Crystallography of aligned Fe-Al eutectoid

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CRYSTALLOGRAPHY OF ALIGNED Fe–Al EUTECTOID

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By applying the Weissenberg technique to small pieces of duplex crystals of FeAl and FeAl₂, produced by directional eutectoid decomposition, it has been found possible not only to establish the previously unknown unit cell parameters of FeAl₂, but also the orientation relationship between FeAl and FeAl₂. The unit cell of FeAl₂ can be described as an A-centred pseudo-monoclinic cell with $a = 7.594$, $b = 16.886$, $c = 4.863$ Å, $\alpha = 89.55^\circ$, $\beta = 122.62^\circ$ and $\gamma = 90.43^\circ$. The orientation relationship between both phases was found to be: $[100]\text{FeAl}_2 \parallel [\bar{1}11]\text{FeAl}$ and $(002)\text{FeAl}_2 \parallel (01\bar{1})\text{FeAl}$. This relationship was confirmed by texture goniometry of larger directionally decomposed eutectoid samples in which the cubic FeAl phase was frequently found to be twinned.

1. Introduction

Over the past few years the crystallographic relations of in situ grown composites have been of increasing interest. These relations are important for the understanding of nucleation and growth of the composites which affect the morphology and thereby the properties of the resulting material. Most studies on crystallographic relations in in situ composites are concerned with unidirectionally solidified eutectics (Kerr and Lewis [1], and Hogan, Kraft and Lemkey [2]). Crystallographic relationships in aligned eutectoids, however, is a field which has had considerably less attention so far.

Carpay [3] and Rao et al. [4] have investigated the Cu–11.8 wt% Al eutectoid by transmission electron diffraction. A recent contribution to the knowledge in this field has been made by Wolff who investigated a number of eutectoids (Cu–Al, Cu–In, Ni–In, Co–Si, Fe–Al and similar eutectoids modified by the addition of a third element). The crystallographic results of these investigations, which were laid down in a thesis [5], were mainly obtained by a texture goniometric method (Schulz Back Reflection Technique) which allowed the investigation of specimens with an area of 1 mm² up to 50 mm² as compared to transmission electron diffraction in which an area of at most 1 μm^2 can be investigated at a time.

The orientation relationship in the Fe–Al eutec-

toid could not be established up to now due to the fact that the unit cell of the FeAl₂ phase was not known. Such knowledge is a prerequisite for the use of the texture goniometric technique in which standard stereographic projections of the constituent phases are essential.

In the present investigation we succeeded in establishing both the unit cell parameters of the FeAl₂ phase and the crystallographic relationship between FeAl and FeAl₂ by making use of the fact that aligned eutectoid decomposition often produces duplex crystals.

These duplex crystals, which can be regarded as interwoven single crystals of the constituent phases, can easily be submitted to single crystal analysis. In the present case the Weissenberg technique has been used for this purpose.

2. Use of the Weissenberg technique

Once a small piece (a few tenths of a mm) of a duplex crystal is mounted on a goniometer head and aligned along a zone axis it is simple to find the axes of rotation which both phases have in common from a single rotation pattern. Furthermore, information is obtained on how the periodicities along both zone axes match.

On a Weissenberg pattern taken about the same zone axes the complete zones in question are

recorded for both phases at the same time. From such a pattern all further information necessary to establish the full orientation relationship can then be taken.

Not only will such a pattern reveal information about crystallographic planes being parallel (as is the case with texture goniometry), it will at the same time show how parallel planes of both phases fit with respect to their spacings; information that otherwise would have to be gathered from the 2θ position in a diffraction pattern and might prove difficult to obtain if one or both phases have low crystallographic symmetry.

3. Experimental

Fe–Al alloys (metals 99.99% pure) of the desired composition were rf melted in a vacuum of better than 10^{-5} Torr in silimanite crucibles with a zirconia lining. When the alloy had molten, argon was admitted until the pressure was about 130 Torr. After 1 h of homogenization in the molten state a silica tube, which via a valve was connected to a vacuum vessel, was lowered into the melt. By opening this valve the molten alloy was forced into the silica tube by the argon pressure.

After switching off the rf generator, the silica tube containing the solidified alloy was lifted from the melt. In this way bars of eutectoid alloy 8 mm in diameter and about 300 mm in length were produced.

The bars were then submitted to directional solidification followed by directional eutectoid decomposition in a Bridgman apparatus. This apparatus consists of an alumina crucible 10 mm in diameter, containing the sample, placed on a water-cooled brass drive rod. Heating was effected by a SiC resistance heating furnace, whereas the cooling was effected – apart from the water-cooled drive rod – by lowering the crucible through a close fitting water-cooled brass toroid. In order to shield the sample from the furnace after its passing through the cooling toroid, a nickel shield was used which was cooled by the water supply and return tubes of the cooling toroid. In most cases hydrogen was used as a protective atmosphere. Temperature gradients of 250–300°C were obtained, depending on the furnace temperature which could be raised to 1200°C.

4. Results

4.1. Eutectoid decomposition

A first attempt to produce aligned eutectoid decomposition was made with an alloy of exactly the eutectoid composition: Fe–43.0 wt% Al according to fig. 1. Alloys of the same composition have previously been subjected to directional eutectoid decomposition by Livingstone [7] and by Van den Boomgaard et al. [8]. After directional solidification and decomposition at a pulling rate of 75 mm/h we found that the sample had been subject to serious segregation. This segregation caused the last part of the sample to solidify to be Al-rich (hyper-eutectoid). As it is this part of the sample which usually shows the largest grains, it seemed advantageous to start with a hypo-eutectoid composition in order to obtain large eutectoid grains in the last part of the sample. With a composition Fe–42.0 wt% Al we indeed succeeded in producing aligned eutectoid morphology in the last part of the sample.

Longitudinal sections of the bar were examined microscopically. Transverse as well as longitudinal sections were analysed by texture goniometry. Small pieces of well-developed regions in the bar were used for taking rotation and Weissenberg patterns.

4.2. Morphology

The FeAl–FeAl₂ eutectoid – as most eutectoids – has a lamellar morphology (see fig. 2). We already mentioned that during solidification of the alloy, which has no congruent melting point (see fig. 1), it is subject to severe segregation resulting in a change of composition over the length of the sample ranging from hypo-eutectoid through eutectoid to hyper-eutectoid. Both hypo- and hyper-eutectoid compositions show dendrites of FeAl and FeAl₂, respectively.

Between the eutectoid and the hyper-eutectoid dendritic region we observed a region of duplex cellular morphology (fig. 3). Apparently deviation of the eutectoid composition caused this duplex cellular morphology prior to the formation of FeAl₂ dendrites.

Examination of the duplex cellular region by texture goniometry showed that here, just as in the Cu–31.9 wt% In–4 wt% Ni eutectoid previously

Fig. 1. Fe–Al equilibrium diagram according to Hansen [6].

studied by one of the authors (Wolff [5]), the duplex cellular morphology did not affect the crystallographic relationship of the phases.

Although lengthwise the directionally decomposed eutectoid samples did not show any zigzag morphology like we found in many other eutectoids (Wolff [5]) the cubic FeAl phase was found to be twinned. Due to a slight carbon contamination of the iron used

for the sample preparation, some Al_4C_3 was formed. This carbide which incidentally also showed up in the directionally decomposed FeAl–FeAl₂ eutectoid samples of Livingston [7] apparently does not affect the morphology of the eutectoid. By reaction with water from the laboratory atmosphere, however, it causes a gradual disintegration of the samples through the formation of $\text{Al}(\text{OH})_3$ and CH_4 .

Fig. 3. Cell boundary of a directionally decomposed duplex cellular Fe–Al eutectoid (longitudinal section).

4.3. Unit cell of FeAl_2

Small pieces of duplex single crystals were used for taking rotation patterns about various prominent zone axes. As the diffraction pattern of FeAl (cubic, $a_0 = 2.9086 \text{ \AA}$ for the Al-rich end of the phase field according to Bradley and Jay [9]) is far less complicated than that of FeAl_2 it was rather easy to assign the recorded diffraction spots to the proper phase.

From the information obtained from the rotation patterns of five zone axes (afterwards indexed as $[100]$, $[101]$, $[001]$, $[011]$ and $[010]$) a preliminary unit cell was chosen for FeAl_2 : an A-face centred pseudo-monoclinic cell.

Fig. 2. (a) Longitudinal section of a directionally decomposed Fe–Al eutectoid (growth direction vertical). (b) Transverse section: deviating lamellar orientation indicates twinning of the FeAl phase; also note Al_4C_3 precipitates (arrow).

Weissenberg patterns of the various zones were used to obtain preliminary cell dimensions. These preliminary data were then used to index diffractometer recordings of FeAl₂ powders from which in turn refined unit cell data were calculated. This resulted in the following data:

$$a = 7.594 \text{ \AA}, \quad b = 16.886 \text{ \AA}, \quad c = 4.862 \text{ \AA}, \\ \alpha = 89.55^\circ, \quad \beta = 122.62^\circ, \quad \gamma = 90.43^\circ,$$

systematic extinction for $k + l \neq 2n$.

The pseudo-monoclinic character of the unit cell is clearly expressed by the values of α and γ which are very close to 90° . Of course, the rather large pseudo-monoclinic cell can be transformed into a smaller triclinic one taking the original [100], [011] and [001] unit cell translations as the new axes but in view of the FeAl/FeAl₂ orientation relationship described below, it is advantageous to maintain the larger pseudo-monoclinic cell.

Table 1 gives the first 30 diffraction lines which

Table 1
List of the first 30 diffraction lines in a powder diffractogram of FeAl₂

<i>d</i> (Å)	<i>hkl</i>	<i>I</i> _a	<i>d</i> (Å)	<i>hkl</i>	<i>I</i> _a
8.492	020	VW	2.789	111	
6.422	100	W		1-11	W
5.125	-120	VW	2.760	-1-51	MW
			2.564	-240	VW
4.667	-111	S	2.529	131	W
	-1-11			1-31	
4.228	040	MS			
3.994	011	MS	2.505	-311	VW
	0-11	MW		-3-11	
3.683	-131	W	2.497	-251	VW
3.653	-1-31	MS	2.469	-2-51	VW
3.582	-211	MS	2.416	-202	MS
	-2-11		2.330	-222	VW
3.531	140	MS	2.319	-2-22	W
	-140			-331	
3.325	031	MS	2.263	-1-22	W
3.311	0-31	W	2.179	-302	VW
3.205	200	W	2.170	151	W
				1-51	
				-171	
3.074	-231	W			
2.997	-220	VW	2.121	-260	M
2.821	060	VW			

a Intensity sequence: S > MS > M > MW > W > VW.

were recorded in a powder diffractogram of the FeAl₂ phase. After these lines a group of very strong reflections occur which to a great extent overlap each other.

4.4. Orientation relationship FeAl/FeAl₂

The Weissenberg technique has proved to be a very successful means to establish orientation relationships. During indexing of the rotation and Weissenberg patterns taken about the various zone axes of FeAl₂ in duplex crystals frequently diffraction spots of FeAl were observed between those of FeAl₂. From these diffraction patterns it is easy to deduce about which zone axis the FeAl crystal has been rotated. Furthermore, the rotation patterns yield information about the fitting of the two lattices in the directions of the zone axes about which rotation has taken place. In this way four sets of coincident crystallographic directions have been established. These are given in table 2 together with the periodicities along these directions.

The fitting of the two lattices in the directions of the coinciding zone axes is clearly expressed by the values for the periodicities. These indicate that, e.g. for the rotation pattern taken about [100]FeAl₂ the second layer line of FeAl coincides with the third one of FeAl₂. Likewise, in the rotation pattern taken about [001]FeAl₂, the second layer line of FeAl coincides with the first one of FeAl₂. Notably in the case of rotation about [101]FeAl₂ all layer lines were found to coincide with those of FeAl. Rotation about [010]FeAl₂, however, yields no coinciding layer lines at all. The complete orientation relationship is

Table 2
Relationship between crystallographic directions of FeAl₂ and FeAl

FeAl ₂		FeAl	
Direction	Periodicity (Å)	Direction	Periodicity (Å)
[100]	7.594	// $[\bar{1}11]$	5.038
[001]	4.863	// $[11\bar{3}]$	9.647
[101]	6.442	// $[\bar{1}20]$	6.504
[010]	16.886	// $[211]$	7.124

Fig. 4. Weissenberg pattern of the zero layer of $[100]$ FeAl_2 . $\text{CoK}\alpha$ radiation, Fe filter. The positions of the FeAl reflections have been indicated by arrows.

demonstrated in fig. 4 which shows the Weissenberg pattern of the zero layer taken about $[100]$ FeAl_2 . The FeAl diffraction spots are clearly visible in this photograph. The reciprocal lattice (fig. 5) constructed from the data of this photograph convincingly shows the excellent fit of the $[100]$ zone of FeAl_2 on the $[\bar{1}11]$ zone of FeAl.

Fig. 5. Zero layer reciprocal lattice of FeAl_2 (rotated about $[100]$) and FeAl (rotated about $[\bar{1}11]$). The size of the dots is a measure for the intensities of the reflections in the case of FeAl_2 .

Fig. 6. Relation between the crystallographic axes (a , b and c) of FeAl_2 and the cubic unit cell of FeAl. The indices refer to the directions within the cubic unit cell. See also table 2.

Note how excellent the sixfold $\{110\}$ and $\{211\}$ planes of FeAl are accommodated by the various planes in FeAl_2 . The pseudo-monoclinic character of FeAl_2 is expressed by the fact that the reciprocal lattice is almost mirrored across b^* and c^* . Some reflections, however, do not come back across the pseudo-mirror plane while others do but with different intensity.

Fig. 6 shows how the directions of the crystallographic axes of FeAl_2 fit into the cubic unit cell of FeAl. A comparison of the angles between the relevant directions in both cases yields the following results:

angle between

$$[11\bar{3}] \text{ and } [211] \text{ is } 90^\circ, \quad \alpha = 89.55^\circ;$$

$$[\bar{1}11] \text{ and } [11\bar{3}] \text{ is } 121.5^\circ, \quad \beta = 122.62^\circ;$$

$$[\bar{1}11] \text{ and } [211] \text{ is } 90^\circ, \quad \gamma = 90.43^\circ.$$

These data also serve to demonstrate how well both lattices match.

Fig. 7, in which the results of Weissenberg photographs taken about the four prominent zone axes of FeAl_2 (see table 2) have been incorporated, gives a survey of the crystallographic relationship between

Fig. 7. Stereographic projection of FeAl_2 and FeAl showing the four coincident zones mentioned in table 2. In addition the positions of the $(\bar{3}91)$ and (351) planes of FeAl_2 , which coincide with (100) and (010) of FeAl , have been drawn.

FeAl_2 and FeAl in stereographic projection. A computer program has been developed by one of the authors (J.W.G.A. Vrolijk) to generate these projections.

It must be mentioned at this point that in some cases, notably the $[101]$ zone axis of FeAl_2 , evidence was found for the twinning of the FeAl phase. This twinning, which invariably occurs on the $(\bar{1}11)$ plane of FeAl , manifests itself by a reflection of the FeAl poles across the trace of the $(\bar{1}11)$ plane (north-south direction through the centre of the stereographic projection in fig. 7). That twinning is not always observed is probably due to the fact that for the Weissenberg technique small-sized (a few tenths of a mm) specimens are used and that apparently in most cases each twin component extends over a larger volume than is investigated by the Weissenberg technique. In the case of texture goniometry, in which much larger portions of the sample are investigated at a time, twinning was observed quite frequently.

4.5. Interface plane

The position of the interface plane was determined by a simple trace analysis of a sample that was sec-

tioned both longitudinally and transversely. By the analysis of a section at the beginning of aligned eutectoid growth we followed a grain which, at the bottom part of the sample, was poorly aligned with the macroscopic growth direction. In fact, the lamellar interface deviated 16° from the direction of the temperature gradient. Nevertheless after only 5 mm of eutectoid growth the same grain showed a perfect alignment of the lamellae with the temperature gradient.

Analysis of a longitudinal section of this part of the sample by texture goniometry showed the same sharp orientation relation between both phases in the grain previously found by both Weissenberg technique and texture goniometry. This implicated that although the interface position did change markedly over 5 mm of sample length the crystallographic orientation did *not*. In view of these results and the previously mentioned duplex cellular morphology which did not affect the crystallography either, it was hardly surprising that we did not find a correlation between the interface position and the crystallography: The position of the interface did not correspond to any low indices plane of either FeAl or FeAl_2 .

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