Saturation Dislocation Microstructures In A Copper Single Crystal During Fatigue In HClO₄ Aqueous Solution

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ABSTRACT: A copper single crystal was tested at room temperature in air and in a 0.1M HClO₄ solution under the symmetric tension-compression load mode, with loading axis parallel to the [013] direction. The dislocation structures were characterised using the electron channeling contrast (ECC) technique of scanning electron microscopy (SEM) and using transmission electron microscopy (TEM). The results show that the saturation dislocation structures in samples subjected to corrosion fatigue in the 0.1M HClO₄ aqueous solution mainly had the form of cells, dislocation wall-like and veins, which differ from the dislocation structures of dislocation wall-like and veins in the air environment.

1 INTRODUCTION

The dislocation structure of a material is directly associated with its mechanical behaviour. The dislocation structures of cyclically deformed specimens [Ackermann et al., 1984; Basinski and Basinski, 1992; Suresh, 1998], especially for single crystals of copper [Laird et al., 1986; Yang et al., 2003; Mughrabi, 1983], have been extensively studied. Cyclic deformation and persistent slip bands (PSBs) are both important to crack initiation and crack propagation [Zhang et al., 2001]. Many investigators have found that the service properties of components subject to corrosion fatigue conditions are considerably degraded compared with the fatigue properties in air environments materials [Ortner et al., 1987; Yan et al., 1985]. Moreover, the corrosion fatigue properties of the materials have been found to be even worse than the simple sum of the separate effects of cyclic loading and corrosion [Yan et al., 1985]. Therefore, a study of environmental effects on cyclic deformation and PSB behavior can be expected to improve our understanding of the mechanism of corrosion fatigue, crack nucleation and life behavior. Unfortunately, this subject has rarely been studied in recent years because the phenomena are complicated. Most attention has been devoted to crack propagation. Contrary to the abundant availability of dislocation structures in specimens cyclically tested in air, TEM and SEM observations of specimens fatigue-tested in corrosive environments are still very limited [Hahn and Duquette, 1978; Yan et al., 1985]. The present investigation examines dislocation structures in a copper single crystal that has been subjected to corrosion fatigue testing, so as to provide a better understanding of environment-cyclic deformation interactions without the complicating factor of the crack path sensitivity of grain boundaries.

Figure 1 shows the location of the orientations of Cu single crystal in the stereographic standard triangle and the classification of different types of slip orientations. In Fig.1, the three pinnacles correspond to [001], [111] and [011] multiple-slip-oriented orientations, respectively, and the three sides correspond to quite different double-slip orientations, i.e., coplanar slip (011/111), conjugate slip (001/111) and critical slip (001/011) orientations, respectively. The [013] orientation locates at the (001/011) side, and corresponds to a critical double slip. In this work, fatigue tests were performed on a copper single crystal with loading axis parallel to [013] double-slip-oriented at room temperature in air and 0.1 M HClO₄ solution respectively, under the symmetric tension-compression load mode. Dislocation structures were observed and characterized using TEM and the ECC technique of SEM.
2 EXPERIMENT MATERIAL AND PROCEDURE

The material used in the present work was a copper single crystal grown from OFHC copper with a purity of 99.999% by the Bridgman technique. Specimens used for corrosion fatigue tests were cut by electric discharge machining, which had the final dimension of $7 \times 10 \times 75 \text{ mm}^3$ and a gauge section of $7 \times 5 \times 15 \text{ mm}^3$, as shown in Fig. 2. The tensile axis of the specimens is parallel to the [013] orientation. The orientation of the specimens was determined by the Laue back-reflection technique with accuracy within $\pm 2^\circ$. To eliminate any residual stress effect, all specimens were electro-polished before testing.

A special apparatus was designed to keep the specimen under well-controlled corrosion fatigue conditions. Figure 3 shows schematically the configuration of the testing system, which consisted of four parts: mechanical testing machine (Parts 5 and 6), solution deaeration system (Part 1), argon purification train (Parts 2 and 3), and potential control electronics (Part 4). Deaerated 0.1 M HClO$_4$ solution was applied as the aqueous environment. Fatigue tests were conducted in symmetric tension-compression load mode at room temperature under the plastic strain control and potential control conditions using an Instron servohydraulic testing machine (8501, 100 kN). A triangular waveform signal with frequencies of 0.05-0.5Hz was used for the constant plastic strain amplitude...
control. The applied plastic shear strain amplitudes were $1.6 \times 10^{-3}$ and $6.8 \times 10^{-3}$, respectively. Stress-strain hysteresis loops were on-time recorded and monitored on an X-Y recorder.

![Diagram](image)

**Fig. 3.** Schematic diagram of testing system.

Specimens were deformed cyclically up to the occurrence of the saturation stage of cyclic deformation. Thin foils for TEM studies were first sliced from the gauge part of the corrosion fatigued specimen parallel to some specific crystallographic planes (111), (111) and (121), by electric discharge machining; then mechanically thinned down to dozens of micron thick and finally polished by a conventional twin-jet method. TEM observations were performed using JEOL-2000FX II electron microscope operated at 200kV. The experiment parameters used in corrosion fatigue are shown in Table 1.

<table>
<thead>
<tr>
<th>Specimen designation</th>
<th>Plastic strain amplitude</th>
<th>Environment solution</th>
<th>Potential (V SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>$6.8 \times 10^{-3}$</td>
<td>Air</td>
<td>N/A</td>
</tr>
<tr>
<td>S2</td>
<td>$1.6 \times 10^{-3}$</td>
<td>0.1N HClO₄</td>
<td>Free Corrosion</td>
</tr>
<tr>
<td>S3</td>
<td>$6.8 \times 10^{-3}$</td>
<td>0.1N HClO₄</td>
<td>0.005</td>
</tr>
<tr>
<td>S4</td>
<td>$1.6 \times 10^{-3}$</td>
<td>0.1N HClO₄</td>
<td>0.005</td>
</tr>
</tbody>
</table>

**3 RESULTS AND DISCUSSIONS**

**3.1 Cyclic hardening curve of specimens tested in air**

Figure 4 shows cyclic hardening curves of the [013] double-slip-oriented copper single crystal which was tested at room temperature in air at plastic shear strain amplitude of $1.6 \times 10^{-3}$ and $6.8 \times 10^{-3}$. It can be seen from Fig. 4 that the shear stress increases with increasing number of cycles and finally reaches constant and enters a saturation state. Moreover, the hardening curves for the different environmental conditions (see Table 1) showed no significant differences. This implies that the environment has no significant influence on the hardening process.
3.2 Surface morphology and saturation dislocation structures in specimens tested in air

Figure 5 shows observations of the surface deformation morphology and dislocation structures of the specimen S1 cyclically loaded in air for 3500 cycles (by this cycle number the specimen was in the saturation stage of cyclic deformation). In Fig.5 (a), the parallel macro deformation bands (DBs), at an angle of 45° with respect to the loading direction, can be seen clearly. These macro DBs can spread over the whole surface. In Fig. 5 (b), the dislocation structure mainly consists of dislocation wall-like and vein structures. The observed plane is (111). Regarding the critical double-slip crystals, Gong et al. [Gong et al., 1996] reported that PSB ladders, veins and labyrinths constitute the main dislocation features in the critical double-slip crystal cycled at intermediate strain amplitudes and cell structures developed at higher strain amplitudes. Jin and Winter (Jin and Winter, 1984) also found PSB ladders and veins in the [012] critical double-slip crystal cycled at an intermediate strain amplitude of $3.0 \times 10^{-3}$. Recently Li et al. [Li et al., 2002] reported that the labyrinth structure becomes the main dislocation configuration in cyclically deformed [017] critical double-slip crystals ($\gamma_{pl} = 1.2 \times 10^{-4}$) and some narrow PSB ladder-like structures are embedded in the labyrinth structures ($\gamma_{pl} = 9.4 \times 10^{-4}$). The present work revealed that the dislocation wall-like and vein structures become the main dislocation configuration in the [013] critical double-slip copper single crystal.

![Fig. 4. Cyclic hardening curves of [013] double-slip-oriented copper single crystals under two different plastic strain amplitudes.](image)

![Fig. 5. SEM images of specimen S1: (a) surface morphology; and (b) SEM-ECC image of dislocation wall-like and vein microstructures](image)
3.3 Surface morphology and saturation dislocation structures in specimen S2

Figure 6 shows observations of the surface deformation morphology and dislocation structures of the specimen S2 which was cyclically tested in a 0.1M HClO₄ aqueous solution at free corrosion potential for 4000 cycles (also being in the saturation stage of cyclic deformation). In the 0.1 M HClO₄ aqueous solution, without any corrosion product that does not dissolve in water was formed on the specimen surface, a copper atom is easy to lose electron to become a copper ion and dissolve in medium solution, is typical active system. Observation shows that the surface has slip traces and partial dissolution of copper atoms, without any apparent oxide films formed (see Fig.6a). SEM-ECC and TEM observations show that the saturation dislocation structures, after corrosion fatigue in 0.1M HClO₄ aqueous solution, are mainly consisted of dislocation walls-like, veins (see Fig.6b) and cells (see Fig.6c).

![Fig. 6. SEM and TEM images of saturation dislocation structures of fatigued copper single crystal in 0.1M HClO₄ solution at free corrosion potential: (a) surface morphologies; (b) SEM-ECC images of dislocation walls-like and vein microstructures; (c) TEM image of dislocation cells.](image)

Yan et al. [Yan et al., 1985] have studied the dislocation structure of copper single crystals oriented for single slip cycled in 0.1M HClO₄ and under different polarization potentials. TEM samples were observed both after saturation and after fracture. They reported that although much higher strain localization was observed in the crystals cycled at anodic potentials, the dislocation structures observed were very similar to those of specimens tested at cathodic potentials and in air. For a plastic shear strain amplitude of $2.0 \times 10^{-3}$, regular loop patches (veins) and dipolar walls (dislocation wall) were observed. For a higher strain amplitude of $4.0 \times 10^{-3}$, dipolar walls associated with secondary slip were found in addition to regular primary walls. We have studied the dislocation structure of copper single crystals oriented for double slip cycled in 0.1M HClO₄ and under free corrosion potential for 4000 cycles (also being in the saturation stage of cyclic
deformation). The present work revealed that the saturation dislocation microstructures, after corrosion fatigue in the aqueous solution of 0.1M HClO$_4$, are mainly consisted of dislocation wall-like, veins and cells, which differ from the dislocation structures in the air.

4 CONCLUSIONS

1) The dislocation walls-like and veins constitute the main dislocation feature in the critical double-slip copper single crystals cycled deformation in open-air condition.

2) For double-slip-oriented copper single crystal cyclically stressed to the saturation stage in a 0.1 M HClO$_4$ aqueous solution, the specimen surface has slip traces and partial dissolution of copper atoms, but without oxide film formed.

3) The saturation dislocation microstructures, after corrosion fatigue in the aqueous solution of 0.1M HClO$_4$, are mainly consisted of dislocation walls-like, veins and cells, which differ from dislocation structures of dislocation wall-like and veins in open-air condition.

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REFERENCES


