

TEXTURES OF PHASES IN $Al_2O_3 - ZrO_2 (Y_2O_3)$ EUTECTIC COMPOSITES

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Crystallographic textures of phases in eutectics $Al_2O_3 + ZrO_2 (Y_2O_3)$ were investigated by means of X-ray diffraction. In all studied eutectic polycrystals (grown from the melt by EFG technique) a preferred orientation [0001] of Al_2O_3 along the growth direction in all the samples was revealed for both initial orientations of Al_2O_3 seeding crystal: $\langle 0001 \rangle$ and $\langle 1011 \rangle$. For a cubic ZrO_2 there were two types of a preferred orientations: sharp ones, close to $\langle 123 \rangle$ with a 6-fold symmetry and more spread $\langle 110 \rangle$. Such a 6-fold symmetry for a cubic phase appears in eutectic due to a joint crystallization.

KEY WORDS: Directional crystallization, macroscopic symmetry, eutectic, alumina, zirconia.

INTRODUCTION

Directional solidification of eutectic composites is of a great interest since it allows to obtain highly anisotropic multiphase structures with regularly arranged components. Such materials are attractive because of their properties but up to date many features of eutectic crystallization and the resulting structures are not clear.

"Crystals" of $Al_2O_3 - ZrO_2 (Y_2O_3)$ eutectics are of an interest first of all because of their high-temperature mechanical properties and corrosion resistance.

In the present investigation the crystallographic texture of a directionally crystallized $Al_2O_3 - ZrO_2 (Y_2O_3)$ eutectics is studied.

EXPERIMENTAL PROCEDURE

Powders of pure (99.9%) Al_2O_3 ; ZrO_2 ; Y_2O_3 ; were dried, weighted (52.9%, 42.7% and 4.4%, respectively) and mixed. Compacted pellets were melted in a molybdenum crucible in vacuum. The rate of directional solidification by EFG (edge-defined film-fed growth) was about 40 mm/h. Seed crystals in these experiments were sapphire single crystals of $\langle 0001 \rangle$ or $\langle 1011 \rangle$ direction along growth direction.

Rods 6 mm in diameter and up to 200 mm in length were obtained. Samples were sectioned and polished at 25, 100 and 200 mm from the seeding crystal. The structure was investigated with the help of SEM and light microscopy. Textures were measured at a computer controlled diffractometer with monochromatised MoK_α radiation. Angular steps of 3 and 5 degrees were used both for φ and ϑ .

PHASES AND STRUCTURES

Only two phases - Al_2O_3 and cubic $ZrO_2(Y_2O_3)$ - were found in all investigated samples and a presence of well defined texture was clear from the diffraction data.

Phases are well defined (Figure 1, ZrO_2 looks white) and 48–58% of the volume are phases in eutectic colonies. Crystallites dimensions are about $1 \times 10 \mu m$ of $ZrO_2(Y_2O_3)$ in eutectic colonies with an average dimensions of these colonies about $60 \times 100 \mu m$. Both phases are aligned in the direction of growth, Al_2O_3 crystallites being often connected with each other forming a binding matrix for eutectic colonies. This colony structure corresponds to a steady-state process and does not change with changing of seed crystal orientation. The presence of ZrO_2 crystalites in two different forms (whiskers in colonies and almost isometrical in intercolony space) is connected with the amount of yttria [1]. It may be assumed that solidification in this case proceeds in two stages: at the first one eutectic colonies consisting of zirconia whiskers in the alumina matrix are formed from the melt similar to primary crystal formation and at the second stage solidification of the melt in the intercolony space occurs resulting in the isometrical form of coarse zirconia crystallites in the binding alumina matrix. Besides, the difference in yttria content in zirconia crystallites inside the colonies and within them confirms the two stage model of crystallization.

TEXTURE INVESTIGATIONS

A 2 mm slit before a counter used in a present experiments permits to resolve a distance between diffraction peaks about 0.65° . Measurements with a slit 0.25 mm have shown, that peaks $\{111\} - 13.74^\circ$; $\{200\} - 15.98^\circ$; $\{220\} - 22.51^\circ$; $\{311\} - 26.48^\circ$ for ZrO_2 and $\{0112\} - 11.71^\circ$; $\{1120\} - 17.15^\circ$; $\{1123\} - 19.59^\circ$; $\{0224\} - 23.53^\circ$; $\{1126\} - 25.59^\circ$; $\{0118\} - 27.15^\circ$ for Al_2O_3 may be well resolved in our investigation (Figure 2).

Defocusing was estimated in a powder sample, but due to the small diameter of the sample and not ideal adjustment of the sample position under X-ray beam these data were not too reliable. After defocusing and background corrections only peaks positions on pole figures (PF) were well defined within angular step accuracy, errors of their intensity could be about 20–50%, or even more for a larger ϑ . For our purposes we have used only levels on PF in 0.1, 0.3, 0.5 etc. of a maximum corrected intensity for a given PF. The size of the irradiated region on a sample was about 3×5 mm, depending on the diffraction and tilting angles, therefore exposure time was 2.5 seconds in every point of a PF, diffraction from dozens of thousands of eutectic crystallites was measured.

In all samples in this investigation, for Al_2O_3 a main texture component was an orientation (Figure 3) close to $[0001]$ aligned to the growth direction (GD). In the case of a seed crystal with the same orientation this may be regarded as an inheritance of the orientation of a seed crystal by the alumina phase. But for $[1011]$ seeding crystals we also found the same orientation of the alumina phase already at a distance of 25 mm from the seed crystal and it was the same on all other samples. Therefore, this preferential orientation is stable for Al_2O_3 in eutectics obtained in our process of directional crystallization and is independent of the seed orientation. The character of corresponding peaks is similar to that from a single crystal, showing a good perfection of the matrix phase in these eutectic samples.

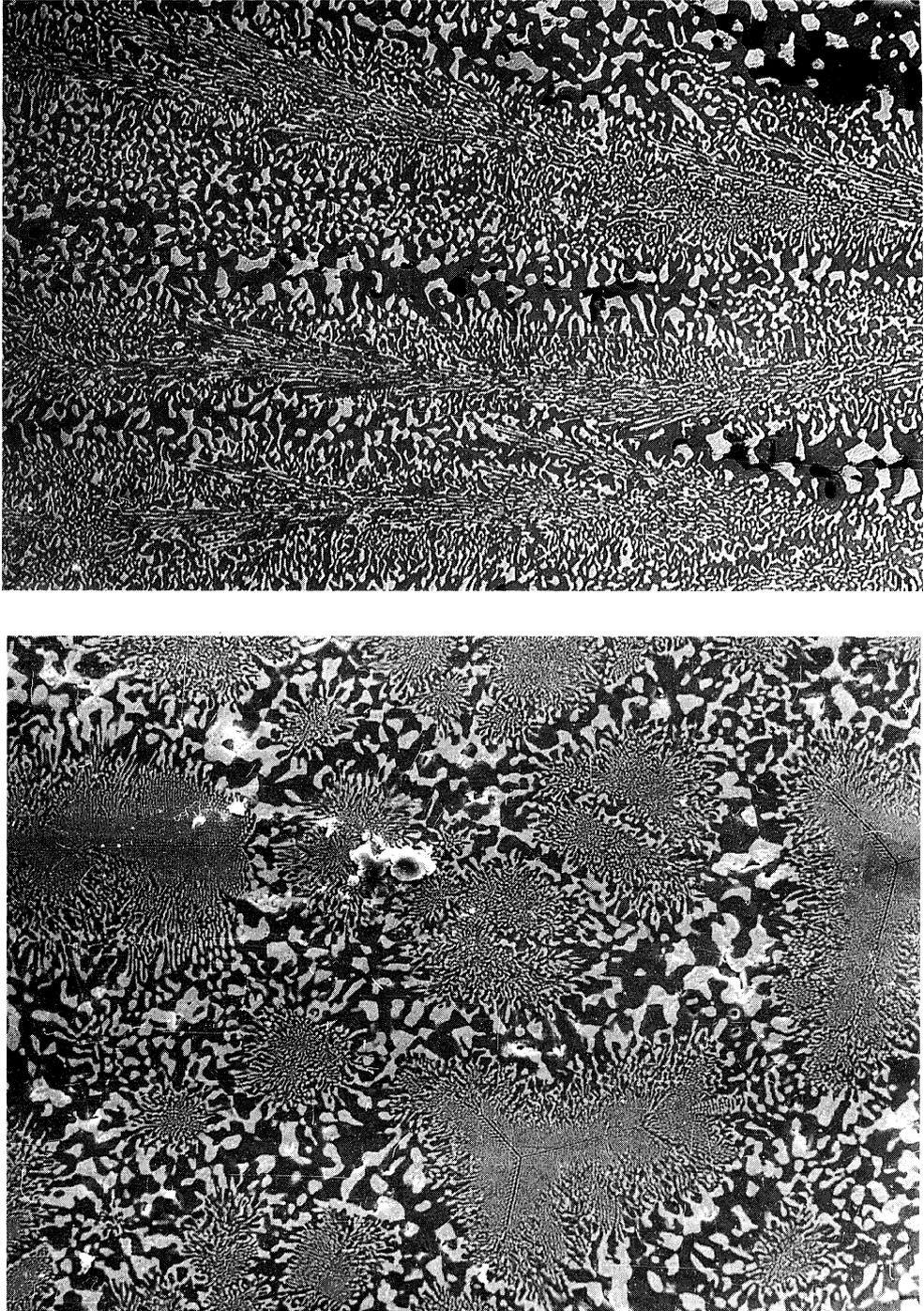


Figure 1 Longitudinal (a) and transverse (b) sections of a sample, x200.

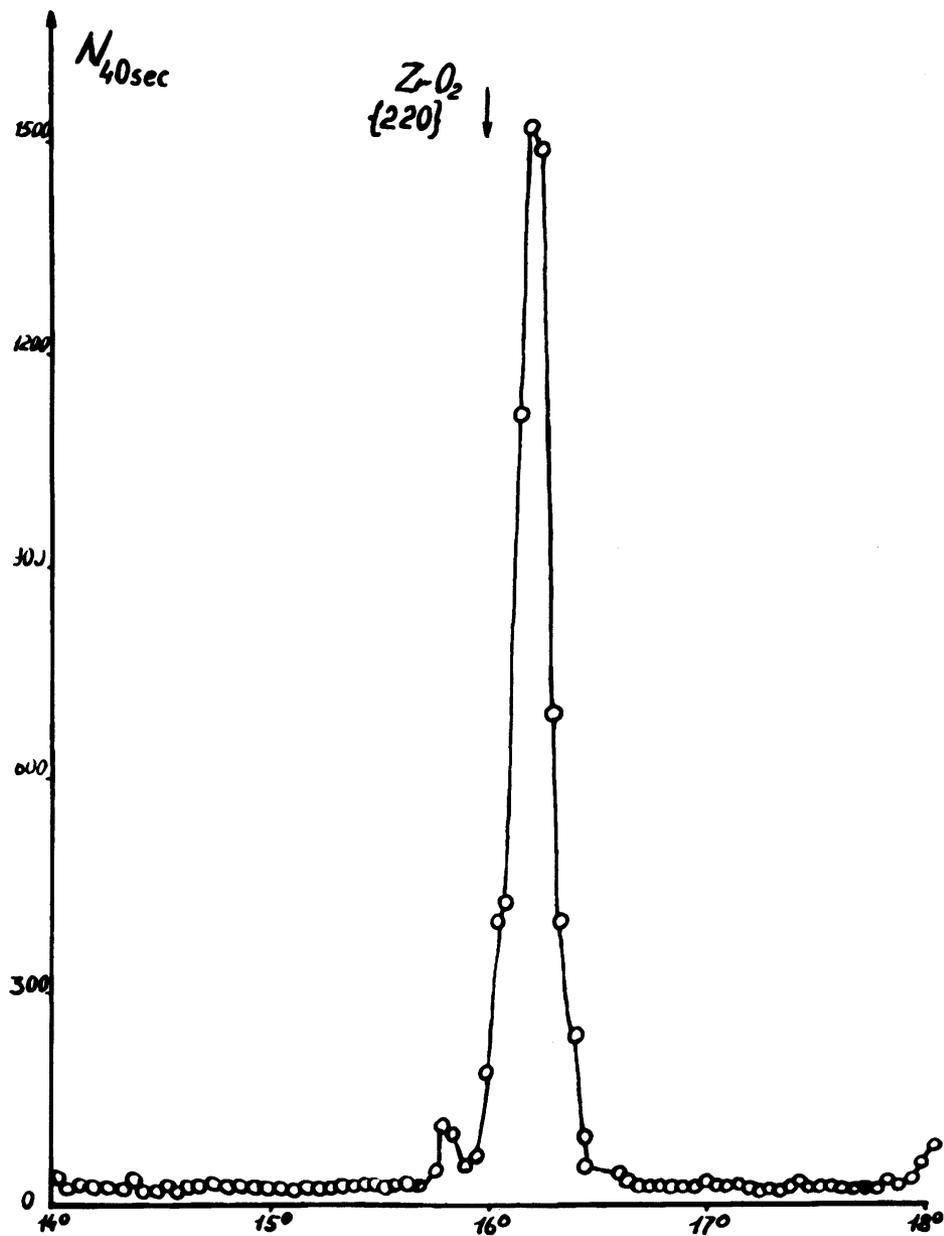


Figure 2 Vicinities of a diffraction peak of $\{200\} ZrO_2$ corresponding to a maximum on the pole figure, tilting angle of the texture goniometer $\vartheta = 35^\circ$.

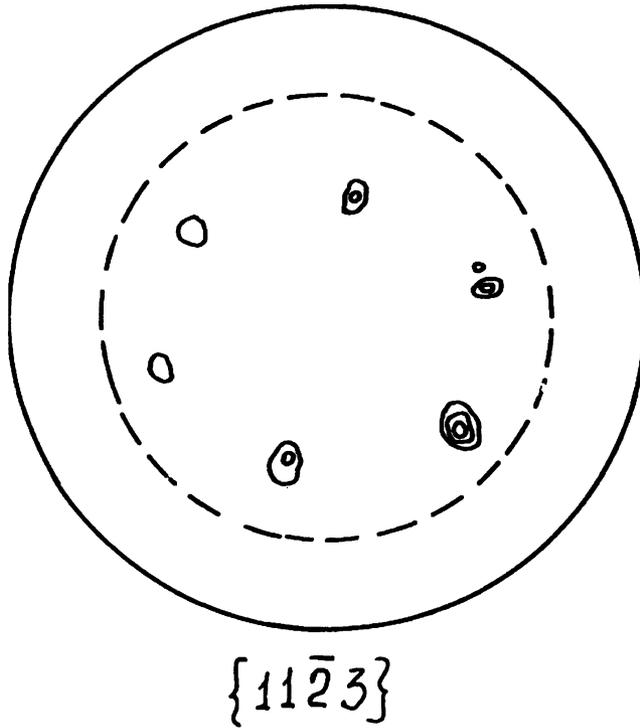


Figure 3 Pole figure $\{11\bar{2}3\}$ of Al_2O_3 , levels corresponding to 0.1, 0.3 and 0.5 of the maximum corrected intensity for a given pole figure are drawn.

On $\{200\}$ PF for ZrO_2 (Figure 4) one can see an evident presence of six-fold symmetry in the arrangement of peaks. These peaks alternate through 60° at the circles $\vartheta = 35^\circ$ and $\vartheta = 55^\circ$ degrees on PF. Such an arrangement of peaks was found for all investigated samples.

It was a possibility to “suspect” that such a surprising symmetry of PF for ZrO_2 was caused by superposition of Al_2O_3 diffraction peaks. To clear this question we have measured the intensity near the peak with $\vartheta = 35^\circ$ on the $\{200\}$ PF (Figure 2). A little discrepancy in the position of the peak and ASTM data was due to tilting of the texture goniometer at 35° and to the presence of Y_2O_3 in the stabilized cubic phase. Also the nearest peak of $\{1120\}$ Al_2O_3 must be located near $\vartheta = 90^\circ$ because Al_2O_3 has $[0001]$ orientation.

In the Figure 5 only the positions of local extremums on the experimental PF $\{111\}$, $\{200\}$ and $\{220\}$ of the ZrO_2 phase are indicated and the presence of six-fold symmetry is evident from all the PF. All peaks are distinctly positioned on circles $\vartheta = \text{const}$. There are 3 such circles within an area $\vartheta \leq 65^\circ$ for $\{111\}$ PF, 2 for $\{200\}$ and 4 for $\{220\}$. Because of the fact that all these PF correspond to axes of symmetry in a cubic crystal, one can conclude that in our case ZrO_2 is oriented with $\langle uvw \rangle \parallel GD$ with $u \neq v \neq w$.

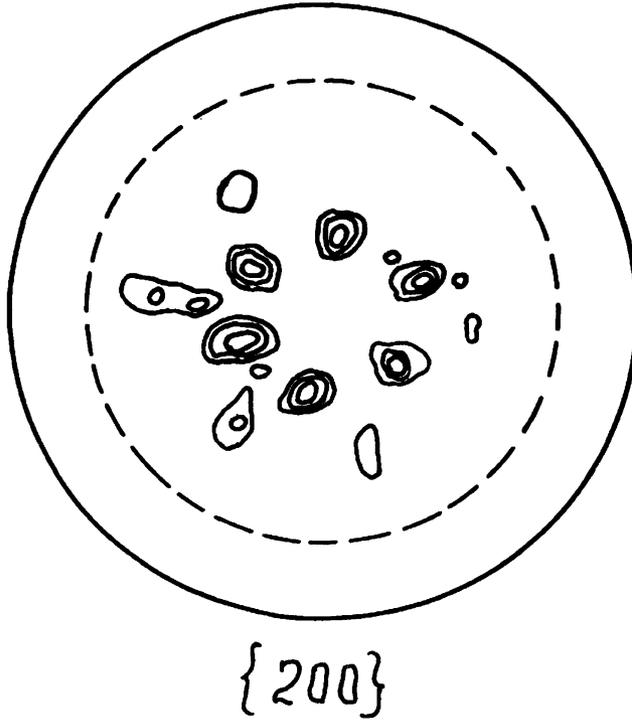


Figure 4 Pole figure $\{200\}$ of the ZrO_2 phase in eutectic, levels 0.07, 0.14 and 0.21 of the maximum corrected intensity for a given pole figure are drawn.

Indexes $\langle uvw \rangle$ of such directions were obtained by the following procedure. Starting from $\langle 123 \rangle$ direction we have calculated the sum of discrepancies S_{hkl}^2 for every PF $\{hkl\}$ as follows:

$$S_{hkl}^2 = \sum_{n=1}^k (\vartheta_{cal} - \vartheta_{exp})^2$$

where ϑ_{cal} and ϑ_{exp} are calculated and experimental values of ϑ for peaks on PF $\{hkl\}$. Then the sum S^2 was calculated:

$$S^2 = S_{111}^2 + S_{200}^2 + S_{220}^2$$

After a simple procedure it was established, that the best fit with experimental data corresponds to $\langle 123 \rangle \parallel GD$. After this it wasn't difficult to determine a direction in ZrO_2 parallel to $[1120]$ direction in Al_2O_3 because both phases were investigated without changing initial sample orientation.

Possible orientation relations between phases are: $[123] \parallel [0001]$; $[153] \parallel [1010]$; $[0110]$; $[1100]$; $[1010]$; $[0110]$ and $[1100]$; $[301] \parallel [1120]$; $[1210]$; $[2110]$; $[1120]$; $[1210]$ and $[2110]$. For ZrO_2 there are 3 indexes and for Al_2O_3 —4.

With the help of these relations peak positions for $\{111\}$; $\{200\}$ and $\{220\}$ PF of zirconia were calculated. As it is clear from Figure 5, positions of peaks are quite similar to that for all 3 experimental PF, average error may be estimated as 7° .

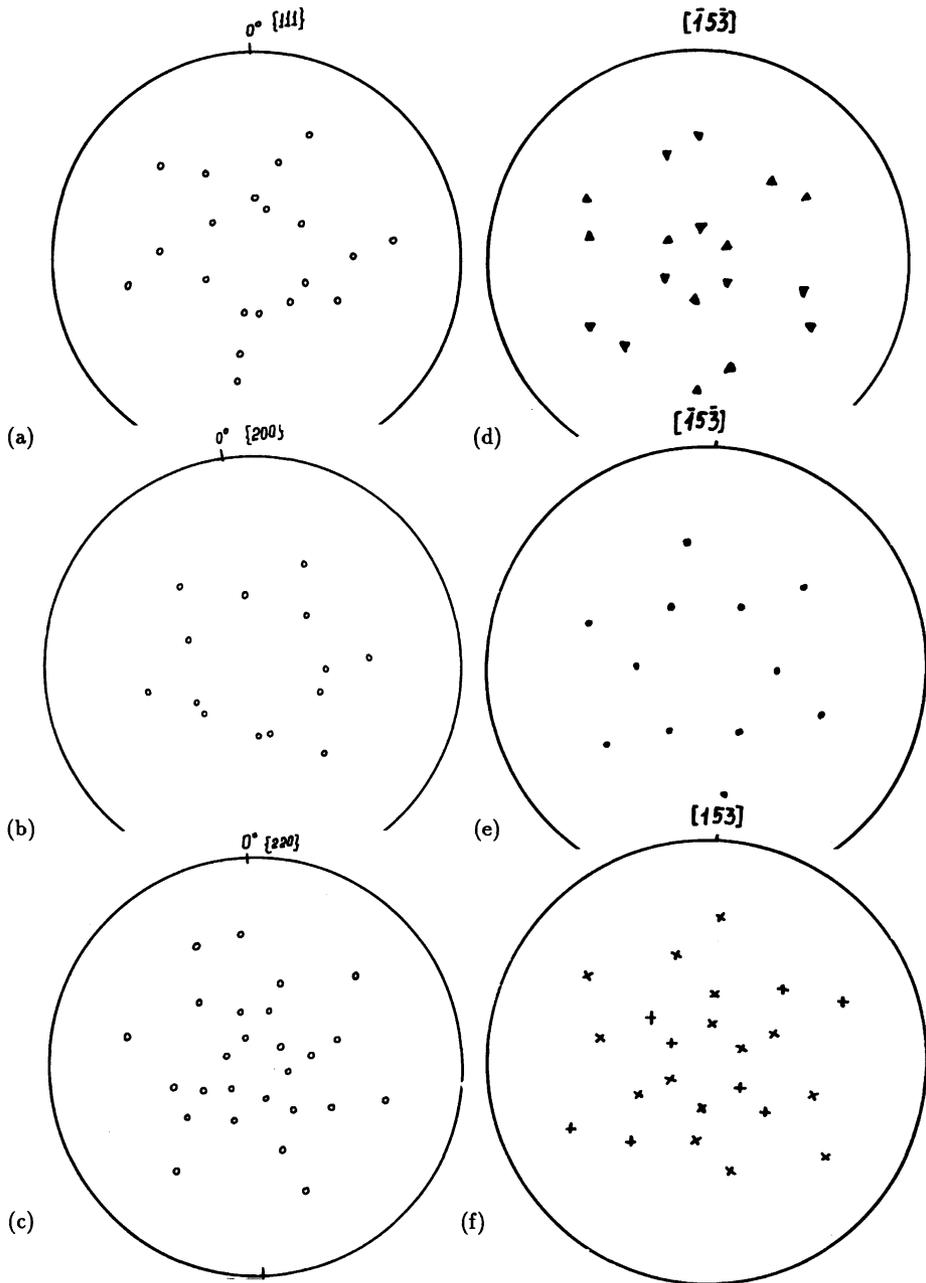


Figure 5 Experimental (a,b,c) and calculated (d,e,f) positions of maximums on a pole figure {111} (a,d), {200}(b,e), {220}(c,f) for the ZrO_2 phase.

The six-fold macroscopic symmetry in the texture of zirconia was forming during the eutectic solidification process under the influence of alumina which was the first phase to nucleate and which controls the solidification of ZrO_2 . The leading role of alumina was established earlier, [2]. The results of the present investigation show that the nucleating phase can determine the texture symmetry of the second phase. Therefore, by analyzing the phase symmetry, one can find what particular phase is the nucleating one in the case that the eutectic comprises phases of the different of crystallographic symmetry.

Also the presence of broad and weaker (about 10 times) peaks was found for both phases. These peaks for zirconia are more significant and they corresponds to $\langle 110 \rangle$ || GD. The intensity of these peaks increases from the seed to the end of the eutectic rods. It is noteworthy that, $\langle 1011 \rangle$ seed crystal orientation strongly affects the intensity of the broad peaks for zirconia in a sample cut from the beginning of the crystal.

The presence of two types of ZrO_2 preferred orientations can be related to the duplex eutectic structure of this phase. Sharp six-fold symmetry peaks can be attributed to the whiskers in colonies, whereas broad peaks can be attributed to the coarse crystallites in intercolony space. In order to prove this fact a local orientation technique must be used.

References

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