shear stress), one assumes $U = U(\Delta F)$, where ΔF is the defect of free energy, then the possibility becomes clear of breaking through obstacles at large supercoolings and of transition to athermal kinetics.

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CITED LITERATURE

1. B. A. Bilby, D. V. Christian, *UFN*, **70**, 515 (1960).
2. G. V. Kurdyumov, O. P. Maksimova, *Izv. AN SSSR, OTN*, No. 6, 4 (1957).
3. G. V. Kurdyumov, *Problems of Metallography and the Physics of Metals*, issue 3, 9 (1952).
4. Ya. M. Golovchiner, *Problems of Metallography and the Physics of Metals*, issue 7, 281 (1964).
5. G. V. Kurdyumov, O. P. Maksimova, *DAN*, **61**, 83 (1963).
6. B. Ya. Sukharevskii, I. I. Vishnevskii, *DAN*, **147**, 882 (1962).
7. W. M. Goldschit, *Naturwiss.*, **14**, 447 (1962).
8. G. I. Clark, D. H. Reinolds, *Ind. and Eng. Chem.*, **29**, 711 (1937).
9. L. N. Komissarova, V. E. Ploshchev, I. N. Kremenskaya, *ZhNKh*, **5**, 586 (1960).
10. V. A. Bilby, *Phil. Mag.*, Ser. 7th., **44**, 782 (1953).
11. Van Buren, *Defects in Crystals*, IL, 1962.
12. G. N. Davydov, F. A. Sidorenko, P. V. Gel' d, *Physics of Metals and Metallography*, **12**, 422 (1961).

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