

SHORT NOTE

FIVEFOLD SYMMETRY IN REAL AND RECIPROCAL SPACES

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Tetrahedrally close-packed structures with juxtaposed pentagonal antiprisms, such as the μ , C14 Laves and the newly found C phases, were studied by means of HREM and SAD. It was found that each bright spot in the structural image corresponds to an antiprism. Differently oriented domains of these phases intergrow frequently with a fairly good match at the interphase boundary. All diffraction patterns of these phases show a fivefold distribution of spot-pairs, and it is shown that this fivefold symmetry comes from the pentagons and spot-pairs from two pentagonal prisms superposed in antisymmetrical positions.

1. Introduction

In the course of a systematic study of the tetrahedrally close-packed (tcp) structures with juxtaposed pentagonal antiprisms by means of high resolution electron microscopy (HREM) and selected area diffraction (SAD), two phenomena of crystallographic interest hitherto unnoticed have been encountered. The first one is the mosaic nature of such tcp phases and very complex domain structures which have been observed by HREM (see fig. 3). This has been reported in a series of publications [1–3]. The second one is the fivefold distribution of diffraction spots in the electron diffraction pattern (EDP) of these phases (see fig. 4). Moreover, these two phenomena seem to be closely related, and it was found that the more faulty the structure, the more obvious is the fivefold symmetry of the EDP. In the present note, the result of a study of this fivefold symmetry of diffraction spots in relation to the assembly of pentagonal antiprisms in heavily faulted tcp phases will be reported.

In superalloys containing Mo and/or W, such tcp phases with juxtaposed pentagonal antiprisms as the C14 Laves, μ and the newly found C [2,4] phases occur in general after long heating at high temperatures. Crystallinities of these phases were extracted electrolytically from some superalloys

(for experimental details, see refs. [1–3]). They were then collected on holey carbon films and examined in a JEOL 200CX electron microscope equipped with high resolution pole pieces. The minimum area selected for SAD is about $0.2 \times 0.2 \mu\text{m}$. Image simulation was carried out using the multislice programme written by Ishizuka [5].

2. Tetrahedrally close-packed structures with juxtaposed pentagonal antiprisms

Fig. 1 is the (110) projection of the structure model of the C14 Laves phase with two nonbasal faults. Both perfect and faulty regions consist of pentagon–triangle sheet at height of 0 and $\frac{1}{2}$ (pentagons superposed antisymmetrically) as the primary or main layers. The atoms at $\pm \frac{1}{4}$ are located inside the pentagonal antiprisms forming the secondary layers. At the $(1\bar{1}\bar{1})$ domain boundary a single slab of the μ structure is formed, which, together with the C14 Laves structure on both sides of it, forms a narrow slab of the C phase. This new C phase can also form at the $(1\bar{1}0)$ domain boundary but it has a different orientation [2]. In the case of the μ phase, a narrow slab of the C14 Laves or C phase can also occur at the $(\bar{1}11)_{\mu}$ domain boundary [3]. These intergrown structures have two most prominent features. First, the match

at the interphase boundary is good, and this explains why these phases can intergrow easily. Second, the pentagonal antiprisms in these phases including the interphase boundaries all have the same orientation (this is only approximately so because two antiprisms may differ by a translation of $\frac{1}{2}$ in the direction of projection).

Thus, the structures of various tcp phases are characterized by the secondary layers, whose atoms represent the centers of these pentagonal antiprisms. Fig. 2 shows the various configurations of interfacial a rectangular Zr_4Al_3 unit on the C14 Laves one of which itself consists of two C15-MgCu₂ parallelogram units in twin position. This is possible because the short (s) and long (ℓ) sides of the Zr_4Al_3 rectangle are of about the same lengths as the sides (s) and long diagonal (ℓ) of the MgCu₂ parallelogram. Since both the structures of the μ and C phases are composed of these units, fig. 2 represents also the various possible ways of formation of these phases on the existing C14 Laves phase unit.

Fig. 3 is the high resolution image of microdomains of these pentagonal tcp structures. Computer image simulations of the μ , C14 Laves and C

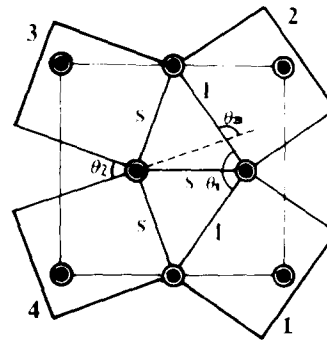


Fig. 2. Schematic diagram shows the growing of four differently oriented Zr_4Al_3 , μ or C units on a C14 Laves unit. Only the atom sites at the secondary layer representing the centers of the pentagonal antiprisms are shown.

phases as well as the $(1\bar{1}\bar{1})$ and $(1\bar{1}0)$ fault models of the C14 Laves phase all confirmed a one-to-one correspondence between the bright dots in the high resolution image and the tunnels inside the pentagonal antiprisms (or the atoms on the secondary layers). The arrangements of these antiprisms in different domains can thus be read directly from the observed image. In fig. 3 at least three rotation domains of the C14 Laves (labeled

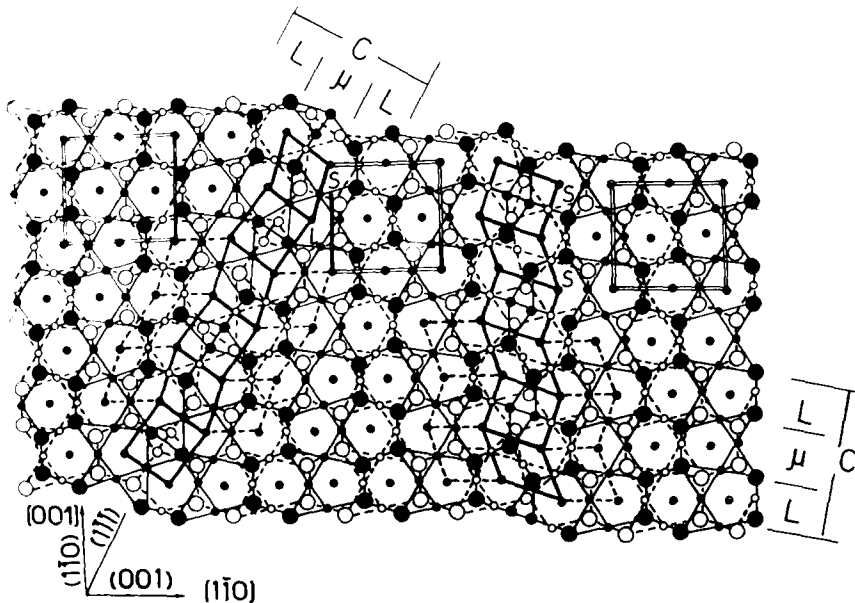


Fig. 1. Structure model of the C14 Laves phase with planar faults on $(1\bar{1}\bar{1})$ and $(1\bar{1}0)$ showing the formation of a narrow μ or C slab at the domain boundary. All these phases are composed of pentagonal antiprisms with the same orientation in this projection.

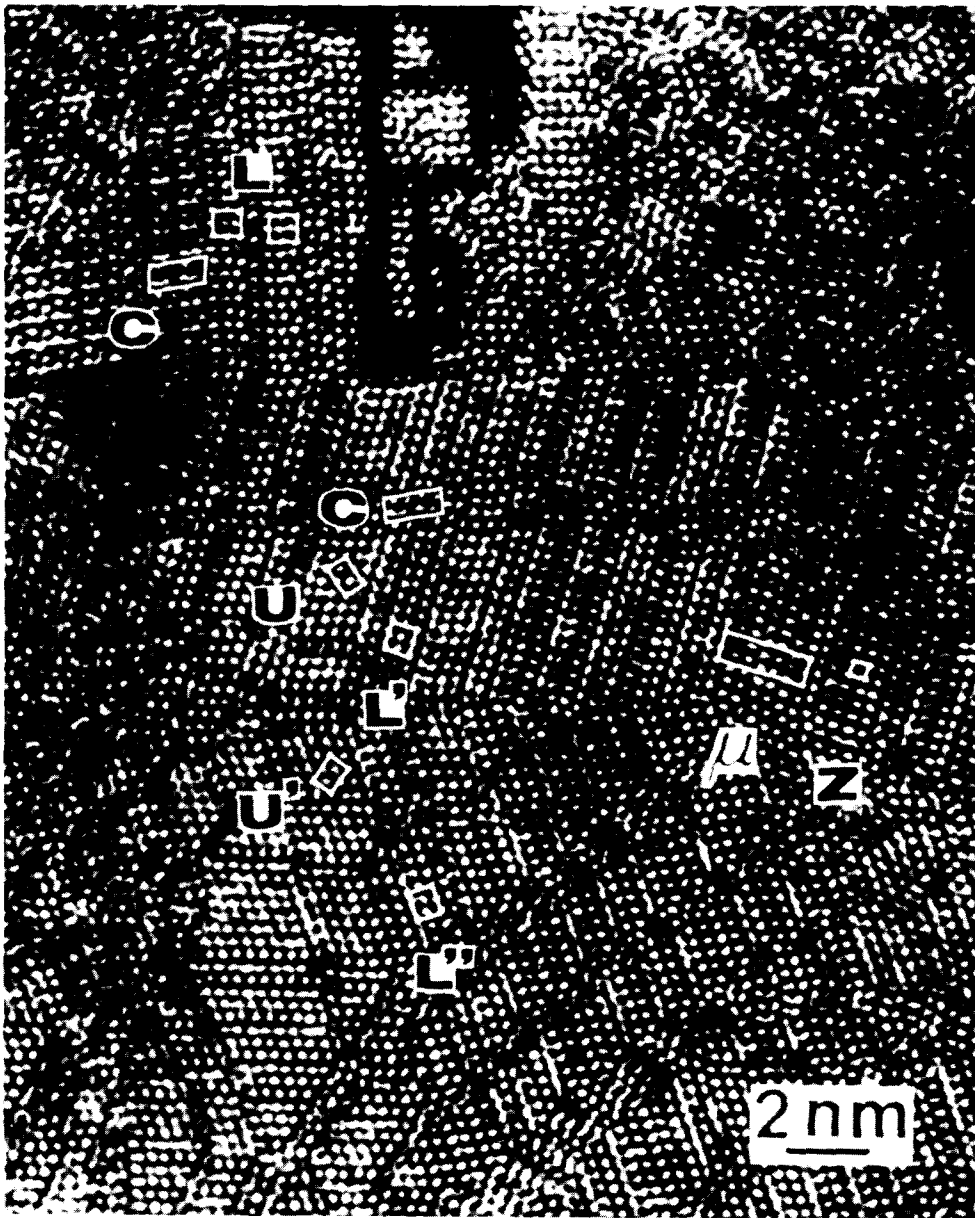


Fig. 3. Structural image of an aggregate of various Zr_4Al_3 (Z), C14 Laves (L), C15 Laves (U), μ and C microdomains in intimate intergrowth.

L, L' and L''), two rotation domains of the C15 Laves or the $MgCu_2$ type of structure (labeled U and U') and several C (C), μ (μ), Zr_4Al_3 (Z) domains can be recognized. These domains intergrow intimately, and in some cases microdomains only a few unit cells in width exist.

From the above discussion it is clear that no matter how complex or faulty the structure is, the underlying building block is the same, i.e. the pentagonal antiprims of the same orientation, and their arrangement is fairly simple, being either rectangular, triangular or a combination [1].

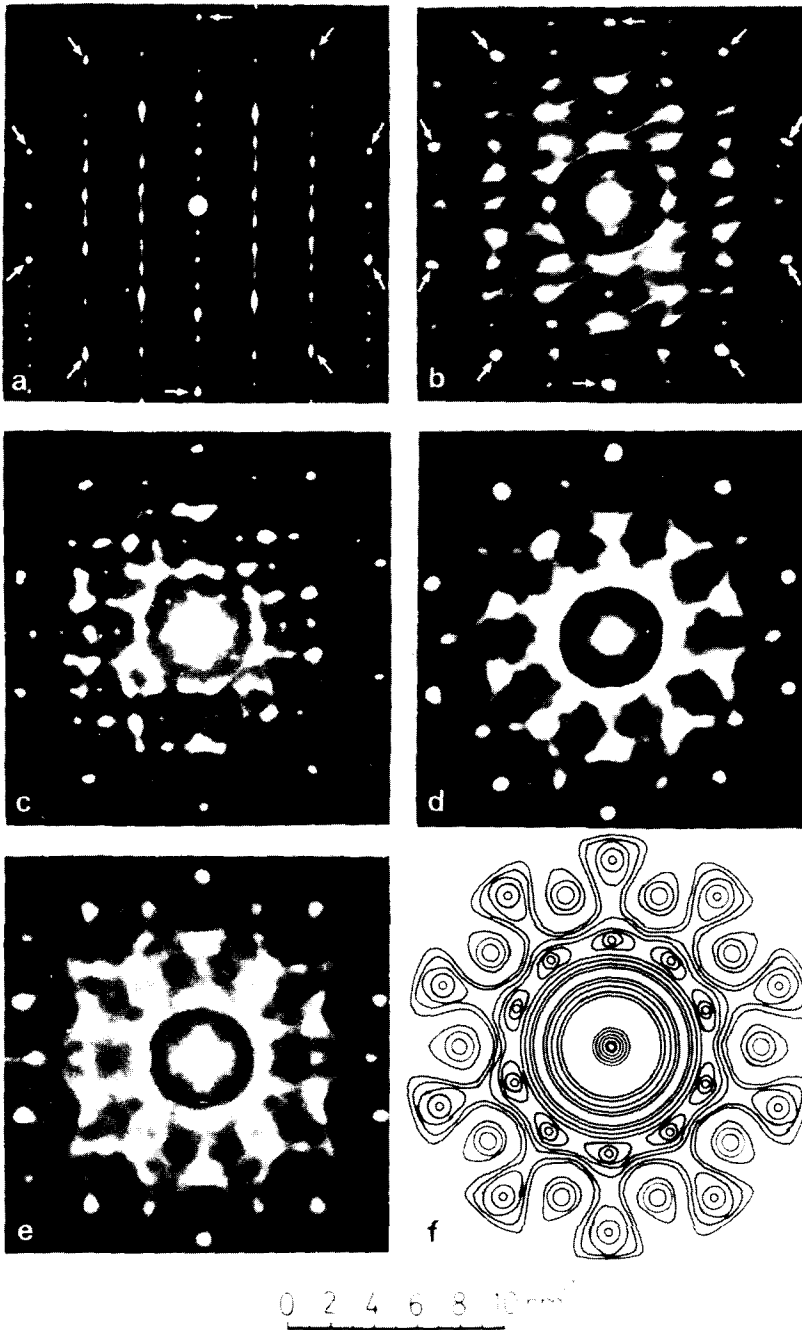


Fig. 4. EDPs of pentagonal top structures with fivefold symmetry: (a) μ : outermost ten spots are marked with arrows; (b) C14 Laves: outermost ten spots are marked; (c) C: fivefold symmetry becomes clearer; (d) mosaic structure with many microdomains: only fivefold distributed diffuse spots appear; (e) composite EDP of differently oriented C and C14 Laves phases: similar to (d); (f) Fourier transform of a single pentagonal antiprism: diffuse halos and fivefold diffuse maxima resembling (d) and (e).

3. Fivefold distribution of electron diffraction spots

Figs. 4a–4c are the EDPs of the μ , C14 Laves and C phases, respectively, taken with the incident beam perpendicular to the juxtaposed pentagonal antiprisms. The distribution of diffraction spots is a representation in the reciprocal space of the space lattices in the real space. Since these phases have different space lattices (μ : rhombohedral; C14: hexagonal; C: monoclinic), it is natural that their EDPs look quite different. However, the outermost ten spots in them (marked with arrows) show a fivefold distribution, and these strong ones all occur at about 8 nm^{-1} , though their indices are quite different. This is indeed quite unexpected. What is more striking is the EDP of a heavily faulted specimen containing many microdomains of these tcp phases as shown in fig. 4d. A crossgrid of spots corresponding to a reciprocal plane no longer can be detected, but the fivefold symmetry now becomes more obvious with spots located on concentric circles with radii of about 2.6, 4.6, 7, and 8 nm^{-1} . The outermost ten spots at about 8 nm^{-1} , though much stronger now, remain at the same positions as the corresponding ones in figs. 4a–4c. This gives a clue for solving this “anomaly” by superposing EDPs from four differently oriented C and three C14 Laves phases as shown in fig. 4e. The resemblance between figs. 4d and 4e is remarkable, and this proves that the former is indeed the EDP of an aggregate of tcp phases with many C and C14 domains whose orientations follow the intergrowth requirements shown in fig. 2. One can see from fig. 3 that these domains in general are only a few tens of nm in size, and this is a kind of “ultrafine grain” structures where long-range order is limited to only several tens of unit-cells. Nevertheless, that such a “mosaic” structure can still give a quite clear fivefold diffraction symmetry is astonishing, and this must result from the pentagonal antiprisms of the same orientation in these tcp phases. To extend this argument one step further, the Fourier transform of a pentagonal antiprism was calculated and is shown in fig. 4f. Both the diffuse halos and fivefold maxima agree well with the EDPs shown in figs. 4d and 4e and this proves beyond any doubt that the fivefold distribution of electron diffraction spots of the pentagonal tcp phases comes from the pentagons and that they are ten in num-

ber from the two antisymmetrically superposed pentagons.

As mentioned above, the projected structure of a pentagonal tcp phase can be visualized as a convolution of a pentagonal antiprism with the atomic sites of the secondary layer which define the space lattice. Therefore, its diffraction amplitude is the product of the Fourier transforms of this pentagonal prism and the second layer. In other words, when a reciprocal lattice point of a tcp phase falls on one of the diffuse maxima of the pentagonal antiprism, the corresponding diffraction spot will appear as a strong one in the EDP. As the reciprocal distance and consequently also the circumference increase, the probability of a set of ten reciprocal points of about the same reciprocal distance superposing on a set of ten diffuse maxima also increases. Perhaps this is the reason why only ten outermost spots with a fivefold symmetry can be detected in figs. 4a–4c. This serves to show the important role played by the pentagonal antiprism in real and reciprocal spaces.

It is of interest to note that several sets of 12 diffraction spots with a sixfold symmetry have been observed in the EDPs of the tcp phases with juxtaposed hexagonal antiprisms, such as σ , H [6], F [7,8] and other σ -related phases [7]. Applying the above reasoning, they are expected to be connected with the hexagonal antiprisms in these structures.

4. Conclusion

A combination of high resolution electron microscopy with selected area diffraction can provide structural information which would be unavailable using either method by itself.

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