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ORIENTATIONAL BONDING OF PHASES ACCOMPANYING DIRECTED CRYSTALLIZATION OF THE EUTECTIC OF THE SYSTEM $Si-TiSi_2$

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The characteristic features of structure formation in cast and direct crystallized alloys of the system $Si-TiSi_2$ were studied. It is shown that the predominant orientation of the bonding of the phases in directionally crystallized eutectics (DE) of the system $Si-TiSi_2$, observed at the stage of steady-state growth, already appears on the surface of nucleation, which apparently indicates that the nucleation of the phases in the alloys of this system is of an epitaxial character.

There are a large number of works on the crystallography of conjugate phases in directionally crystallized eutectics (DE) [1, 2]. Their results, however, do not always agree, which is primarily a result of the local nature of the methods of study employed and the fact that only the stage of steady-state growth was analyzed. In [3] the stages of formation of orientational bonding of phases in several metallic DE with a low entropy of melting of the phases were studied by the method of texture diffractometry, which has the advantage that the information is integrated over a large cross-sectional area of the sample. The crystallography of nucleation of DE is in most cases random and the orientational bonding is established in the course of subsequent growth. Epitaxial bonding of phases on the nucleation surface was observed only in DE of the system Al–ξ(AlAg). Directionally crystallized eutectics with a high entropy of melting of the phases ($\Delta S_{melt} > 23$ J/(g·atom·K) [4]), having a tendency toward limitation during growth, have been virtually unstudied in this respect. In this work the formation of orientational bonding of phases in DE of the high-entropy system $Si-TiSi_2$ was studied. The entropies of melting of its phases equal $S^{Si}_{melt} = 27.59$ [5] and $S^{TiSi_2}_{melt} = 33.8$ J/(g·atom·K) [6] (estimated based on the latent heat of fusion), respectively.

MATERIAL AND EXPERIMENTAL PROCEDURE

The experiments were performed on alloys of the system $Si-TiSi_2$ with the eutectic (22% Ti by weight) and hypo- and hypereutectic (1-30% Ti by weight) compositions. The starting materials were titanium and silicon iodide of semiconductor purity. Directed crystallization was achieved following the procedure of [7] on a silicon seed with <111> orientation. A crystallization rate in the range $1.7\text{-}2\cdot10^{-2}$ mm/sec was chosen, while the temperature gradient G on the crystallization front (qualitatively estimated from the angle of growth of the ingot) was varied by varying the magnitude of the overheating of the melt. The microstructure was determined by the procedure of [8] and studied under an MIM-7 microscope. The texture was determined on a DRON-3 diffractometer with a GP-2 attachment in Cu_K radiation with back-and-forth motion of the sample in its own plane. The pole figures for the silicon phase were constructed for both the {220} and {111} reflecting surfaces, whose x-ray intensity is high. Because of the weakness of the reflection from the (040) plane, the normal to which, according to the data of [8] is the axis of growth of $TiSi_2$, the pole figures were

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Fig. 1. Sectoral boundaries in $Si-TiSi_2$.

TABLE 1

d, Å	*hkl*	*d*, Å	*hkl*	*d*, Å	*hkl*
2,967	202	1,386	315	1,19	040
2,292	311	1,359	206	1,084	317
2,131	004	1,307	602	1,071	008
2,082	022	2,239	333	1,020	800
1,824	313	1,221	026		

constructed for the reflecting planes (022) and (313) of $TiSi_2$. As for the slits used in making the pictures, their Bragg angles did not overlap with those of the planes of the lattice of the silicon phase, which was confirmed by additional studies on Si single-crystals.

RESULTS AND DISCUSSION

It is well known that the nucleation of a eutectic colony (grain) in each system of alloys is initiated by one of the phases only — the base phase. Metallographic studies of cast thermally etched alloys of the system $Si-TiSi_2$ with different concentration showed that in all cases the eutectic colonies appear only on crystals of titanium disilicide, which is thus the base phase in the system under study. This is confirmed by the forms of the sectoral boundaries (Fig. 1), determined by the crystal geometry of the base phase, which has an orthorhombic symmetry, and the formation of a ring of a solid solution of titanium in silicon (in what follows, for brevity, called silicon) around the base of $TiSi_2$ crystals. The faceted forms of growth of titanium disilicide, characteristic of phases with a high entropy of melting, are striking in hypereutectic alloys with slow growth rates. This is most often a pyramid with a rhombus at the base. As the rate of crystallization increases (i.e., as the supercooling on the crystallization front increase), the faceted forms of growth of the branches of $TiSi_2$ dendrites and the striking anisotropy of their growth are lost.

The starting section of a directionally crystallized ingot with the eutectic composisition has a typically hypoeutectic structure. Silicon dendrites with a partially faceted form do not have a ring, and the eutectic colonies are not genetically related with them. The length of this section is all the longer, the lower the value of G is. The direction of heat removal and the direction of growth of Si dendrites are not always parallel especially at the start of crystallization. At the steady-state stage of growth the microstructure of DE becomes regular and lamellar and is oriented in the direction of heat outflow. Numerous surfaces of misalignment are observed in the transverse sections. As crystallization proceeds the grains in DE grow larger, but the defectiveness of the structure remains.

The data presented show that the DE studied is a normal eutectic with a regular lamellar structure. There are several criteria for predicting the character of the structure of DE. According to [10] the formation of normal structures in DE with a high entropy of melting of the phases is possible if the ratio of the entropies of melting of the phases $S_\beta/S_\alpha \leq 1.5$. According to [11] the criteria determining the morphology of the eutectic phases under conditions of directed crystallization are their growth characteristics, and double eutectics combined with the forms of growth of free crystals of the phases can be divided into three groups: faceted—faceted, faceted—unfaceted, and unfaceted—unfaceted. An analogous classification was proposed in [9]. Normal regular structures, according to [11], are formed only if both phases grow in an unfaceted fashion. According to [9], however, regular structures can also form in eutectics of the faceted—faceted group (polyhedron—polyhedron), if dendritic growth of one of the phases with a partial transition from faceted to spherical forms of growth can occur.

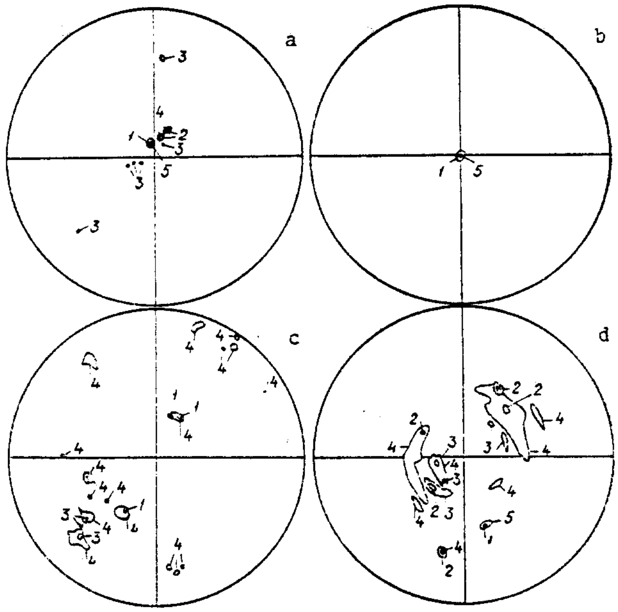

Fig. 2. The pole figures α from 0 to 70° with sections at different distances from the seed: a) 220 – 2 mm, b) 220 – 250 mm, c) 022 – 2 mm, d) 022 – 250 mm. Regions of reflections with intensity (%) (100-80) (1), (80-60) (2), (60-40) (3), (40-20) (4), and (20-10) (5).

The observed faceted forms of growth of the phases as well as the existence of sectoral boundaries indicates that DE of the system Si–$TiSi_2$ are, according to the classification of [9], of the polyhedron–polyhedron type. As the supercooling increases, however, the striking anisotropy of growth vanishes, spherical forms of growth of the branches of $TiSi_2$ dendrites appear, and the DE acquires a classical lamellar structure, which confirms the results of [9, 10] and does not agree with the criterion of [11].

The study of the crystallography of growth was started with a refinement of the information on the crystal lattice of the $TiSi_2$ phase, since the available data of [12] are inconsistent. The powder patterns showed that the indicated phase has an orthorhombic lattice (structural type S54 with constants a = 8.279 Å, b = 4.819 Å, c = 8.568 Å). Table 1 gives the series of interplanar distances, identified with the indicated values of the constants.

Figure 2 shows the pole figures of the phases of DE for different stages of crystallization. At the starting stage of growth the silicon crystals have different orientation. The strongest reflections are concentrated, however, within 10° of the <110> direction. During further growth the silicon is oriented so that the <110> direction becomes parallel to the direction of heat outflow. The pole figures {220}, constructed from sections at the steady-state stage of growth, are distinguished by more intense textural peaks, indicating grain growth. Even at the final stage of crystallization, however, up to 20% of the relative intensity of the {220} Si reflection falls within 4-8° (in different ingots) of the direction of heat outflow.

The $TiSi_2$ phase at the starting stage of growth also contains crystals of all possible orientation, but even for this phase the strongest reflections are concentrated within 10° of the orientation for which the [010] direction is parallel to the direction of heat outflow. This is apparently caused by the curvature of the crystallization front (the crystal grows at an angle of approximately 10°). During the growth the intensity of these reflections increases, indicating that the mechanism of competitive growth of grains is operating, but new strong reflections with different orientation of $TiSi_2$ also appear. The (022) pole figures of $TiSi_2$, obtained at the final stage of growth, confirm the presence of the orientational bonding [010] $TiSi_2 \parallel \langle 110 \rangle$ Si [8], but the reflections are smeared over 25-30°. At the same time grains with a different orientation of $TiSi_2$ are also present at this stage of growth. Thus a multigrain lamellar structure with predominant orientational bonding [010] $TiSi_2 \parallel \langle 110 \rangle$ Si both at the moment of nucleation and at later stages of growth forms in the DE of the system Si–$TiSi_2$. The existence of a predominant bonding of the phases on the nucleation surface and the fact that it is preserved at subsequent stages of growth can be regarded as an indication of epitaxial nucleation of one phase on the other [3] (in the case of silicon crystals on $TiSi_2$ studied here).

As already pointed out, epitaxial nucleation was observed only in metallic eutectics with a low entropy of melting of the phases. According to [9] the high-entropy phases nucleate differently and come into contact in the course of further growth. The data obtained in this work show that epitaxial nucleation is apparently possible also for eutectics with a high entropy of melting of the phases.

CONCLUSIONS

1. Eutectic grains (colonies) in alloys of the system Si–$TiSi_2$ nucleate only on crystals of the $TiSi_2$ phase, which is the base phase for this system. This is confirmed by the form of the sectoral boundaries, which inherit the orthorhombic symmetry of $TiSi_2$, and the appearance of rings of the silicon phase around the base crystals.

2. The predominant bonding [110] Si ‖ [010] $TiSi_2$ in DE of the system Si–$TiSi_2$ already arises on the surface of nucleation, which apparently indicates that the nucleation is of an epitaxial character. Aside from grains with the indicated predominant bonding of the phases both at the stage of nucleation and at the stage of steady-state growth there occur grains with a different orientation of $TiSi_2$. The orientation of the silicon phase at the steady-state stage is the same in all grains.

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