On the high-temperature plasticity of cubic-C rare-earth oxides

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High-temperature plasticity of cubic-C rare-earth oxides is studied through a study of the behaviour of two different dislocations. One is largely dissociated by glide; the other dissociates by climb. In both case the stacking fault is the same and is characteristic of the cubic-C structure. In the first part, a non-stoichiometric climb model of extended dislocation is suggested. Such a model may lead to a recovery process through an unpinning mechanism of the dislocations. It has been shown that, depending upon the size of an initial cluster, a "super"-jog may be obtained without any activation energy. It is suggested that such a climb mechanism may be particularly likely in oxides containing a large amount of impurities. In the second part, the climb dissociation is considered. The influence of the surrounding network of dislocation has been studied. The results show an increase in the climb dissociation width due to the nearest dislocations. As a consequence the dislocation is sessile and therefore plays an important role in the high-temperature plasticity of these oxides.

1. Introduction

There are 15 rare-earth elements in the Periodic Table, from lanthanum to lutetium. Most of the corresponding oxides are sesquioxides, M_2O_3, where M represents the rare-earth elements. Structures of the rare-earth sesquioxides and their possible crystallographic transformations have been extensively studied on either bulk material [1] or on thin films [2, 3]. The most important structures found have been called A (hexagonal), B (monoclinic) and C (cubic), respectively. Some very-high-temperature structures, H (hexagonal) and X (not well defined) have also been reported. For a given temperature, the structure passes from A to B to C with increasing atomic number.

In this work, attention will be focused on the cubic-C structure which is sometimes called the low-temperature stable modification of cubic lanthanide sesquioxides ($C-Ln_2O_3$). In fact, the rare-earth oxides having the highest atomic numbers exhibit stable C-structure up to 1800 or 2000° C [1].

Hitherto, the plastic properties of those oxides have not been studied. Furthermore, it is very difficult to grow sufficiently large single crystals of rare-earth oxides for classical deformation tests to be carried out. The problem of cubic rare-earth oxide plasticity is therefore dealt with by making a close parallel with a sesquioxide which exhibits the same structure, the same chemical properties, the same point-defect disorder, but which is not a rare-earth oxide. This is the yttrium sesquioxide, Y_2O_3.

It has been possible only recently to grow relatively large yttrium oxide single crystals by the Verneuil method. These crystals have been used in a study of plastic proporties of Y_2O_3 covering a wide range of temperatures and stresses [4, 6]. Both the theoretical and experimental aspects of Y_2O_3 plasticity have revealed interesting features from which generalizations may be made concerning the cubic-C rare-earth oxides.

2. The cubic-C structure

The cubic rare-earth Type-C structure belongs to the space group Ia_3. This structure may be described as a modified fluorite structure where one fourth of the sites in the anion sub-lattice

are missing. The unoccupied anion sites form non-interecting strings along the four $\langle 1\,1\,1 \rangle$ directions of the cubic cell. These strings provide relatively unimpeded pathways for the migration of oxygen ions through the material. The cation sub-lattice is f c c and the lattice parameter is near 1 nm. From these crystallographic considerations, and taking into account point-defects disorder, a clear difference in the diffusion behaviour of the two components of those oxides may be expected.

3. Structure and plasticity of the cubic-C oxides

From a crystallographic point of view, the shortest Burgers vector of such a structure is $b_1 = a/2 \langle 1\,1\,1 \rangle$ which is approximately 0.9 nm in length. In fact, it has been experimentally shown [4] that at least three Burgers vectors intervene in the plasticity of the cubic-C structure of Y_2O_3. These vectors are:

$$b_1 = a/2 \langle 1\,1\,1 \rangle\, 0.9\,\text{nm};$$
$$b_2 = a \quad \langle 1\,0\,0 \rangle\, 1.0\,\text{nm; and}$$
$$b_3 = a \quad \langle 1\,1\,0 \rangle\, 1.5\,\text{nm}.$$

Furthermore, the longest Burgers vector b_3 is responsible for the easy glide system of the structure which is $(0\,0\,1) \langle 1\,1\,0 \rangle$.

On the other hand, possible stacking faults due to imperfect shear have been extensively studied [7]. Despite the fact that the stacking faults which may be possible in this structure seem generally energetic and therefore unlikely, an interesting result was obtained with one stacking fault which may be described by either the shear system $a/2 \langle 1\,1\,0 \rangle (0\,0\,1)$ or by the removal of four successive planes in the $(0\,0\,1)$ stack.

A theoretical calculation on the basis of a purely ionic crystal has therefore been carried out on Y_2O_3. The corresponding stacking-fault energy, E_{SF}, has been found to be surprisingly low for an oxide (80 mJ m^{-2} in Y_2O_3). The simple explanation is that only the fourth plane–plane interactions are modified by this fault. Owing to the stacking-fault energy effect on the fine structure of the dislocations concerned, this important result strongly suggests that the $(0\,0\,1)$-type planes of the cubic-C structure are of prime interest in the study of the plastic behaviour of the rare-earth oxides. Experimental consequences of these particular aspects of the structure have been shown in Y_2O_3. In fact, depending upon stress and temperature range, two

Burgers vectors, b_2 and b_3, respectively, play the major role in the plastic behaviour.

4. Dislocation motion in the cubic-C oxides
4.1. Burgers vector, $b_3 = a \langle 1\,1\,0 \rangle$
It has been experimentally shown that dislocations whose Burgers vector is $b_3 = a \langle 1\,1\,0 \rangle$ are the physical origin of the easy glide system $(0\,0\,1) \langle 1\,1\,0 \rangle$ of the cubic-C structure in the high-stress and "low"-temperature range [4]. Owing to the Burgers vector length (1.5 nm), and the corresponding self energy, this result is quite surprising. The physical explanation is the dissociation of these dislocations into, at least, two partials, separated by the stacking fault ribbon mentioned above. It is a glide dissociation which takes place in the $(0\,0\,1)$ planes of the structure. Both high-voltage electron microscopy [8] and observations using a weak-beam contrast technique [9] support these results and show, almost exclusively, edge dislocations. The problem now arises of how such a largely-dissociated edge dislocation can escape when stopped by some obstacle or internal stress, in other words, is there any recovery process possible with such a configuration of dislocations.

The problem is dealt with by the application of two models:

(a) A non-stoichiometric climb model of dislocations based on the different behaviour of the two sub-lattices [10]; and

(b) A climb model of largely-extended dislocations previously developed for low stacking-fault energy metals [11].

4.1.1. Climb model of extended dislocations in the cubic-C structure
The climb model of extended dislocations in the cubic-C structure can be outlined by the following points:

(1) An extended gliding dislocation is stopped by an obstacle, for instance an impurity (see Fig. 1a).

(2) Oxygen, which is the faster moving ion, diffuses towards or along the dislocation and aggregates to form clusters in the lower part of the extra half planes of one of the partial dislocations (see Figs 1b, 2a and 3a). Owing to the electrical neutrality of the crystal, it is suggested that the clusters correspond to eight extra half planes of either neutral or molecular oxygen. Such clusters are postulated to be coherent with the matrix
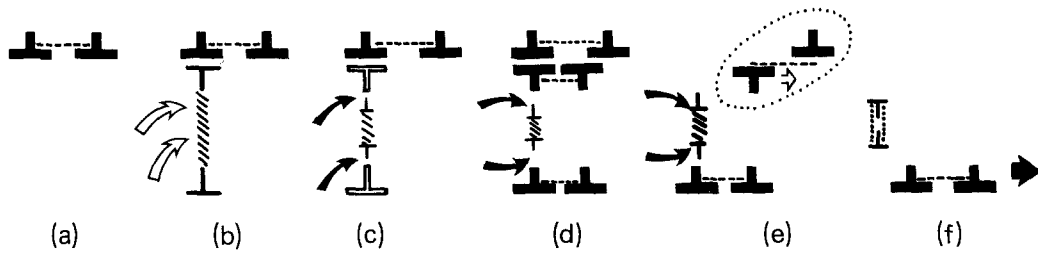
Figure 1 The different steps of the non-stoichiometric climb model of a dislocation dissociated by glide. White arrows: diffusion and aggregation of the faster ion; black arrows: diffusion of the slower ion.

and their description in terms of interstitial loops is then possible.

(3) Each of the "interstitial dislocation loops" dissociate into two dislocations by means of the slowest ion, the cation. A crown of perfect crystal is created between the two dislocation loops (see Figs 1c, 2b and 3b). The Burgers vector of the outer loop is perfect and corresponds to $b_3 = a$ $\langle 1\,1\,0 \rangle$.

(4) The outer loop dissociates by glide and gives the configuration shown in Figs 1d, 2c and 3c.

(5) The initial partial dislocation reacts with the dissociated outer loop (see Figs 1f, 2e and 3d).
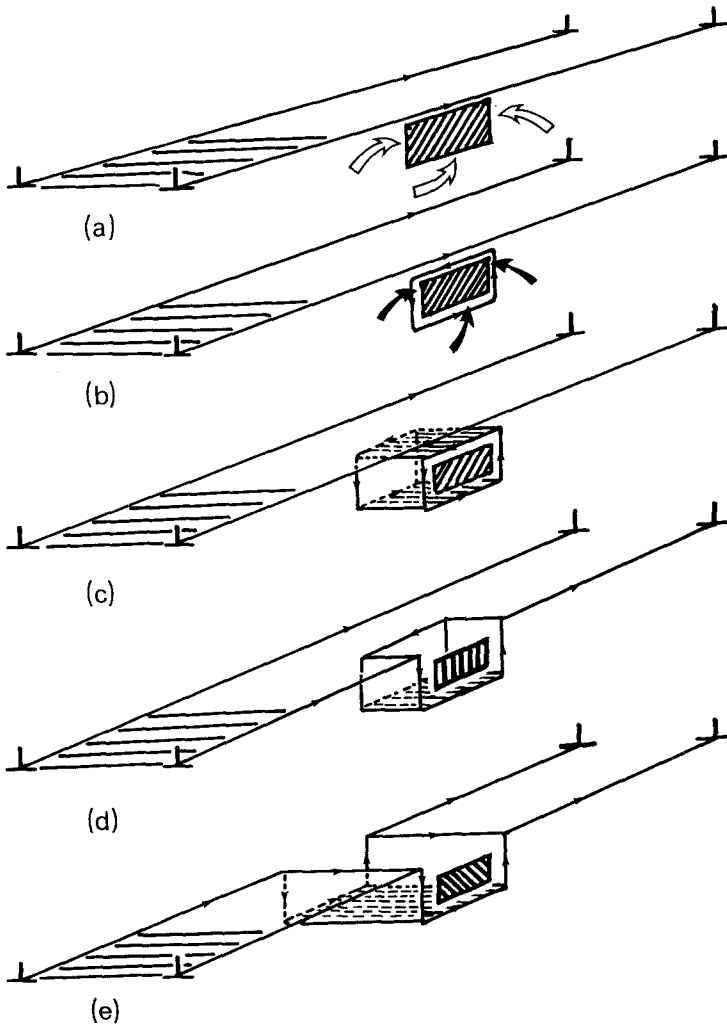

Figure 2 Geometry of the different steps of the climb mechanism. White arrows: diffusion and aggregation of the faster ion; black arrows: diffusion of the slower ion.
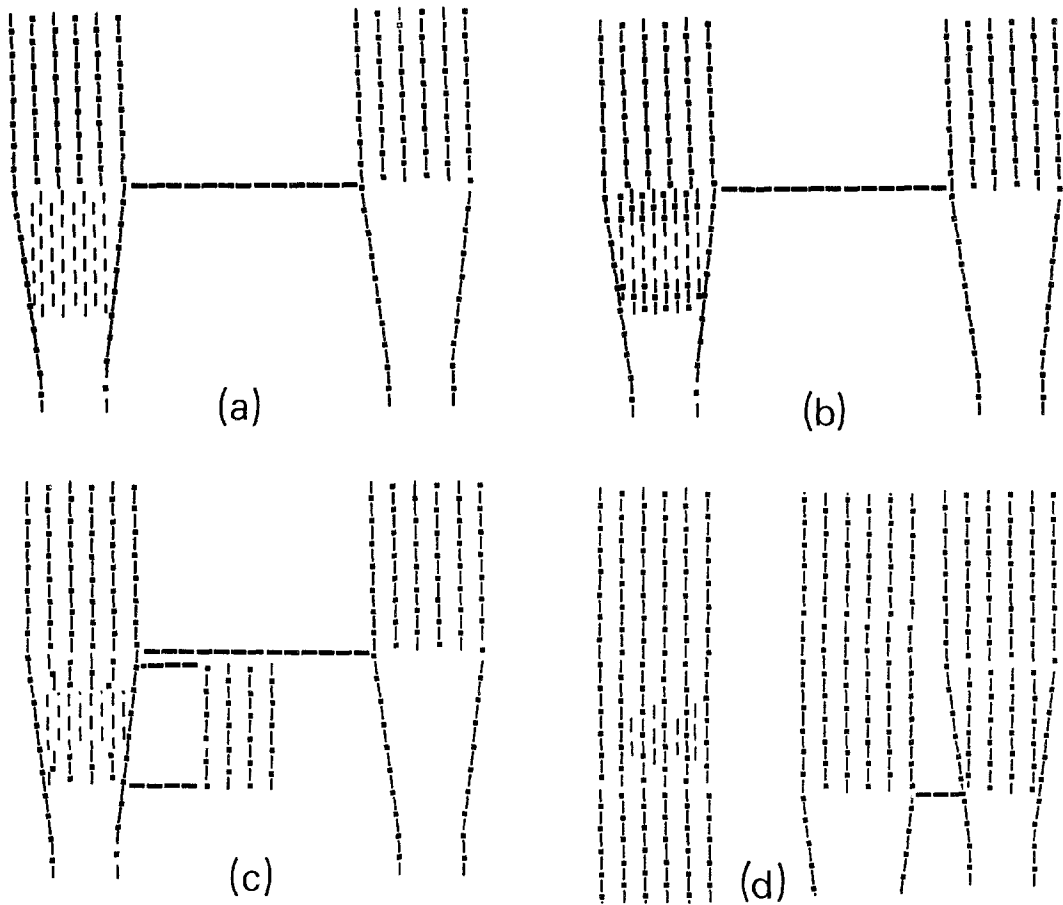
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Figure 3 Schematic view of the climb mechanism in terms of extra half planes.

(6) Under the action of stress, the dislocations could glide again together with the "super"-jog, leaving behind interstitial loops (see Fig. 1f).

Such a process may have a linear extension along the core of one of the initial partial dis-

locations and lead to the whole climb of the dislocation. This non-stoichiometric climb model of dislocations might be particularly possible in impure crystal where impurity sites are not only hardening sites through the pinning of the
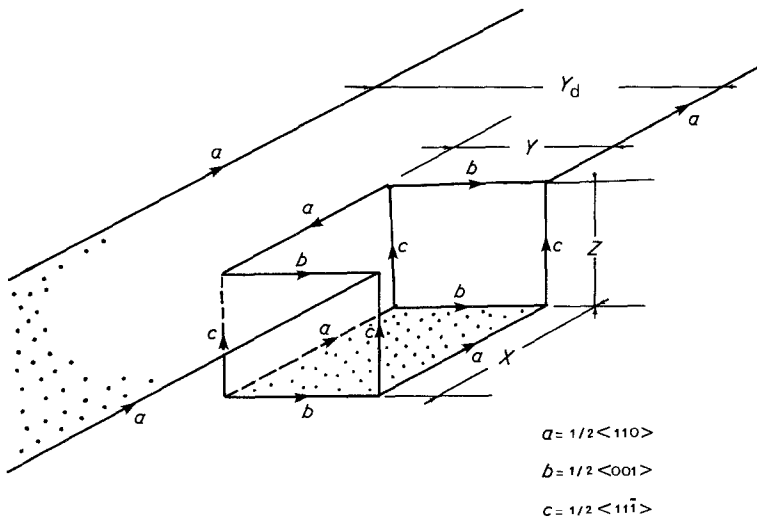

$a = 1/2 <110>$

$b = 1/2 <001>$

$c = 1/2 <11\bar{1}>$

Figure 4 Geometry of the box-like configuration used in the elastic-energy computations. Y_D is the dissociation width and x, y and z are the sides of the box.
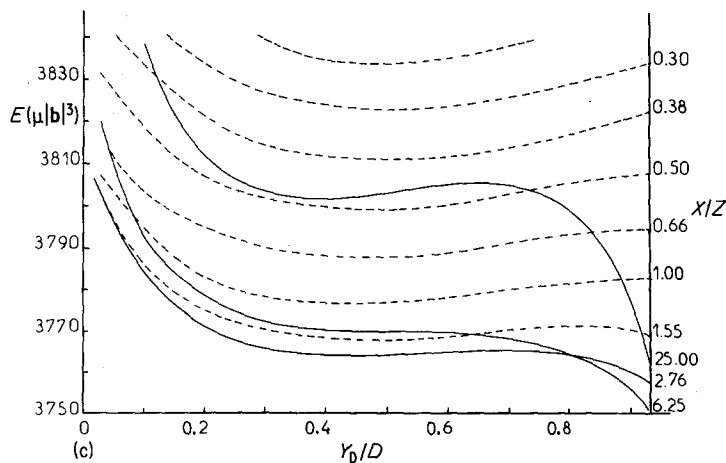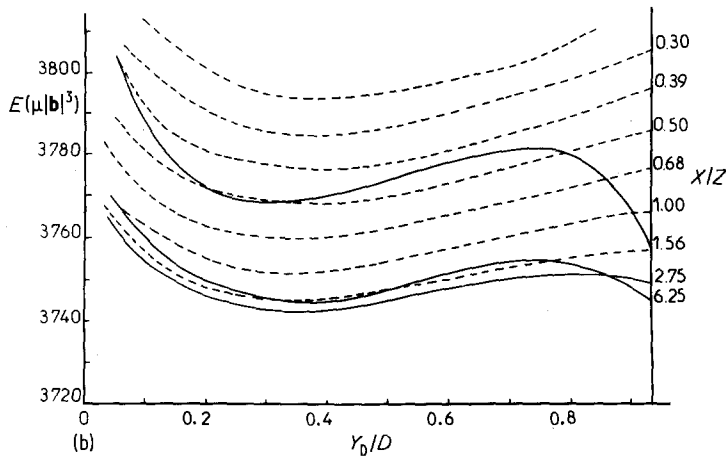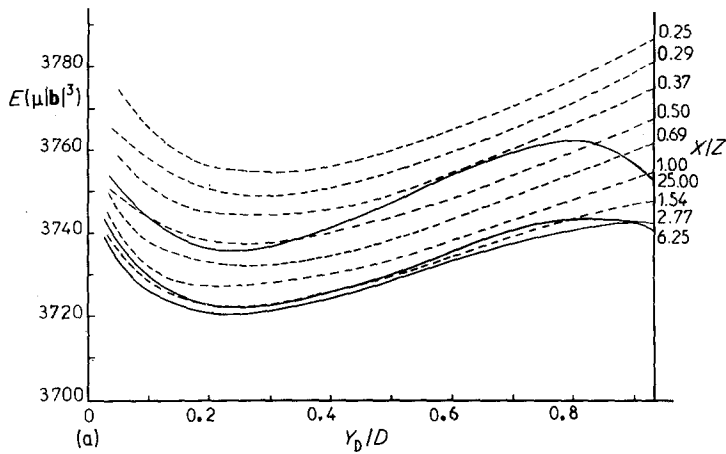
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Figure 5 Results of the energy computations. Elastic energies, E, plotted against the dissociation of the box-like configuration. $E_{sf} = 80 \text{ mJ m}^{-2}$, $\mu = 6.5 \times 10^{10}$ Pa, (a) $S = (30 |\mathbf{b}|)^2$; (b) $S = (40 |\mathbf{b}|)^2$; (c) $S = (50 |\mathbf{b}|)^2$.

dislocations but also favourable sites for the nucleation of the clusters which trigger the climb mechanism.

In the description of the model, a simplified box-like configuration is obtained (see Fig. 2d). If such a configuration does not fully extend from one partial dislocation to the other the super-jog is not obtained and the trapped dislocation cannot escape by further glide. In order to have some idea of the critical size from which the box-like configuration leads by glide dissociation to a wholly extended super-jog, the corresponding elastic energy has been computed. The computer program and the method used have
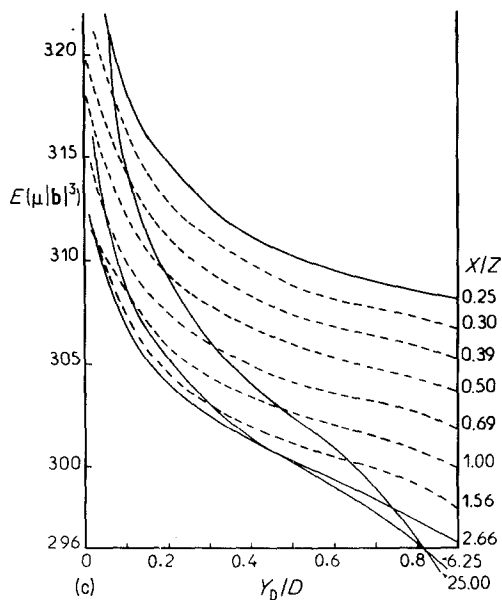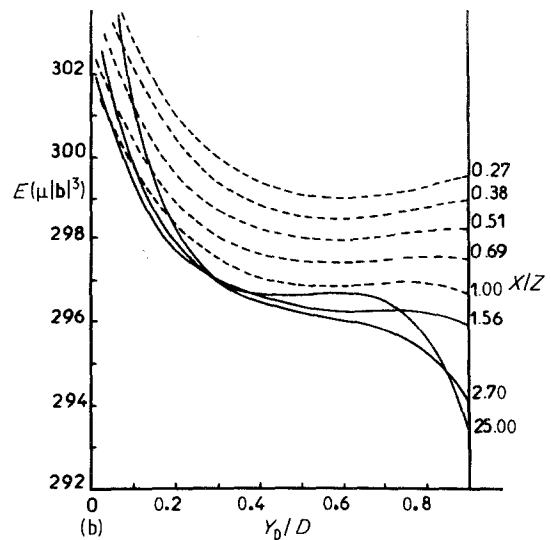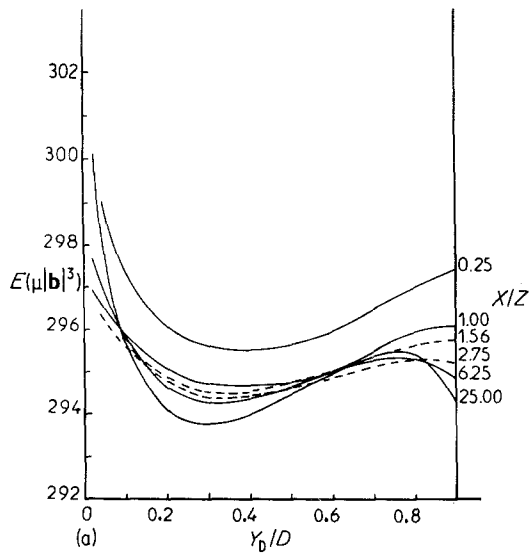
Figure 6 Energy computations of the box-like configurations. $E_{sf} = 350 \, \text{mJ m}^{-2}$ and $\mu = 3.5 \times 10^{10}$ Pa. (a) $S = (4 \, |b|)^2$; (b) $S = (6 \, |b|)^2$; (c) $S = (10 \, |b|)^2$.

realistic. Results of the computations are shown in Figs 5a, b and c and 6a, b and c. On those curves the elastic energy is plotted against the dissociation width of the box-like configuration (Fig. 4). The right-hand axis indicates the shape of the initial cluster through the x/z ratio. Each figure corresponds to one cluster surface.

In the first case, where the stacking-fault energy is taken to be equal to $80 \, \text{mJ m}^{-2}$ and the shear modulus μ, is taken to be equal to 6.5×10^{10} Pa, it is shown that for an initial surface, s, of $(30 \, |b|)^2$ and $(40 \, |b|)^2$ it is impossible to obtain a whole extended super-jog without any activation energy.

From a surface, s, of $(50 \, |b|)^2$ it is possible to obtain such a super-jog only by glide dissociation

Figure 7 Dislocation associated with loops observed in plastically-deformed Y_2O_3 Burgers vector is $b_3 = a \langle 1\,1\,0 \rangle$.

been described elsehwere [11]. Geometry of the problem and the corresponding Burgers vectors are shown in Fig. 4. For the sake of simplicity, the remaining interstitial loop involved in the process is not taken into account. The physical parameters used are those of yttrium sesquioxide.

Two cases are considered:

(i) In the first, room-temperature shear modulus and a theoretical prediction for the stacking-fault energy are employed;

(ii) in the second, high-temperature shear modulus and stacking-fault energy deduced from electron microscope observations are used.

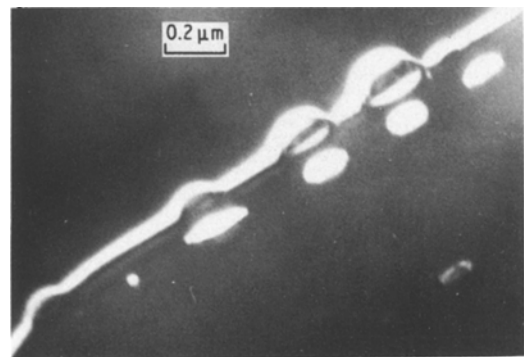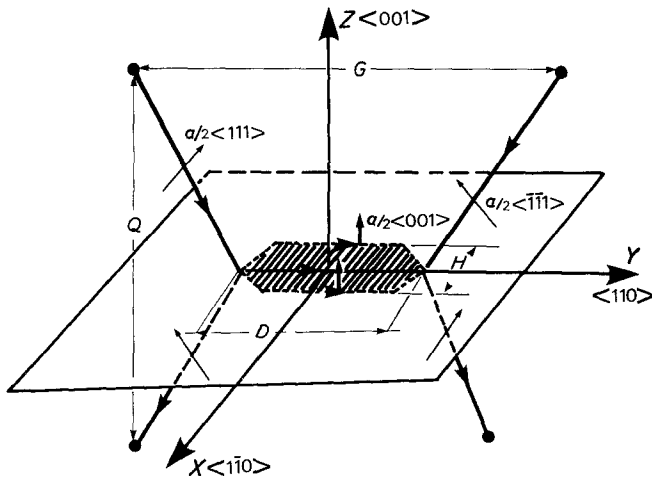This second case seems, in fact, the more

Figure 8 Geometry of the dislocation junction used in the energy computations.

from one partial dislocation to the other. The more favourable shape corresponds to ratio of x/z higher than two. This means that the initial cluster must be an elongated rectangle along the dislocation core. The parameters of Y_2O_3 used in the computation give then a critical surface, s, of $(50 |\mathbf{b}|)^2$ ($\sim 5 \, nm^2$) and a dissociation width of the initial dislocation corresponding to $56 |\mathbf{b}|$ (56 nm). In this case, those results show that the defects involved in the climb mechanism are very large and seem therefore to be not very realistic.

In the second case, the stacking-fault energy is taken to be equal to $350 \, mJ \, m^{-2}$ and μ is taken to be equal to 3.5×10^{10} Pa. It is shown that the whole super-jog is impossible for a surface, s, of $(4 |\mathbf{b}|)^2$ but possible for a surface of, $s = (6 |\mathbf{b}|)^2$ and an elongated shape. For $s = (10 |\mathbf{b}|)^2$, the

super-jog is possible whatever the shape. For the critical surface of $s = (6 |\mathbf{b}|)^2$, the more favourable shape is a rectangle of length $10 |\mathbf{b}|$ and width $3.6 |\mathbf{b}|$. The dissociation width of the initial dislocation corresponding to $350 \, mJ \, m^{-2}$ is $6.8 |\mathbf{b}|$. In this case, the size of defects involved in the model seems more realistic.

In fact, in each case, the critical sizes of the cluster leading to a whole super-jog is of the same order of magnitude as the dislocation width of the initial dislocation. This result is in good agreement with those obtained in low stacking-fault energy metals [11].

The micrograph shown in Fig. 7 has been observed by electron microscopy in plastically-deformed Y_2O_3. The configuration of both the dislocation whose Burgers vector is $\mathbf{b}_3 = a \langle 1\,1\,0 \rangle$
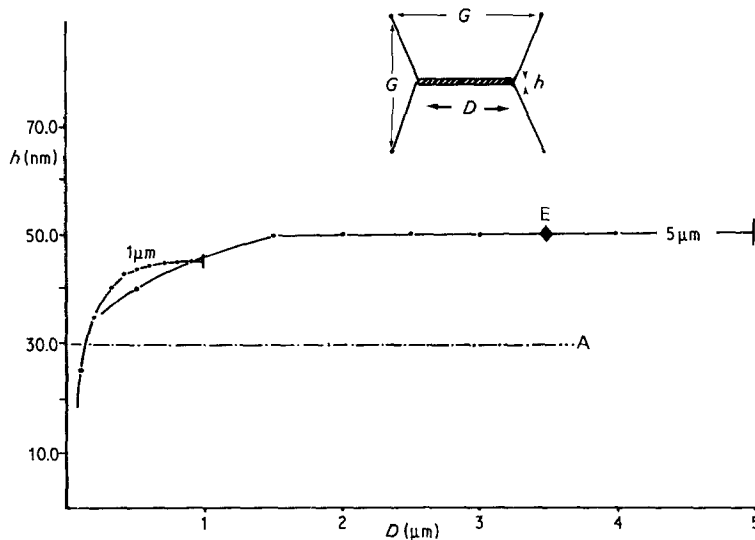

Figure 9 Dissociation width, h, plotted against the dislocation, D, length for two sizes (1 μm and 5 μm) of the dislocation network, G. Each point corresponds to the equilibrium energy. Point E indicates the minimum energy of the whole configuration for $G = 5 \, \mu m$. The broken line, Curve A is the dissociation width predicted by the classical analytical relation for infinite dislocations. In these results the value of the stacking-fault energy predicted by theoretical computations ($80 \, mJ \, m^{-2}$) is used.
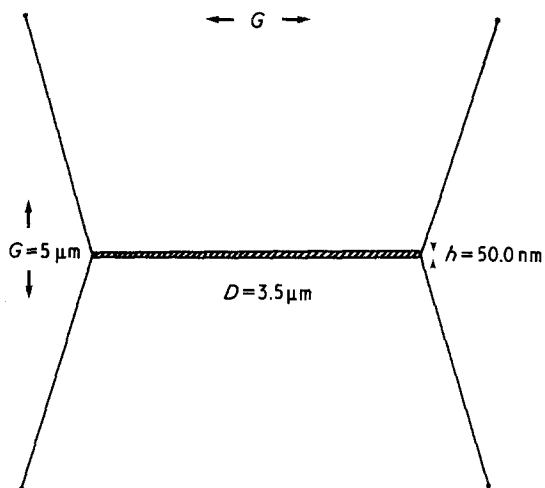
Figure 10 Equilibrium shapes obtained by the computations for $E_{sf} = 80 \text{ mJ m}^{-2}$ and $G = 5 \mu m$.

Figure 11 Equilibrium shape obtained with the stacking-fault energy deduced from electron microscopy observations.

and of the associated loops might be explained by the non-stoichiometric climb model suggested above.

4.2. Burgers vector $b_2 = a \langle 1\,0\,0 \rangle$

It has been experimentally shown that edge dislocations whose Burgers vector is $b_2 = a \langle 1\,0\,0 \rangle$ play a major role in the low-stress and high-temperature plasticity of the cubic-C structure. A very interesting aspect of such a dislocation is its climb dissociation possibility [6]. The initial dislocation dissociates into two partial dislocations having co-linear Burgers vectors. The stacking-fault ribbon belongs to the climb plane of the dislocation. Furthermore, the associated stacking fault corresponds to the removal of four extra $(1\,0\,0)$ planes. It is the stacking fault of low energy described above. This non-stoichiometric dissociation leads to a hardening process in terms of glide and is interpreted as the physical origin of of the rate-controlled high-temperature creep mechanism.

A fundamental process which could give either this climb dissociation or, conversely, its constriction has been developed in detail elsewhere [10]. In fact, such a dislocation appears mainly from the reaction of two other dislocations whose Burgers vectors are of the $b_1 = a/2 \langle 1\,1\,1 \rangle$-type and which form a three-dimensional network inside the crystal. It is a dislocation of junction.

One of the most important factors governing the behaviour of this dislocation is its dissociation width. It is therefore interesting to study the influence of the surrounding dislocation network
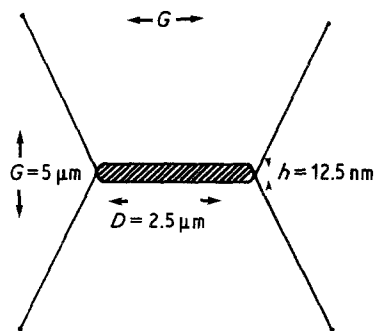
on this parameter. This has been performed in a simplified way by means of the same computer program as that used above. The geometry of the computed configuration is shown in Fig. 8 and the results are shown in Figs 9, 10 and 11. In Fig. 9 the climb dissociation width, h, is plotted against the dislocation length, D, for a given size of dislocation network, G. Dissociation width predicted by the classical analytical relation is shown by the broken line, Curve A. The curves corresponding to $G = 1$ and 5 micrometers show, with increased D, an increase followed by a plateau of constant dissociation width. The minimum energy shape of the whole configuration is indicated by Point E in Fig. 9. Both values, due to either the theoretical or the experimental prediction of stacking-fault energy have been used and lead, respectively, to the equilibrium shapes shown in Figs 10 and 11. From those results it may be deduced that a surrounding network tends to substantially increase the climb dissociation width of the junction dislocations. Also, the dislocation seems elongated compared with the other parts of the network. A more sophisticated surrounding network gives approximately the same results showing that the major part of the interaction energy comes from the nearest dislocations.

The larger the climb dissociation, the more difficult a constriction is. Further glide of such a dissociated dislocation is questionable. In fact, electron microscopy studies have shown that these dislocations seem to move easily in a pure climb motion. It is still uncertain if a large climb dissociation width plays an important role in the pure climb motion of a dislocation; it has been suggested that non-stoichiometric processes could act in this way through faulting—unfaulting mechanisms, but all these assumptions are open to discussion.

5. Conclusion

Two different dislocations of the cubic-C structure which are dissociated by glide and climb, respectively, have been studied. A non-stoichiometric climb model of the dislocation dissociated by glide has been proposed and discussed and the influence of the surrounding network on the climb dissociation width of a dislocation has been studied. The models and processes described are developed through the example of yttrium sesquioxide. Nevertheless, since exactly the same characteristics appear with the rare-earth oxides having the cubic-C structure, the discussion may therefore be generalized to those structures. It is emphasized that all the assumptions suggested in this work are open to discussion and the conclusion are, of course, yet to be supported by experimental evidences.

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