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Self diffusion of cation in yttria stabilized zirconia single crystal

Deock-Soo Cheong†

Department of Materials Science and Engineering, Dankook University, Cheonan 330-714, Korea

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Abstract Dislocation dipoles were formed in the early stage of deformation of Y-CSZ single crystal at high temperatures. And the dipoles were pinched off to break into dipoles loops by dislocation climb. Dislocation loop annealing was peformed in Y-CSZ single crystal to evaluate the diffusivity of cation which was the rate-controlling ion.

Key words Self diffusion, Yttria stabilized zirconia single crystal, Dislocation loop annealing experimenta, Prismatic dislocation loop, Diffusivity of cation, Rate controllin gion, High temperature deformation

1. Introduction

ZrO_2 has been used for oxygen sensor materials because diffusivity of anion is higher than cation unlike other ionic oxide ceramics. Therefore the diffusion of cation has been received many attention since the cation in ZrO_2 is rate-controlling species in diffusion in this crystal.

Y-CSZ (Yttria fully stabilized Zirconia) single crystal were deformed by dislocation movement during high temperature deformation which showed yield drop by activation secondary slip system [1, 2]. And yield drop was occurred after the yield point by activating the secondary slip system. The dislocation structures in this crystal were studied comprehensively by Cheong *et al.* [3]. The yield drop can be occurred when dislocation movement in the sample were faster than cross head speed [4]. In the early stage of deformation, dislocation dipoles were formed by cross slip [4] and edge trapping mechanism [5]. And the dipoles were pinched off to break into dipoles loops by dislocation climb. The dislocation loops can be either vacancy or interstitial type.

Since shrinkage of the dislocation loops was occured by diffusion of ions in this crystal with the heat treatment, diffusivity of ions in this crystal was investigated by dislocation loop annealing experiments.

Since the diffusion of anion is faster than that of cation, an cation can be the rate controlling ion in Y-CSZ single crystal.

2. Experiments

Y-CSZ single crystals were receive from Ceres Company (Waltham, MA) which were doped with 9.4 mol% Y_2O_3 grown by skull melting process. The crystals were rod shape, about 40 mm diameter and 100 mm in length. The orientation were determined by Laue X-ray back reflection. The geometry and orientation of the specimen were shown in Fig. 1. The compress axes was <112> to activate the primary slip plane, {001}. Three Laue X-ray back reflection pictures showed 3 axes of the sample and the size of sample was $3 \times 3 \times 8\ mm^3$, as shown in Fig. 1.

Plastic deformation experiments were carried out in a screw-driven Instron machine equipped with compression apparatus, consisting of deformation rods surrounded by high temperature furnace. The cross head speed of the compression tests were $2.08 \times 10^{-6}\ sec^{-1}$. The deformation tests were performed at 1400°C in the air.

TEM samples were prepared from the sample deformed at 1400°C which gave good dislocation structures with many dislocation loops.

All the foils were cut parallel to the primary slip plane, (001) in order to study the dislocation structures. Then the samples were polished, cutted into 3 mm disk, dimple polished and finally ion-bean thinning following the conventional TEM sample preparation procedure.

The TEM sample was annealed in a furnace between TEM observations. Small alumina sample chamber was used for the annealing process to prevent thermal shock to the sample. The sample chamber was preheated at 100°C for 30 seconds, and inserted completely into the center of the furnace to minimize the thermal damage to the sample. Thin area of TEM samples was easily bro-

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†Corresponding author
Tel: +82-41-550-3530
Fax: +82-41-550-3530
E-mail: dscheong@gmail.com

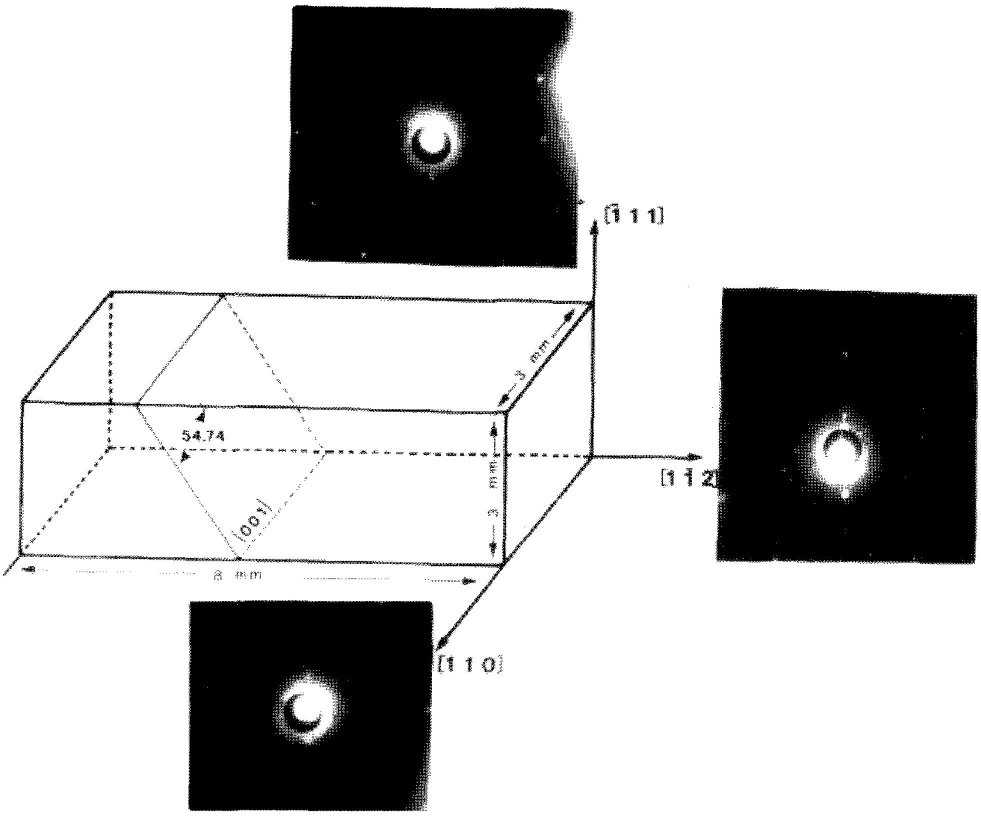


Fig. 1. The geometry of compression sample. Three X-ray Laue back photographs show the orientation of the sample. The primary slip plane, (001) was shown in this figure.

ken during the annealing process and TEM work. The annealing temperatures in this experiments were 1200, 1250, 1275, 1300°C and periods were 0, 10. 30, 70, 120 minutes.

The analysis of dislocation loops in this study was performed in Philips 400T, operating at 125 kV. Conventional diffraction contrast experiments using dynamical two-beam conditions [6] were carried out to determine the Burgers vector and study the dislocation structures and interaction. In theses two beam conditions, each of the Burgers vector can be determined from g·b analysis, with at least two g vectors. During TEM observation, 20~50 loops dislocation loops at each sample were selected and characterized for this experiments. After each heat treatment, the same loops were observed and characterized in TEM.

3. Results and Discussion

The oxide ceramics exhibit plastic deformation by the activation of dislocation movements at high temperatures. ZrO_2 showed the plastic deformation by the dislocation movements at high temperatures, as shown in Fig. 2 [2, 3]. Y-CSZ sample showed plastic deformation with.

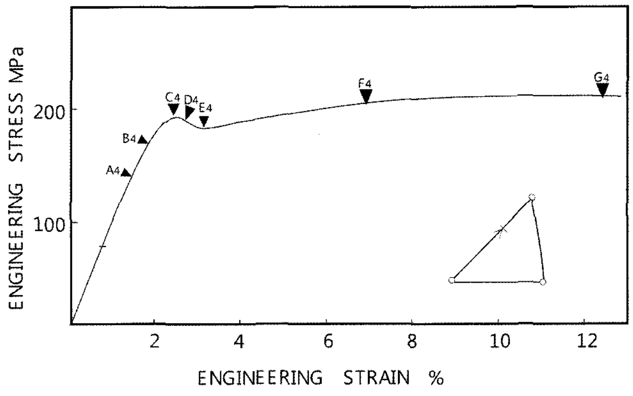


Fig. 2. Stress-Strain curve of the sample deformed along [112] at 1400°C. The arrowed stage A_4 to G_4 are where the deformation experiments were stopped and dislocation structures studied by TEM.

The yield drop which was caused by the activation of secondary slip system [1, 2] Cheong *et al.* [7] also was reported the dependence of temperatures on plastic deformation in Y-CSZ single crystal. In the early stage, B4 of deformation, many dislocation dipoles were formed and the dipoles were pinched off and became

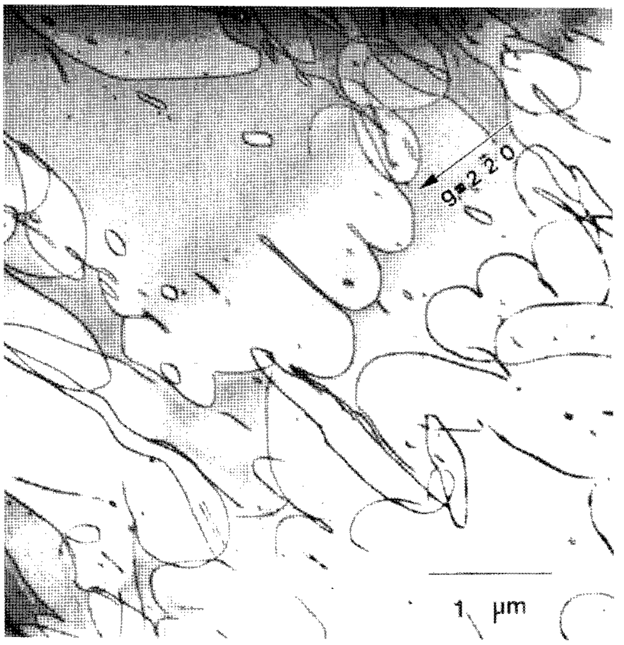


Fig. 3. Dislocation structure at the early stage, B_4 of deformation which showing many dislocation dipoles and prismatic loops.

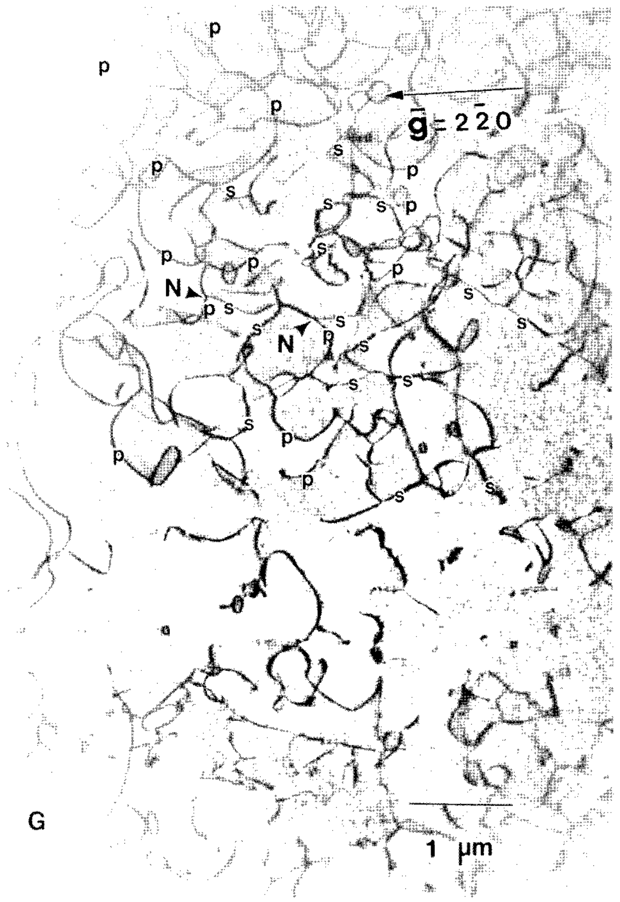


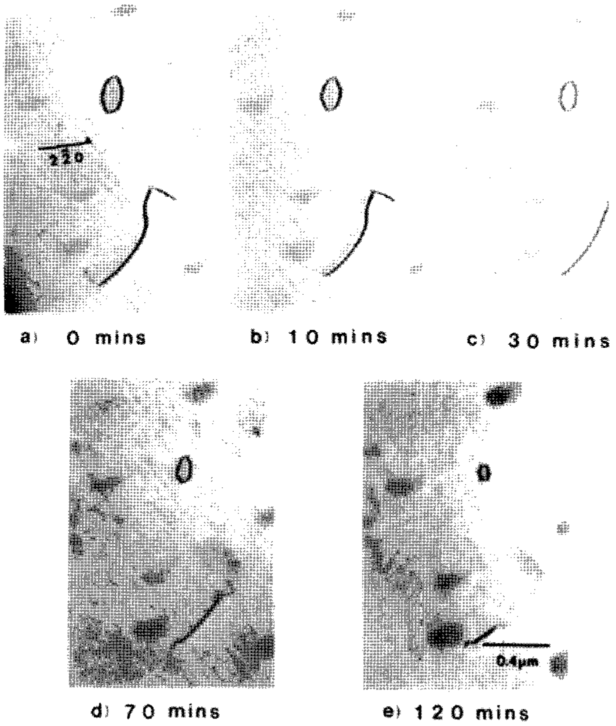
Fig. 4. Dislocation structure in the sample deformed to zero-work hardening region, stage G_4. p, s, and N refer to primary, secondary dislocation and nodes, respectively.

prismatic loops, as shown in Fig. 3. Earlier scientists reported [8, 9] that there is a significant movement of screw dislocation and resulted in large amount of dislocation dipole formation. Prismatic loops formed from dislocation dipole by pinching off by dislocation clim or cross slip [10, 11].

At this stage, most of dislocations was in the primary slip system, {001}<110>. The secondary slip system, {111}<110> started to act at this stage, which cause the yield drop later [2].

As plastic deformation progressed, density of dislocations were increased and the dislocations with many slip systems were operating through convention dislocation multiplication [12]. At this stage this sample showed dislocation networks with many dislocation nods which caused work-hardening at the stage G_4. The dislocation network and nods indicate that multiple slip system was activated, as shown in Fig. 4. More dislocations in other slip system in stead of the primary slip system were observed.

Dislocation loop annealing experiments were performed in order to estimate the diffusivity of the rate controlling species of Y-CSZ single crystal. According to the dislocation model of Friedel [13], the shrinkage of prismatic loops was controlled by the vacancy emission from jogs along th loop. Other scientists [14-16] con-



a) 0 mins b) 10 mins c) 30 mins

d) 70 mins e) 120 mins

Fig. 5. TEM micrographs display the sequential shrinkage of a prismatic dislocation loop after annealing at 1275°C for 0, 10, 30, 70 and 120 minutes.

firmed that the prismatic loops shrinkage by the diffusion of vacancies. Fig. 5 exhibits a series of TEM micrographs of one loop during the sequential annealing of 0, 10, 30, 70 and 120 minutes at 1275°C.

The simplified theory predicts the relationship between the annaling period and the change of loop radius squared, $r_1^2 - r_2^2$ with the following equation [17],

$$r_1^2 - r_2^2 = G{\cdot}D_m{\cdot}Q/(1 - \nu)\ K_a{\cdot}T{\cdot}t_{a{\cdot}\S} \tag{1}$$

where r_1 = radius of the loop before annealing, r_2 = radius of the loop after annealing, G = shear modulus, D = diffusion coefficient, Q = activation energy, ν = Poisson's ratio, K_a = gas constant, T = absolute temperature, t_a = annealing time, respectively.

To find a better approximation of the diffusivity of the rate controlling species, it was determined for each loop studied using the numerical integration. The resulting values of diffusivity for four different temperatures were summarized in Fig. 6 which showed large scatter of the data, about a factor of 10 to 20. Even though the results show the large scattering due to the measurement error, the collection of the date is reasonably correlated showing 68 % of correlation factor.

The resulting diffusivity of the rate controlling species is

$$D = 6.3(\pm 1.1) \times 10^{-3} \exp\{5.13 \pm 0.58(\text{ev})/kT\} \tag{2}$$

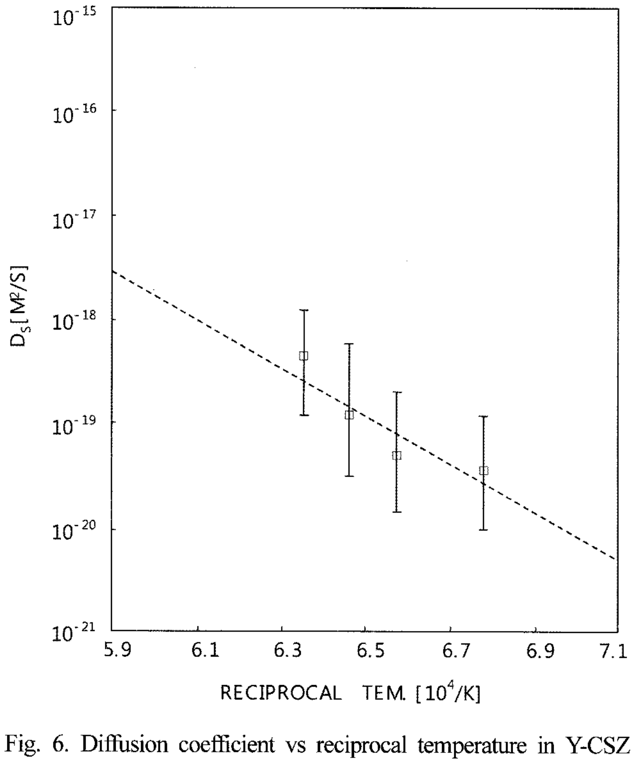


Fig. 6. Diffusion coefficient vs reciprocal temperature in Y-CSZ single crystal.

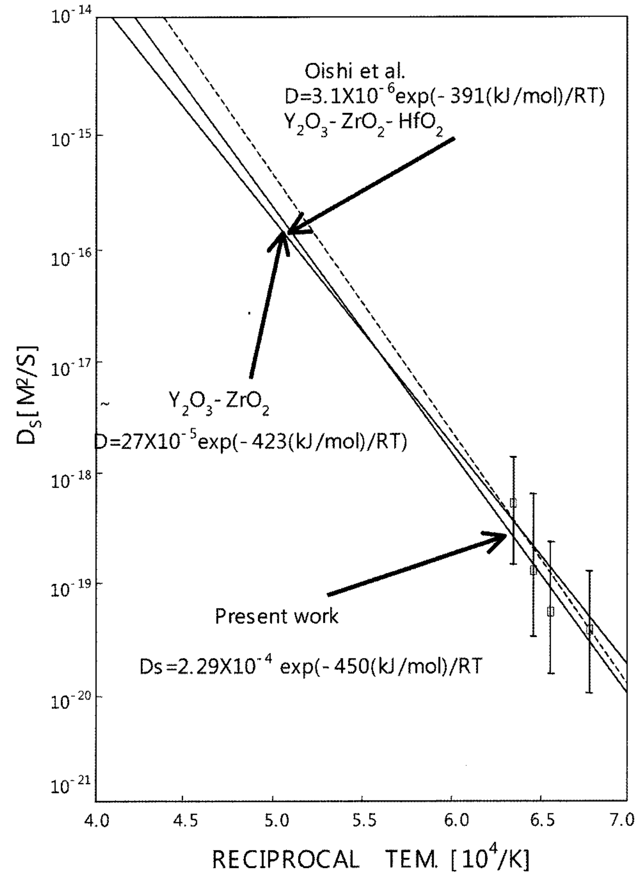


Fig. 7. Diffusion coefficient vs reciprocal temperature in Fig. 6 with the diffusion results of Oishi *et al.* [18] in the high temperature region.

The extrapolation of the dislocation loop annealing date to high temperatures showed the good agreement with the inter-diffusion experiments of Oishi *et al.* [18] The activation energy of the dislocation loop annealing experiments was 5.13 ± 0.58 eV/atom, while it was 4.5 eV/atom for the inter-diffusion experiments [18]. The cause of the large uncertainty may be due to the narrow temperature range of this annealing experiments. In the dislocation loop annealing experiments, it is impossible to determine which is the rate controlling ion. Oishi *et al.* [16] also reported that the activation energy of cation in this crystal are proportional to the atomic size suggesting that Y is the slower moving ion.

4. Conclusion

Y-CSZ single crystal showed plastic deformation by the movement of dislocations at high temperatures. The shrinkage of the prismatic loops in this study was accomplished through the diffusion-controlled kinetics.

Diffusion coefficient of the rate controlling species in this crystal was determined from the dislocation loop annealing experiments. The result is

$$D = 6.3(\pm 1.1) \times 10^{-3} \exp\{5.1 \pm 0.6(\mathrm{eV})/kT\} \qquad (3)$$

Since size of Y atom is larger than one of Zr, the diffusion coefficient is for Y instead of Zr.

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