Fractal Aspects of the Martensitic Transformation in Zirconia

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Introduction

The martensitic transformation of Zirconia has a great importance for practical applications. The properties of ceramic materials can be improved by the use of the transformation toughening [1]. Especially ZrO_2 is used for this purpose because it transforms from a tetragonal (t) phase (slightly distorted CaF_2 -structure) to a monoclinic (m) phase at 1150 K. This transformation shows all phenomena of a martensitic transformation [2]. The transformation is reversible and the amount of the transformed phase depends on the temperature.

Martensitic transformed microstructures can be described with the fractal theory [3]. The fractal analysis was done for example on a Fe-31.4Ni-4.2Al(wt%)-alloy. In this paper the fractal aspects of the microstructure of pure m- ZrO_2 are shown.

After describing the experimental observations a model is given how the fractal microstructure was formed. Then the microstructure will be characterized with a few geometric parameters which leads to an easy determination of the fractal parameters. The result will be discussed.

Experimental observations

Specimens of pure, skull-melted Zirconia were prepared for transmission-electron-microscopy (TEM). The material has at room temperature the monoclinic structure and contains many twin lamellae with a thickness of about 100 nm to 1 μm . They are formed during the martensitic tetragonal to monoclinic transformation at 1150 K. The twins reduce the strain resulting from the shape change and volume expansion (approx. 6 %) during the transformation.

Triangular shaped regions can be observed at every second end of such twins (fig. 1). Above a critical size these triangles are twinned in a finer manner. At the end of every second end of these twin lamellas again triangular shaped regions can be observed. It is assumed that the twins in the small triangles are formed in a second step. In the fractal analysis [3] of this selfsimilar microstructure these steps are called generations. Triangles containing smaller ones were observed until the fourth generation (fig. 1). The crystallographic orientations of the twins and the twin boundaries can be analysed and were published elsewhere [4,5]. Below a critical size of about 20 nm the triangles are not twinned any more but consists of single phase regions.

These regions appear with a darker contrast in micrographs (e.g. fig. 2) obtained by high resolution electron microscopy (HREM). The lattice constants of this phase were found to differ significantly from monoclinic Zirconia. This phase was indicated as a phase with orthorhombic symmetry [6] ($\text{o}'\text{-ZrO}_2$). Probably

Fig. 1)

Triangular shaped regions are formed at every second end of the twin lamellae in pure, monoclinic Zirconia. The triangles are twinned in a finer manner with smaller triangles at the end. Up to four generations can be observed.

Fig 2)

- a) HREM-micrograph at the tip of a twinned triangle. At every second twin smaller triangles of orthorhombic ZrO_2 can be observed.
- b) Geometric parameters of the fractal microstructure.

this phase is formed during the martensitic transformation $t \rightarrow m$ -ZrO₂ as an intermediate step. In the following chapter a model will be introduced how Zirconia transforms.

Model of Transformation

Above 1150 K Zirconia consists of the tetragonal phase (fig. 3a). By cooling below the M_s -temperature ZrO₂ transforms into the monoclinic phase by a volume expansion of about 6% [2]. Since each part of the material is surrounded by the stiff ZrO₂-matrix (and the melt crucible) rather high internal forces act inside the material introducing a lot of twins. At the end of every other twin boundary either tensile or pressure stress fields are produced. At the later ones the orthorhombic phase occurs (fig. 3c), which is probably a high pressure phase compensating the internal pressure stress partly. At the tensile stress regions cracks can be observed.

Fig. 3)

During cooling Zirconia transforms at 1150 K from the tetragonal phase (a) to the monoclinic phase introducing twin lamellae (b) and triangular shaped regions of the orthorhombic phase (c), which continues to transform by further cooling (d,e) into the fractal microstructure.

By further cooling the orthorhombic phase transforms into small twins of $m\text{-ZrO}_2$. This transformation may be compared with the martensitic transformation in the Fe-Ni-Al-alloys. The resulting smaller triangles of the $o'\text{-ZrO}_2$ transform during a following step into monoclinic twins also (fig. 3e). Up to four generations were observed as can be seen in fig. 1. Several selfsimilar triangles with twin boundaries are inserted into each other. This arrangement of twin boundaries in a triangular shape is described by a geometrical model in the following chapter.

Geometrical Description

The observed microstructure can be described geometrically by a few parameters only. This model is useful for the fractal analysis later. The opening angle of the triangles was found to be nearly constant for both the twinned and the untwinned (orthorhombic) triangles ($\alpha \sim 40^\circ$). The width of the next twin lamellae (b_{v+1}) depends on the length of the previous lamella l_v , where v is counted beginning from the triangle tip. This can be expressed by the equation

$$b_{v+1} = m \cdot l_v, \quad (1).$$

where the factor m was experimentally determined to be $1/4$, unless there are no disturbances due to some irregularities in the twinning. Together with another condition (2) equation (1) can be used as a recursion formula to evaluate equation (3).

$$l_v = 2 \cdot \tan \frac{\alpha}{2} \cdot \sum_{u=1}^v b_u \quad (2).$$

$$l_v = l_0 \cdot c^v \quad (3).$$

$$\text{with } c = 2m \cdot \tan \frac{\alpha}{2} + 1 \quad (4).$$

Equation (3) allows to determine the length of each twin lamellae. l_0 is the length of the smallest twin at the tip of the triangle. Since $c > 1$, equation (3) shows that the length of each twin increases by a small increment until a final length l_n is reached.

For the fractal analysis the volume fraction is needed. The observed microstructure is assumed to be isotropic. Hence, the volume fraction can be calculated simply by adding the area of each small triangle. This area is expressed in fig. 2b by the dotted area. The size of the small triangles has to be introduced as a new parameter. It makes sense to express the (upper) half width of the triangle base line as a part (p) of the twin width (fig. 2b). This allows to calculate the area of a small triangle F_{iv} :

$$F_{iv} = p^2 \cdot b_v^2 \cdot \frac{\cos \alpha + 1}{\sin \alpha \cos \alpha} = F_{i1} c^{2v-2} \quad (5).$$

$$\text{with } F_{i1} = p^2 \cdot m^2 \cdot l_0^2 \frac{\cos \alpha + 1}{\sin \alpha \cos \alpha} \quad (6);$$

where F_{i1} is the area of the first triangle near the tip of the big triangle. The big triangle has the area

$$F_0 = F_{up} \cdot c^{2n} \quad (7).$$

$$\text{with } F_{up} = \frac{l_0^2}{4 \tan^2 \frac{\alpha}{2}} \quad (8).$$

where F_{up} is the area of the already transformed triangle at the tip of the big triangle. Hence, the amount of the orthorhombic phase s at all twins in a specimen ($n \rightarrow \infty$) results from forming the limit:

$$s = \frac{F_1}{F_0} = \lim_{n \rightarrow \infty} \frac{\sum_{v=1}^{n-1} F_{1v}}{F_0} = \frac{F_{11}}{F_{up}} \cdot \frac{2-c^2}{c^2(c^2-1)} < 1 \quad (9).$$

The serie can be transformed to the geometric serie with a finite limit. The observations showed that the limit has to be smaller than 1 otherwise the parameters α , m , p were measured in the wrong way. Especially the parameter p should be estimated carefully because it effects s quadratically.

The volume fraction of the original phase should decrease after one fragmentation ($x=1$) in the same manner:

$$\frac{V_{x+1}}{V_0} = s \quad (10).$$

From the micrographs the parameters α , m , p can be obtained by averaging over different triangles. In table 1) the parameters of the martensitic microstructure for $m\text{-ZrO}_2$ are shown. The Fe-31.4Ni-4.2Al(wt%) -alloy has the same geometry and was analysed as well from figure 4 in reference [3] for comparision.

Parameter	α	m	p	c	s (calc.)	s (exp.)
ZrO ₂	40°	1/4	0.5	1.1819	0.613	?
Fe-Ni-Al-alloy	22°	1/7	0.96	1.0555	0.566	9/16 = 0.5625

Table 1)

Geometric parameters of fractal microstructures.

For the Fe-Ni-Al-alloy the volume fraction $V_{x+1}/V_0 = s$ was also measured experimentally. This value fits quiet well to the calculated s from the geometric model in this paper. Since the experimental measurement of the volume fraction is rather difficult, the geometric model gives a possibility for easy determination.

Fractal analysis

The fractal theory was first developed in the streology [7]. A measured line length l_x increases if the resolution limit ϵ_x decreases:

$$l_x = l_0 \cdot \epsilon_x^{1-D} = l_0 \cdot (N \cdot n)^{-D} = l_0 \cdot N^D \cdot \epsilon_x \quad (11).$$

with

$$D = -\frac{\log N}{\log n} \quad (12).$$

D is the fractal dimension and may be experimentally determined from the fractal plot ($\log l_x$ vs. $\log \epsilon_x$) using (11). On the other hand D can be calculated by (12) from a fractal model. There fractal structures are composed by one fractal motif which appears, reduced in size, x times repeated (s. fig 1) in ref. [3]). The fractal motif consists of N segments of the same length $l_0 \cdot n$.

The fractal theory for two- or three-dimensional objects has still to be developed. The example of the martensitic microstructure of Zirconia as shown in this paper is clearly a fractal microstructure. During each generation of transformation x the volume fraction of the original phase decreases:

$$V_x = V_0 \cdot s^x = V_0 \cdot (N \cdot n)^x \quad (13).$$

compared to eq. (11) $s = Nn$ is found. That means the product Nn can be estimated from the experiment but not n or N alone, which would be needed to calculate the fractal dimension. The calculation of the fractal dimension would allow to characterize different types of martensitic transformations.

Discussion

It was shown that the microstructure of martensitic transformed ZrO_2 has fractal character. By further cooling below the M_s -temperature the amount of the original phase residual phase decrease. In the model the generation number x is related to the temperature, while s should not depend on the temperature. This implies that the angle α , m and p are temperature independent, as can be seen from the micrographs. In all generations the same values were measured. In contrast to this external stress fields might effect p .

In the opposite direction, however, for long-time annealing a few degree below the A_s -temperature the fractal microstructure will be destroyed, because fast diffusion processes will minimize the interfacial energy.

The fractal analysis is mainly a mathematical description. A physical meaning arises, if both the original and the transformed phase show significant differences in some properties. In this case the temperature dependence of the particular property, which is related to the volume fraction of the two phases, can be predicted in a easy way.

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