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Classification
Physics Abstracts
81.30M

Study of the precipitation in $MgO.3.5\ Al_2O_3$ during creep experiments

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(*Reçu le 16 octobre 1978, révisé le 10 janvier 1979, accepté le 15 janvier 1979*)

Résumé. — L'influence d'une contrainte sur les plans de précipitation de l'alumine α dans des monocristaux de spinelle $MgO.3,5\ Al_2O_3$ a été étudiée à 1 220 °C et 1 250 °C. On trouve que les plans de précipitation sont les plans { 111 } de contrainte normale maximum. L'énergie d'activation, mesurée par sauts de température, varie de 3 à 3,5 eV.

Abstract. — The influence of stress on the planes of precipitation of α-Al_2O_3 in $MgO.3.5\ Al_2O_3$ single crystals is studied at 1 220 °C and 1 250 °C for three orientations of the compression axis. We find that the planes of precipitation are the { 111 } planes which have a maximum normal stress. An activation energy, as measured by temperature jumps, is found ranging from 3 to 3.5 eV.

1. **Introduction.** — The solubility of alumina in the spinel $MgO.Al_2O_3$ is very high and a whole series of solid solutions $MgO.nAl_2O_3$, with n varying from 1 to 5, forms at high temperature as shown in the phase diagram (Fig. 1). These solid solutions can be retained at room temperature in a metastable form by quenching from the growth temperature; such is the case for single crystals grown by the Verneuil process.

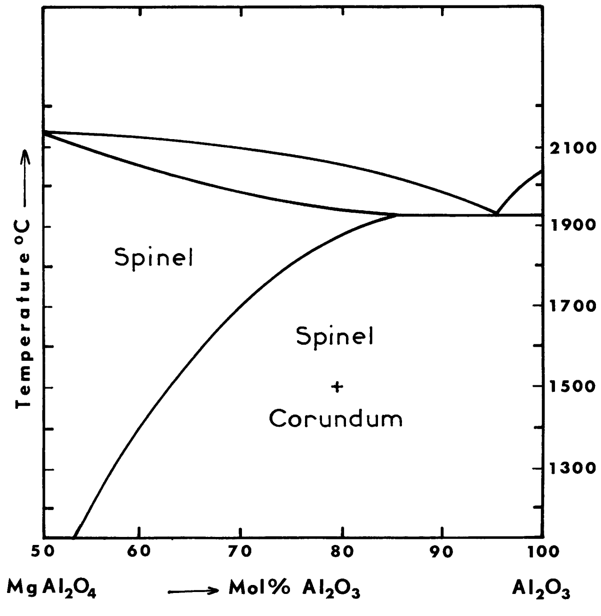

Fig. 1. — Phase diagram for the $MgO.Al_2O_3$ system.

By heating these crystals, precipitation of the alumina phase occurs until the spinel phase reaches the equilibrium stoichiometry ratio n of Al_2O_3 : MgO at the test temperature.

While the different stages which lead from the initial solid solution to the two-phase composite have been studied, either by X-ray diffraction over a large range of stoichiometries by Saafeld and Jagodzinski [1], or by transmission electron microscopy by Lewis [2] and Bansal and Heuer [3] (n = 3.5), the influence of stress on the precipitation structures, in particular the relation between the stress axis and the planes on which the precipitation takes place, is poorly documented. Only the precipitation of hematite from nickel ferrite during creep has been recently studied in this way by Veyssière *et al.* [4].

In the present work, the precipitate structure of alumina from Al-rich spinel is studied during creep of $MgO.3.5\ Al_2O_3$ single crystals.

This leads to a different picture at least for our alumina spinels from the one proposed by Veyssière *et al.*

2. **Experimental techniques.** — A large single crystal boule of $MgO.3.5\ Al_2O_3$, grown by the flame fusion technique, was obtained from Cristal Tec (L.E.T.I. Grenoble).

Creep samples were cut, after orientation by the Laue technique, with a diamond impregnated saw

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into $2 \times 2 \times 6\ mm^3$ cubes. Three orientations have been used for the compression axis (C.A.) : [001], [110] and [111]. After cutting, the sample faces were polished with 1 μm diamond paste.

Creep experiments were performed in compression in air. The creep apparatus has been already described elsewhere [5].

After the creep test, because of thermal etching, the faces of the specimen were again mechanically polished to allow observation of the precipitate structure by optical microscopy using Nomarski contrast.

3. **Results and discussion.** — Samples were subjected to creep at 1 220 °C and 1 250 °C at stresses from 120 MPa to 160 MPa.

The creep curves of all the specimens are S-shaped, as shown in figure 2. They can be divided into two parts. Part 1 consists of an initial inflection, resulting from a decreasing creep rate immediately after loading, followed by a region where the creep rate increases with increasing creep strain up to a maximum $\dot{\varepsilon}_M$. In part 2, the creep rate increases continuously decreases to values of order $10^{-8}\ s^{-1}$, indicating the difficulty of deforming these samples after precipitation.

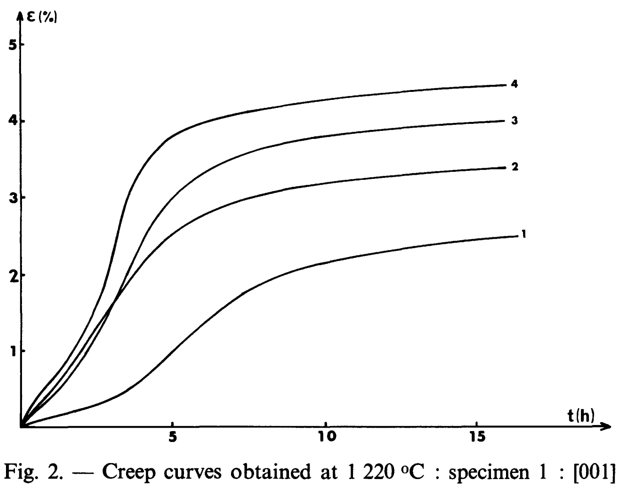

Fig. 2. — Creep curves obtained at 1 220 °C : specimen 1 : [001] C.A. 120 MPa ; specimen 2 : [001] C.A. 160 MPa ; specimen 3 : [110] C.A. 160 MPa ; specimen 4 : [111] C.A. 160 MPa.

Figure 3 represents a plot of $\dot{\varepsilon}$ *versus* time t. The duration and the maximum creep rate $\dot{\varepsilon}_M$ reached at the end of part 1 depend on the test temperature and stress.

Near to the initial inflection, alumina precipitates can be seen by optical microscopy, and are nucleated on { 111 } planes (Fig. 4). At the end of test the precipitation appears as coarse lamellae in { 111 } planes, crossing the sample. Their thickness is about 20 microns (Fig. 5*a*, *b*, *c*).

The { 111 } planes on which precipitation of the α-Al_2O_3 phase is observed vary with the compression axis.

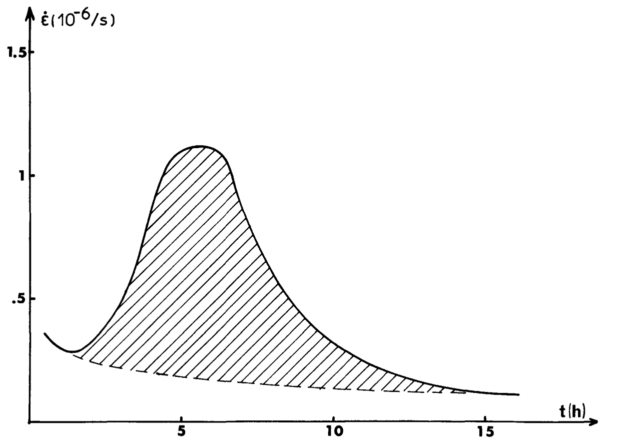

Fig. 3. — Curve $\dot{\varepsilon}$ *versus* time t for specimen 1.

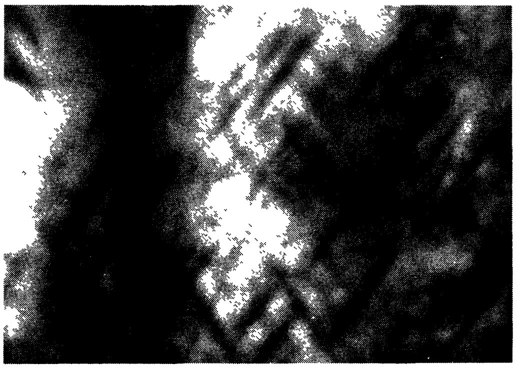

Fig. 4. — Precipitation structure after creep, stopped near to the initial inflection, at 1 220 °C, 160 MPa, face $(1\bar{1}0)$, [001] C.A. vertical.

For [001] C.A., precipitates are found in all the four { 111 } planes (Fig. 5*a*).

In the case of [110] C.A. (Fig. 5*b*), only the two { 111 } planes oblique to the C.A. contain precipitates, in agreement with the observations in nickel ferrite [4].

However, when the stress is applied along the [111] axis precipitates lie in the (111) plane perpendicular to C.A. (Fig. 5*c*) (except near the surfaces).

This plane is a plane of zero glide stress.

This is in contradiction with Veyssière's hypothesis [4] in which the precipitates would expand by slip in those { 111 } planes which have the highest Schmid factor for the { 111 } ⟨ 112 ⟩ glide systems. These are the systems favouring the transformation F.C.C. (spinel) → H.C.P. (α-Al_2O_3) by a shear $a_0/12$ ⟨ 112 ⟩ every two { 111 } anionic planes in the spinel phase.

Finally, the composition n of the resulting spinel phase hence the completion of the precipitation process, can be determined by simple X-ray analysis. The lattice parameter in the spinel $MgO.n\ Al_2O_3$ varies with n from 7.960 Å ($n = 3.5$) to 8.085 Å ($n = 1$) [6]. This allows n to be known from measurement of this parameter on a Debye-Scherrer diagram. For a specimen after 16 hours creep at 1 220 °C, this

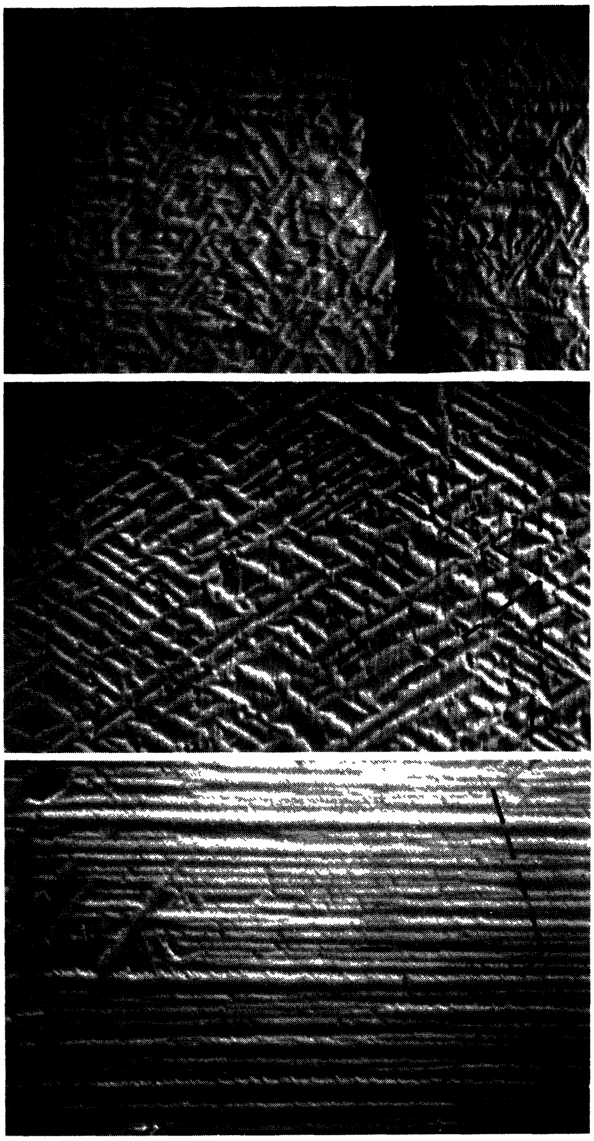

Fig. 5. — Precipitation structures after creep at 1 220 °C, 160 MPa. Duration of the test 15 hours ; face $(1\bar{1}0)$ compression axis vertical. *a*) [001] C.A. specimen 2 ; *b*) [110] C.A. specimen 3 ; *c*) [111] C.A. specimen 4 ; traces of { 111 } planes in dotted lines.

gives a value $n = 1.3$, that is the equilibrium composition of the spinel phase at this temperature. It follows that the precipitation process can be considered as terminated at the end of test.

The accelerated creep rate observed here is interpreted as being partly due to the precipitation of α-Al_2O_3 from the matrix. This effect has also been observed in nickel ferrite by Veyssière [4] but his tests were stopped near to the inflection $\dot{\varepsilon}_M$ and the decreasing creep rate was not recorded.

Some estimation of the precipitation induced strain in the crept samples can be tentatively obtained from figure 3. A correlation is observed between the peak in the $\dot{\varepsilon}$ *vs*. t plot and the duration of precipitation, since { 111 } precipitates are seen appearing at its foot while X-ray determinations of n show completion of the process at its end. Assuming then the whole precipitation takes place during the peak, a reasonable guess of the contributed extra-strain is to take it equal to the hatched area comprised between the peak and the dotted line in figure 3, which extrapolates the steadily decreasing pure creep rate. This yields for the three C.A. investigated, [001], [110] and [111], estimated strain values $\varepsilon_{app} = 2\,\%$, $2.8\,\%$ and $3.3\,\%$ respectively. Note that they do not seem to depend on the applied stress.

In the model of phase transformation by a shear $\frac{a_0}{12}\langle 112 \rangle$ every two (111) anionic planes, the strain component produced along the compression axis is :

$$S\left(\frac{a_0}{12}\langle 112 \rangle\right)/2\left(\frac{a_0}{2\sqrt{3}}\right) = \frac{S\sqrt{2}}{4} \qquad (1)$$

S being the Schmid factor and $a_0/2\sqrt{3}$, the spacing between two consecutive { 111 } anionic planes. The total strain carried out by the shear process which produces a given volume ratio of alumina phase equal to k is :

$$\varepsilon = kS\sqrt{2}/4\,.$$

Writting the decomposition reaction as :

$$MgO.3.5\ Al_2O_3 \rightarrow 2.2\ Al_2O_3 + MgO.1.3\ Al_2O_3 \qquad (2).$$

it is seen that 57 % oxygen ions are in the alumina phase after completion of the reaction, so that $k = 0.57$ at 1 220 °C. It follows $\varepsilon = 8\,\%$ for [001] and [110] C.A. This is much larger than the strain of our samples after complete precipitation.

On the other hand precipitation of alumina from the matrix reduces the sample volume. Alumina is more compact than spinel and this entails a volume reduction of about 4.2 % when comparing the volume occupied by the same number of oxygen ions in equation (2). This reduction corresponds to the lattice parameters change between corundum and spinel, particularly marked along the C axis : $\Delta e/esp = (ecor - esp)/esp = -0.06$ ($ecor$ being the spacing between two consecutive (0001) anionic planes and $esp = a_0/2\sqrt{3}$).

This contraction produces a shortening of the sample. To calculate it, let us consider only the contraction along the C axis $\Delta e/esp$, neglecting the slight differences in lattice parameters of the initial and final spinel phases. Then the strain along the compression axis is written as :

$$\varepsilon = k\frac{\Delta e}{esp}\cos^2\alpha \qquad (3)$$

α being the angle between the C direction and the compression axis.

We obtain for the three C.A. orientations considered, [001], [110] and [111] respectively :

$$\varepsilon = 1.1\,\%,\quad 2.3\,\% \quad \text{and} \quad 3.4\,\%.$$

Except for the first, these values are about the same as the estimated compression strains produced by precipitation. The observed precipitation planes for [110] and [111] C.A. are those planes which give a maximum shortening of the sample length in agreement with the above behaviour.

Temperature jumps of $\pm$ 30 °C were performed during the precipitation near to the maximum creep rate $\dot{\varepsilon}_M$. Thermal equilibrium is reached about ten minutes after the jump and the new creep rate is extrapolated to zero time. We found values of the activation energy ranging from 3 to 3.5 eV.

These values are definitely smaller than the ones found either for mass transport by creep in the stable or quasi-stable aluminate spinels $MgO.n\,Al_2O_3$ ($n = 1.8$ [5], $n = 1.1$ [7]), which is 5.3 eV, or for oxygen self diffusion, 4.5 eV [8]. This difference should be ascribed to the need of oxygen transport, since here only the counter diffusion of Al^{3+} and Mg^{2+} (controlled by the slowest moving cation) is involved, resulting in unoccupied tetrahedral sites and finally in volume reduction).

In conclusion, both the strain after complete precipitation, and the precipitation planes correspond in our aluminate spinels much more to a simple crystallographic rearrangement on those { 111 } planes which have a maximum normal stress, than to a shear process as proposed by Veyssière *et al.*

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