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## GRAIN BOUNDARY STRUCTURE IN HCP METALS

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**Résumé:** La structure des joints de grains dans le zinc a été étudiée par microscopie électronique à transmission. Les joints de forte désorientation contiennent souvent des réseaux de dislocations et dans ces conditions l'orientation des deux grains est proche d'une position de coïncidence. Celle-ci peut être obtenue exactement par simple rotation autour de l'axe [0001] comme pour les cristaux à structure cubique. Pour tous les autres cas il est nécessaire d'ajuster la valeur du rapport  $c/a$ : les structures de grain observées sont alors reliées à ce réseau de coïncidence "contraint" de même façon qu'elles le sont d'habitude avec un réseau de coïncidence parfait. Malheureusement la très forte hétérogénéité de distribution de ces réseaux de coïncidence dans les cristaux hexagonaux complique l'analyse: il y a de nombreux réseaux possibles pour une seule observation expérimentale.

**Abstract:** A transmission electron microscope study of the structures of grain boundaries in zinc has been performed. Dislocation structures are observed in many high angle boundaries, and in most cases, the boundaries that exhibit such structure are close in misorientation to a coincidence site lattice (CSL) forming misorientation. In some cases, the CSL can be formed exactly, by a simple rotation, as in the familiar cubic crystal cases, but this can only occur for rotations about the [0001] axis. For all other cases there must also be a slight constraint of the  $c/a$  ratio to some ideal value. Grain boundary structures are found to be related to constrained CSLs just as they are for exact CSLs in the more familiar cases. A serious complication for the analysis, however, is that the distribution of CSLs in misorientation space is very inhomogeneous for the HCP materials, so there are many candidate CSL systems for the analysis of any experimentally observed boundary.

### 1. Introduction

High angle grain boundary structures have been studied extensively in cubic crystal systems over the past several years by means of transmission electron microscopy, among other techniques. There have been relatively few studies of grain boundary structure in HCP materials, however, although these interfaces present very interesting cases for which the well known O-lattice theory must be extended (1). It is also notable that three-dimensional coincidence site lattices (CSLs) cannot be formed, in general, so the "preferred states" corresponding to CSL orientations are more complicated to create.

Bruggeman, Bishop and Hartt (2) pointed out that three dimensional CSLs can only be obtained when  $(c/a)^2$  is a rational fraction, except for rotations about [0001]. It is therefore necessary to constrain the value of  $(c/a)^2$  to a rational value in order to obtain a three dimensional CSL, which we will call a constrained CSL or CCSL, such that a set of DSC lattice vectors becomes available. Even at the exact coincidence orientation, a grain boundary generally must contain intrinsic dislocations to accommodate the constraint of the  $c/a$  ratio, as though the grain boundary were made up of two semi-coherent interfaces between the natural and constrained crystals, and the coincidence boundary itself. When there is also a rotational deviation from coincidence, the usual misorientation-accommodating arrays of dislocations are superimposed upon the constraint-accommodating arrays to make up the total dislocation structure of the interface.

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Although the structure of such CCSL interfaces has received some discussion in the past, there have hitherto been no experimental confirmations of the hypothesis that CCSL structures form preferred boundaries in the same way that CSL structures do for cubic crystals.

The HCP structure also provides the possibility of forming "partial" DSC dislocations because it has two atoms per lattice site. Translations from one atom site to another may not be structure conserving if at least one of the atom sites is not a lattice site. Grain boundary dislocations of this type have been discussed by various authors (3,4,5).

## 2. Experimental

Polycrystalline zinc sheet was cold rolled to a thickness of 0.23mm, and 3mm discs were punched from it. These discs were annealed at 85°C in vacuo for 30 minutes to produce an experimentally convenient grain size and well equilibrated grain boundary structures. The specimens were then double-jet electropolished in a 10% nitric acid - methanol solution at -10°C. Electron microscopy was performed at 200kV, using a JEOL 200CX, and the crystallographic details of the boundaries were determined with high accuracy using specially developed techniques (3).

## 3. Results

Detailed observations have been obtained from several high angle grain boundaries in zinc, including exact-CSL-related boundaries, with [0001] rotation axes, and CCSL boundaries, as described above. In this paper, we shall describe and discuss some of the CCSL-related boundaries.

Fig.1. Transmission electron micrograph of a high angle grain boundary in zinc. The boundary is close in misorientation to the constrained CSL misorientations listed in Table 1, and it contains two sets of dislocations, marked A and B. The Burgers vectors are discussed in the text.

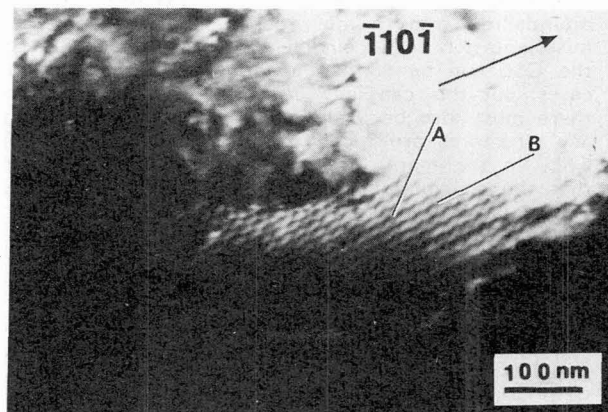


Figure 1 shows a TEM image of a grain boundary containing two sets of dislocations, which are labeled "A" and "B". The misorientation of the boundary was 85.38° about the axis [98,-3,0] which is close to the misorientations required to produce CCSLs with  $\Sigma$  values of 13, 15, 17, 24 and 28, as listed in Table 1. The boundary plane was determined to be (-7,43,-36,72) which is close to a common {0112} plane in each of the coincidence systems listed. A significant experimental problem is caused by the multiplicity of CCSL systems close in misorientation to the experimental boundary, because each CCSL has a DSC lattice associated with it. This means that the determination of the Burgers vectors of the dislocations requires the elimination of many more possibilities than in the case of a single CSL, such as is found in cubic crystals (4). The problem is further exacerbated by the fact that the various DSC vectors associated with the different CCSLs are very close in magnitude and direction, since they are effectively vectors joining the lattice sites of the two crystals in very slightly different reference orientations.

On the basis of eleven different two-beam diffracting conditions and two "simultaneous two-beam" conditions, the image behavior of the dislocations of set A is consistent with a Burgers vector equal to  $1/3 [2110]$ , which is parallel to the rotation axis, hence common to both crystals, and a DSC vector for any of the candidate CCSLs. The dislocations of set B have image behavior which is consistent with a  $DSC_3$  vector for any of the CCSL systems. These vectors are:

$$\begin{aligned}\Sigma 13: & 1/39 [-13 -4 17 -9] \\ \Sigma 15: & 1/15 [-5 -2 7 -3] \\ \Sigma 17: & 1/51 [-17 -5 22 -12] \\ \Sigma 24: & 1/24 [-8 -3 11 -5] \\ \Sigma 28: & 1/84 [-28 -13 41 -15]\end{aligned}$$

All of these vectors are very close in magnitude and orientation, as discussed above, and there is no substantial difference between their image behaviors upon which to differentiate between them, even when image matching techniques are used. Clearly, the Burgers vector analysis provides no basis upon which to judge whether one CCSL is the basis for the preferred structure that the dislocation arrays conserve. It is clear, however, that some form of preferred structure does exist, and that it is preserved even at the expense of the strain energy of the dislocation arrays.

In order to further distinguish between the structures expected for the different CCSLs, we note that the constraints required to form them are different, and that the dislocations necessary to accommodate the constraint vary from one system to another. The array spacings and dislocation line directions can then be calculated for each of the dislocations, using the five different reference structures. The array spacings are found to be error-laden in this calculation, but the dislocation directions are relatively reliable, and much less sensitive to small errors in the measured misorientation or the constraint. In practise, the O-lattice vectors are calculated and used to determine the O-cell walls. The dislocations should then lie at the intersections between the O-cell walls and the boundary plane. Figure 2 summarizes these calculations for the experimental case described here. The O-cell walls corresponding to dislocations A and B are indicated on the stereographic projection, for each CCSL system, along with the experimentally determined trace of the boundary plane. It can be seen that the match between the measured and calculated dislocation line directions is quite good for the  $\Sigma 13$  calculation, but is very poor for all of the other CCSLs. We note that in this case the best match is for the CCSL exhibiting the smallest value of  $\Sigma$ , which is not the one exhibiting the smallest constraint.

Figure 3 is an image of another grain boundary showing two sets of dislocations, one of which is straight while the other is sharply curved. The misorientation of this boundary was  $[100 \ 1 \ 1]/85.22^\circ$ , which is very close to that of the first boundary discussed in this paper. The boundary plane is  $(14,36,-50,78)$  which is again close to  $\{01\bar{1}2\}$  for both crystals. Interpretation of the structure of this interface is again based on the CCSL systems listed in Table 1. The image behavior of the straight dislocations is consistent with the Burgers vector  $1/3 [12\bar{1}0]_2$ , i.e. the shortest lattice vector of crystal 2, which must also be a DSC vector for any of the CCSL systems. The image behavior of the curved dislocations is consistent with a Burgers vector perpendicular to the plane  $(01\bar{1}2)_1/(01\bar{1}2)_2$ , i.e. the boundary plane. Possible Burgers vectors for each of the candidate CCSL systems areas follows:

$$\begin{aligned}\Sigma 13: & 1/26 [ 0 7 -7 6] \\ \Sigma 15: & 1/30 [ 0 8 -8 7] \\ \Sigma 17: & 1/34 [ 0 9 -9 8] \\ \Sigma 24: & 1/48 [ 0 13 -13 11] \\ \Sigma 28: & 1/56 [ 0 15 -15 13]\end{aligned}$$

Each of these vectors joins atom sites in one crystal to those in the other crystal, but they do not join lattice sites. They are therefore not DSC vectors, but partial-DSC vectors, as described by Smith (4). Image matching for the curved dislocations was performed using the  $\Sigma 13$  case, and it was found that the simulated images closely match the experimental ones if the Burgers vector is twice as large as the one listed above, i.e. if we use a perfect DSC vector. That the curved dislocations have DSC Burgers vectors is also strongly suggested by the fact that the contrast of the boundary does not change from one side of the defect to the other in the common diffracting condition shown in Fig.3.

TABLE 1  
Constrained CSL Systems Close in Misorientation to the Experimental Boundaries

System	$(c/a)^2$	Rotation Axis	Angle	Constraint
$\Sigma 13$	7/2	[100]	$85.57^\circ$	0.5%
$\Sigma 15$	24/7	[100]	$86.17^\circ$	-0.5%
$\Sigma 17$	27/8	[100]	$86.62^\circ$	-1.3%
$\Sigma 24$	39/11	[100]	$85.22^\circ$	1.2%
$\Sigma 28$	45/18	[100]	$85.90^\circ$	0.02%

Fig.2. Stereographic projection summarizing the geometry of the grain boundary illustrated in Fig.1. The solid line is the trace of the boundary plane and the points a and b represent the line directions of the dislocations A and B. The various dashed lines are the traces of the calculated O-cell walls based upon the available CCSLs.

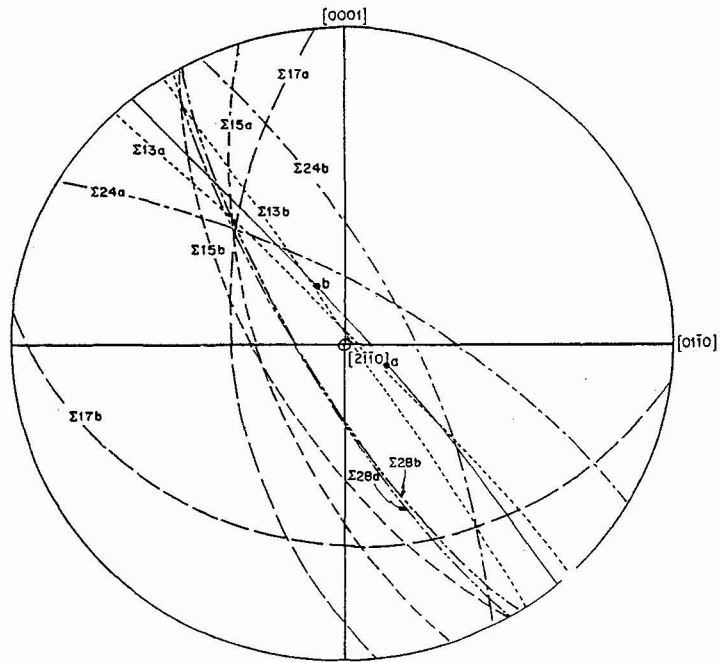
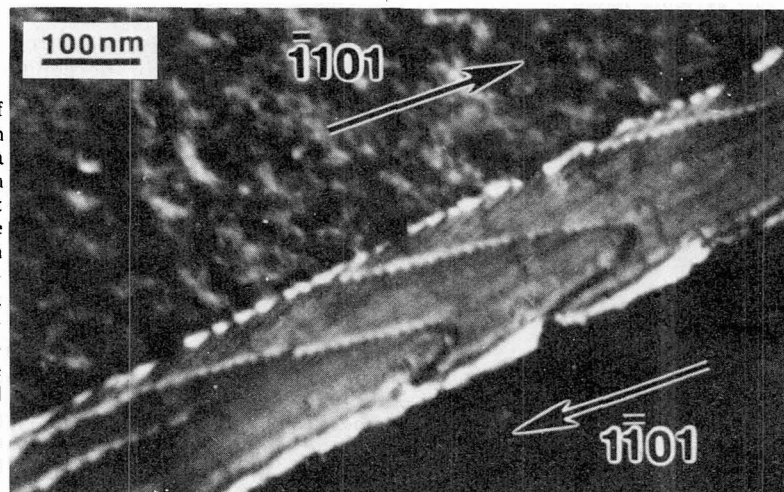


Fig.3. Image of another grain boundary having a misorientation close to that required for the CCSLs listed in table 1. This interface contains a fine, straight array of dislocations and a coarse set of curved ones. The Burgers vectors are discussed in the text.



As in the previous case, it is not possible to distinguish between the different CCSL systems on the basis of the Burgers vector analysis alone, and it is necessary to determine the quality of the match between the experimental and predicted array structures. The curved dislocations must be considered to be extrinsic to the structure of the boundary, but the line direction of the straight dislocation array can be compared with the O-lattice calculations. The angles between the measured and calculated line directions for the five CCSLs are  $18.76^\circ$ ,  $40.47^\circ$ ,  $90.16^\circ$ ,  $13.49^\circ$  and  $27.13^\circ$ , respectively, so the fit between theory and experiment is reasonable for  $\Sigma 13$  and  $\Sigma 24$ , but poor for all other cases.  $\Sigma 13$  is the highest coincidence density CCSL, but  $\Sigma 24$  has no apparent special features, embodying both a lower coincident site density, and a larger constraint than the  $\Sigma 13$  system does.

#### 4. Discussion

The boundaries described here are only two out of the many that have been studied in this research, but they serve to illustrate some of the problems that can be encountered in studying non-cubic materials. They also provide some indication of the ways in which the familiar geometrical theories on grain boundary structure need to be generalized. There are two significant experimental difficulties associated with the study of grain boundaries in hcp metals that are not present for fcc and bcc metals. The first of these is that there is usually more than a single CCSL system upon which to build the analysis of the observed structures. Each CCSL has its own associated DSC lattice, and therefore the range of Burgers vectors which must be considered is much larger than in the more familiar cubic cases. In practise, as in the cases described here, the Burgers vectors appropriate to the various CCSLs may be indistinguishable. The second of the problem is that partial-DSC dislocations may exist in the hcp system because of the crystal geometry. In many cases, the partial-DSC Burgers vectors lie in the same directions as the perfect DSC vectors, but have lengths equal to one half or one third of the perfect vectors. In these cases it is not sufficient merely to determine the orientation of the Burgers vector, but its length must also be established, and this may be a non-trivial exercise.

The solution to the latter problem is available through a variety of experimental techniques, two of which have been discussed here. It is possible to estimate the length of the Burgers vector by means of image matching, and it is possible to reveal relative shifts of one crystal with respect to another by use of common diffracting conditions. In the one case described in this paper, both of these techniques indicated that the dislocations were in fact perfect, and not partial. We have not yet found any cases in which it was possible to establish the existence of partial DSC dislocations in any grain boundary in zinc.

The problem of multiple CCSL systems is rather more difficult, and indeed it begs the question of whether or not there is a real distinction to be drawn between the structures based upon the various systems. Since the DSC vectors essentially join the same lattice sites irrespective of the CCSL system, the differences between them arise from slight differences of reference system, which, in turn arise from small differences in the choices of idealized  $c/a$  ratio. Since the DSC vectors are essentially identical, then so are the dislocations with Burgers vectors corresponding to them: the cores are indistinguishable on the basis of the geometry, since the Burgers vectors connect the same lattice sites in every case, and the long-range strain fields are essentially identical because of the similarity of the Burgers vectors. Since the defects in the boundaries are identical, is there any basis upon which to distinguish between structures belonging to any particular CCSL system? In the two cases presented here, the dislocation array structures were shown to match certain predicted structures better than others, and the differences are associated with the fact that the dislocation arrays exist not only to accommodate differences between ideal and actual orientations, but also between ideal and actual  $c/a$  ratios. It is the latter component of the arrays that causes the measurable differences between the various structures. In both of the cases described in this paper, the dislocation arrays appear to accommodate the constraints associated with one or two of the CCSL systems rather better than any of the others. In both of these cases, the  $\Sigma 13$  CCSL provides a good match between the theoretical and actual dislocation structures, so we presume that the dislocations exist in order to preserve a grain boundary structure related to that particular geometry.

For the particular case of an exactly symmetrical grain boundary, there need be no constraint of the  $c/a$  ratio at all, because the two crystals will match perfectly in two dimensions. However, if there is any deviation from the plane of exact symmetry, then lattice matching is required in three dimensions and the CCSL ideas discussed here must be considered. For both of the boundaries described in this paper (and indeed for two others studied in this research) the boundary plane was very close to an exact symmetry plane, but was never precisely aligned with it. It would appear, from the frequency with which we have observed them, that boundaries close to low index symmetrical grain boundary planes may be energetically favored in the hcp metals. Such boundaries will frequently correspond to a variety of CCSL systems, as in the cases described in this paper, and the behavior of such boundaries may be determined by the properties of the dislocations in them. Whether or not the structure of the boundary is better described by one or other of the available CCSL systems, the dislocation-related properties such as grain boundary sliding, migration and point-defect absorption/emission would probably be unaffected because the dislocations are so similar for all of the different CCSLs.

#### 5. Conclusions

High angle grain boundary structures corresponding to constrained coincidence site lattices have been observed in zinc. There are usually several available CCSL systems upon which to base the analysis of the structure, but the Burgers vectors of the dislocations may be indistinguishable. It was confirmed, however, that the line defects in these boundaries were dislocations of the DSC type. The line directions of the dislocations appear to be consistent with accommodation of the orientation and constraint differences between the 'ideal' and observed boundaries for the case of  $\Sigma=13$ , rather than any of the other CCSLs. This represents the smallest CCSL unit cell.

Partial DSC dislocations have not yet been observed in this material.

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