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Abstract

Strain-rate cycling tests associated with ultrasonic oscillation were carried out between the strain rates ($\dot{\varepsilon}$) of 1.1×10^{-5} s^{-1} and 5.6×10^{-5} s^{-1} for NaBr:Li$^+$ or K$^+$ single crystals from 77 K up to the room temperature. Superposition of oscillatory stress during plastic deformation causes a stress drop ($\Delta\tau$). By using the stress change ($\Delta\tau'$) due to the strain-rate cycling keeping the stress amplitude constant, $\Delta\tau'/\Delta\ln\dot{\varepsilon}$ was given as a measurement of the strain-rate sensitivity (λ) of flow stress. The relative curve of $\Delta\tau$ and λ has a stair-like shape for the two kinds of crystals at low temperature (T). That is to say, the curve has two bending points and two plateau regions and λ between the two bending points decreases gradually with increasing $\Delta\tau$. The activation energy (G_0) etc. concerned with the break-away of a dislocation from the isotropic strain around additive cation could be obtained on the basis of three relative curves (τ_p vs. T, λ_p vs. T, and τ_p vs. V) fitting the Cottrell-Bilby relation to the experimental results. τ_p is $\Delta\tau$ value of first bending point at low stress decrement and λ_p is the difference between λ at first plateau place and at second one on the curve of $\Delta\tau$ vs. λ. V is the activation volume obtained from λ_p. As a result, it was found that Li$^+$ ions are slightly weaker than K$^+$ ones as weak obstacles to dislocation motion in the crystals. Furthermore, the additive Li$^+$ or K$^+$ ions act as still weaker obstacles to dislocation motion in NaBr host crystal as against NaCl because of a slight reduction in G_0.

1 Introduction

Strength and plastic deformation of crystalline materials are dependent on dislocation motion, which is hindered by obstacles in a crystal. Here is considered two types of obstacles, i.e. weak obstacles such as additive ions and strong ones such as forest dislocations. The weak obstacles are considered not to be vacancies here, because the vacancies in a crystal have low density in contrast to the additions. For example, the concentration of vacancies at thermal equilibrium state is about 1.6×10^{-15} % for alkali halide crystal at room temperature. The mechanical property of materials is influenced by the interaction between dislocation and the weak obstacles. This has been widely investigated by the yield stress measurements (see, e.g., Refs. [1-4]), the direct observations of dislocation (see, e.g., Refs. [5-7]), the internal friction measurements (see, e.g., Refs. [8-10]) or the stress relaxation tests (see, e.g., Refs. [11, 12]). However, these methods do not provide the information on the interaction between dislocation and obstacles in bulk during plastic deformation. On the other hand, combination method of strain-rate cycling tests and the Blaha effect measurement would be possible to overcome the weak points in the widely known methods and has the merit different from these methods.

The Blaha effect is the phenomenon that static flow stress decreases when an ultrasonic oscillatory stress is superimposed [13]. Blaha and Langenecker found it when the ultrasonic oscillatory stress of 800 kHz was superimposed during plastic deformation of Zn single crystals. The same phenomenon has been confirmed in many metals [14-16] and has been widely made to apply to the plastic working technique for industrial purpose such as wire drawing, deep drawing, rolling and another metal forming techniques, since this phenomenon has an industrial significance [17-19].

It has been reported so far that the measurement of strain-rate sensitivity under

application of ultrasonic oscillatory stress during plastic deformation gives useful information on the interaction between a mobile dislocation and point defects in alkali halide crystals [20-22]. A large number of investigations on strength of materials have been made with alkali halide crystals [7, 23, 24]. This may be because the single crystals are readily available and have simple crystal structure and transparency. Alkali halide containing additive, therefore, is an excellent material for an investigation of mechanical properties. We report the influence of additive and host ions on the interaction between dislocation and additive ion in alkali halide crystals through the use of data obtained by the original method (strain-rate cycling tests associated with ultrasonic oscillation).

2 Experimental Procedure

The specimens used in this study are NaBr single crystals doped with Li^+ or K^+ as monovalent impurities. Each concentration of the impurities was 0.5 mol% in the melt. Two kinds of the specimens were prepared by cleaving out of single crystalline ingots, which were grown by the Kyropoulos method in air. The specimens cleaved to the size of $5\times5\times15mm^3$ were annealed immediately below the melting point for 24 h and were cooled to room temperature at a rate of 40 Kh^{-1} in order to reduce dislocation density as much as possible. The preparation method of specimens is the same as described in the previous paper for NaCl:Li^+, K^+, etc. single crystals [25].

Figure 1   A schematic illustration of the apparatus is shown in figure 1. A resonator composed of a vibrator and a horn with the resonant frequency of 20 kHz was attached to the testing machine, Instron 4465. The specimens were lightly fixed on a piezoelectric transducer and then cooled down to a test temperature. The specimens were deformed by compression along the <100> axis and the ultrasonic oscillatory

stress was intermittently superimposed for one or two minutes by the resonator in the same direction as the compression. The amplitude of the oscillatory stress was monitored by the output voltage from the piezoelectric transducer set between a specimen and the support rod. The strain of the specimen is considered to be homogeneous, because the wavelength, which is 226 mm by calculating from the data of Ref. [26], is about 15 times as long as the length of the specimen.

Figure 2   The strain-rate cycling test during the Blaha effect measurement is illustrated in figure 2. Superposition of oscillatory stress (τ_v) during plastic deformation causes a stress drop (as $\Delta\tau$, in MPa). Keeping the stress amplitude of τ_v constant, strain-rate cycling between the strain rates of $\dot{\varepsilon}_1$ (1.1×10^{-5} s^{-1}) and $\dot{\varepsilon}_2$ (5.6×10^{-5} s^{-1}) was carried out. Then, the stress change due to the strain-rate cycling is $\Delta\tau'$. The tests were performed from 77 K up to the room temperature. The temperature measurement was achieved by heater controlled using thermocouples of Ni-55%Cu vs. Cu. For the tests at 77 K, the specimen was immersed in the liquid nitrogen. Each specimen was held at the test temperature for 30 min prior to the compression test and the stability of temperature during the test was kept within 2 K. The strain-rate sensitivity ($\Delta\tau'/\Delta\ln\dot{\varepsilon}$) of the flow stress, which is given by $\Delta\tau'/1.609$, was used as a measurement of the strain-rate sensitivity (as $\lambda = \Delta\tau'/\Delta\ln\dot{\varepsilon}$, in MPa).

3 Results and Discussion

3.1 Relative curves of $\Delta\tau$ vs. λ for various crystals

Figure3(a)(b)   The variations of $\Delta\tau$ and λ with shear strain, ε, are shown in figure 3a and b for NaBr:Li$^+$ (0.5 mol%) single crystal at 193 K. The numbers besides each symbol represent the output voltage from the piezoelectric transducer on the support rod, which is proportional to the stress amplitude. $\Delta\tau$ is almost constant independently of

shear strain but increases with stress amplitude at a given temperature and strain. λ decreases with stress amplitude and the variation of it is small at low and high stress amplitude at a given shear strain. The relations between $\Delta\tau$ and λ at shear strains of 10

Figure 4 and 14 % in figure 3a and b are plotted in figure 4. The $\Delta\tau$ vs. λ curves have stair-like shape, i.e. first plateau region ranges below the first bending point at low $\Delta\tau$ and second one extends from the second bending point at high $\Delta\tau$. λ gradually decreases with $\Delta\tau$ between the two bending points. As indicated in the figure, $\Delta\tau$ at first bending point is referred to as τ_p, in MPa. Similar result as figure 4 is also

Figure 5 obtained for NaBr:K$^+$ (0.5 mol%) single crystal at 193 K as shown in figure 5. Figure

Figure 6 6 corresponds to the case of nominally pure NaBr single crystal at the same temperature (193 K) and shear strains (10, 12 and 14 %) as figure 4 for NaBr:Li$^+$ and figure 5 for NaBr:K$^+$. λ decreases with increasing $\Delta\tau$ at low stress decrement and no first bending point (i.e. τ_p) is on the relative curves of $\Delta\tau$ and λ for NaBr crystal. Therefore, τ_p is due to the additive ions (Li$^+$ or K$^+$) in the crystals. Stair-like relation

Figure7(a)(b) curve of $\Delta\tau$ vs. λ is obtained for NaBr:Li$^+$ or K$^+$ at any other temperature. Figure 7a and b shows the relative curves at various temperatures for the two kinds of single crystals. At the higher temperature, the smaller first bending point (τ_p) is observed in the figures. And τ_p disappears near room temperature. τ_p has been explained as the effective stress due to the weak obstacles such as the point defects which lie on the dislocation when a dislocation begins to break-away from the weak obstacles with the help of thermal activation during plastic deformation [22, 28, 29]. If this can be applied also to the case of NaBr:Li$^+$ or K$^+$ single crystals, the value of τ_p should depend on temperature. This is revealed as in figure 7a and b. These figures suggest that additive ions (Li$^+$ or K$^+$) are weakening still more as the weak obstacles to

dislocation motion at higher temperature and cannot act as the obstacles any more almost above room temperature.

The numbers besides each symbol in figures 4 to 6 represent the shear strains of these single crystals. Relative curves of $\Delta\tau$ and λ shift upward with increasing strain for all the crystals as can be seen in the figures. As can be observed in figure 3b, the result of slight increase in λ with strain leads to this phenomenon. It seems to be caused by λ which depends on dislocation cuttings, in other words, the reduction in the average length ($\bar{l}$) of dislocation segments pinned by obstacles (forest dislocations) with strain, because λ is inversely proportional to $\bar{l}$.

3.2 Influence of additive and host ions on deformation characteristics

Figure8(a)(b) Figure 8a and b shows the dependence of effective stress on temperature in which the solid circles correspond to τ_p for the each crystal. Isotropic strains are expected to be produced around the additive cations in the crystals, because their size is different from that for the host ions (Na^+). The force-distance profile between dislocation and the isotropic strain can be approximated to the Cottrell-Bilby relation [30] taking account of the Friedel relation [31]. Then, the relation between the effective stress and temperature is represented by the solid lines in figure 8a and b, which are determined by numerical calculation with the parameters (τ_{p0}, T_c, and G_0). τ_{p0} is the value of τ_p at absolute zero. T_c is the critical temperature T at which the relative curve of τ_p and temperature intersects the abscissa and τ_p is zero. G_0 is the Gibbs free energy for breaking away from the strain field around the additive ion by a dislocation at absolute zero. These curves agree with the data (τ_p) based on the analysis of relations between $\Delta\tau$ and λ at a given strain. In figure 4, the difference between λ at first plateau place and at second one on the curve of $\Delta\tau$ vs. λ is indicated as λ_p in MPa, which has

been considered the strain-rate sensitivity due to additive ions [20, 32] and is given by:

$$\lambda_p = \frac{kT}{bl_p d},$$

(1)

where k is the Boltzmann constant, b the magnitude of Burgers vector, l_p the average space of additive ions on a dislocation, and d the activation distance. The values of λ_p

Figure9(a)(b) for the each crystal are denoted by solid circles in figure 9a and b. When a dislocation overcomes the isotropic strains with the help of thermal activation during plastic deformation, the interaction between a dislocation and additive ions in the crystals is represented by the variations of τ_p and λ_p with temperature. Furthermore, observation of the activation volume V obtained from Eq. (1) (i.e. $V = kT/\lambda_p$) would provide the information on it, as well as them. The relation between τ_p and V is

Figure10(a)(b) shown in figure 10a and b for the crystals. On the basis of above-mentioned model and by using the least squares method with the parameters, solid lines in figures 9 and 10 are determined so as to fit to the experimental data (solid circles). The parameters

Table 1 used here are given in Table 1 for NaBr:Li$^+$ or K$^+$. The values of T_c and G_0 for NaBr:Li$^+$ are somewhat smaller than those for NaBr:K$^+$. The result implies that K$^+$ ions are slightly stronger as weak obstacles to dislocation motion on the slip plane containing many additive cations and a few forest dislocations during plastic deformation, compared with the case of Li$^+$ ions in the crystal. This may be because the isotropic strain around K$^+$ ion is larger than that around Li$^+$ one in NaBr single crystal. Its interaction energy with edge dislocation is much larger than that with screw dislocation, so that G_0 values in the table relate to the movement of edge dislocation in

the crystals and the yield strength is determined by the resistance to the motion of it. The parameters for NaCl single crystals containing Li^+ or K^+ ions are listed in the same table, where those are estimated by similar method as NaBr:Li^+ or K^+. The values of T_c and G_0 become larger and are influenced also by the different anions (i.e. Cl^- and Br^-) of the host crystals. That is to say, the additive Li^+ or K^+ ions act as still weaker obstacles to edge dislocation motion in NaBr host crystal as against NaCl. The differential G_0 values for the movement of edge dislocation in the different host crystal containing the same additions would be caused by the ionic radii of solvent, the rigidity modulus, and the Poisson's ratio according to the Cottrell equation [30].

With regard to alkali halides doped with monovalent impurities, it is well known that the dislocation motion is controlled by size-effect due to the isotropic strains around them rather than modulus-effect between solvent and solute ions [2, 33]. When the additive ion is at a distance of h ($h \approx b/2$) above edge dislocation on a slip plane, the interaction energy for the movement of dislocation due to the size-effect is expressed by [33, 34]

$$G_0 = \frac{1}{\pi} K_1 \varepsilon_b \Omega \left(\frac{b}{h} \right) \tag{2}$$

$$\left(K_1 = (C_{11} + 2C_{12}) \left\{ \frac{C_{44}(C_{11} - C_{12})}{C_{11}(C_{11} + C_{12} + 2C_{44})} \right\}^{\frac{1}{2}}, \varepsilon_b = \frac{1}{a} \cdot \frac{da}{dc} \right),$$

where C_{ij} is the elastic constants, a the lattice constant, c the concentration of additive ion and Ω ($\Omega \approx b^3$) the volume of additive one. Calculations of G_0 by using Eq. (2) are given in Table 2 for the crystals. A tendency for G_0 values to be variable in different host crystal containing the same additions agrees with that for experimental

results denoted in Table 1, as well as the same host crystal containing the different ones.

4 Conclusions

Relative curves between $\Delta\tau$ and λ have stair-like shape for NaBr:Li$^+$ or K$^+$ single crystals, which are obtained by the original method, i.e. combination of strain-rate cycling tests with the Blaha effect measurement during plastic deformation. By analyzing the three relationships (τ_p vs. T, λ_p vs. T, and τ_p vs. V) on the basis of data obtained from $\Delta\tau$ vs. λ, the activation energy G_0 for NaBr:Li$^+$ is found to be 0.50 eV and less than 0.53 eV for NaBr:K$^+$. This leads to the phenomenon that K$^+$ ions are slightly stronger as weak obstacles to dislocation motion in contrast to the case of Li$^+$ ions in NaBr crystals. Furthermore, the value of G_0 for the overcoming of edge dislocation from the isotropic strain around Li$^+$ or K$^+$ ion is influenced also by the different anions of the host crystals (NaBr or NaCl) because of variant characteristics such as the ionic radii of solvent, the rigidity modulus, and the Poisson's ratio. Not only the experimental G_0 values are near calculations of it by using Eq. (2) but also variations in its experimental value with different additive cations or anions of the host crystals agree with them for the crystals, as given in Tables 1 and 2.

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Table 1 Parameters used for calculation.

Crystal	τ_{p0} (MPa)	T_c (K)	G_0 (eV)
NaBr:Li$^+$ (0.5 mol%)	1.08	469	0.50
NaBr:K$^+$ (0.5 mol%)	1.12	483	0.53
NaCl:Li$^+$ (0.5 mol%) [25]	0.57	1201	0.55
NaCl:K$^+$ (0.5 mol%) [25]	0.75	704	0.60

Table 2 Interaction energy with edge dislocation due to size-effect by using Eq. (2).

Crystal	G_0 (eV)
NaBr:Li$^+$ (0.5 mol%)	0.52
NaBr:K$^+$ (0.5 mol%)	0.67
NaCl:Li$^+$ (0.5 mol%)	0.59
NaCl:K$^+$ (0.5 mol%)	0.77

Figure captions

Fig. 1 Schematic illustration of the apparatus.

Fig. 2 Variation of applied shear stress, τ_a, when the strain-rate cycling between the strain rate, $\dot{\varepsilon}_1$ (1.1×10^{-5} s^{-1}) and $\dot{\varepsilon}_2$ (5.5×10^{-5} s^{-1}), is carried out under superposition of ultrasonic oscillatory shear stress, τ_v.

Fig. 3 Variation of (a) the stress decrement ($\Delta\tau$) and (b) the λ ($\Delta\tau'/\Delta\ln\dot{\varepsilon}$) of flow stress with shear strain at 193 K and various stress amplitude for NaBr:Li$^+$ (0.5 mol%) single crystal. The numbers besides each symbol represent the output voltage from the piezoelectric transducer on the support rod, which is proportional to the stress amplitude τ_v.

Fig. 4 Relation between the stress decrement ($\Delta\tau$) and the λ for NaBr:Li$^+$ (0.5 mol%) at 193 K and the strains of 10 % and 14 %. The numbers besides each symbol represent the strain of the crystal. The plotted points are obtained from figure 3a and b.

Fig. 5 Relation between the stress decrement ($\Delta\tau$) and the λ for NaBr:K$^+$ (0.5 mol%) at 193 K and the strains of 8 %, 10 % and 12 %. The numbers besides each symbol represent the strain of the crystal.

Fig. 6 Relation between the stress decrement ($\Delta\tau$) and the λ for NaBr single crystal at various strains [27]. The numbers besides each symbol represent the strain of the crystal.

Fig. 7 Relation between the stress decrement ($\Delta\tau$) and the λ for (a) NaBr:Li$^+$ (0.5 mol%) and (b) NaBr:K$^+$ (0.5 mol%) single crystals at various temperatures. The numbers besides each symbol represent the temperature of the crystal.

Fig. 8 Dependence of τ_p on temperature for (a) NaBr:Li$^+$ (0.5 mol%) and (b) NaBr:K$^+$ (0.5 mol%) single crystals. The solid curves are given by numerical calculation.

Fig. 9 Dependence of λ_p on temperature for (a) NaCl:Li$^+$ (0.5 mol%) and (b) NaCl:K$^+$ (0.5 mol%) single crystals. The solid curves are given by numerical calculation.

Fig. 10 Relation between τ_p and activation volume (V) for (a) NaCl:Li$^+$ (0.5 mol%) and (b) NaCl:K$^+$ (0.5 mol%) single crystals. The solid curves are given by numerical calculation.
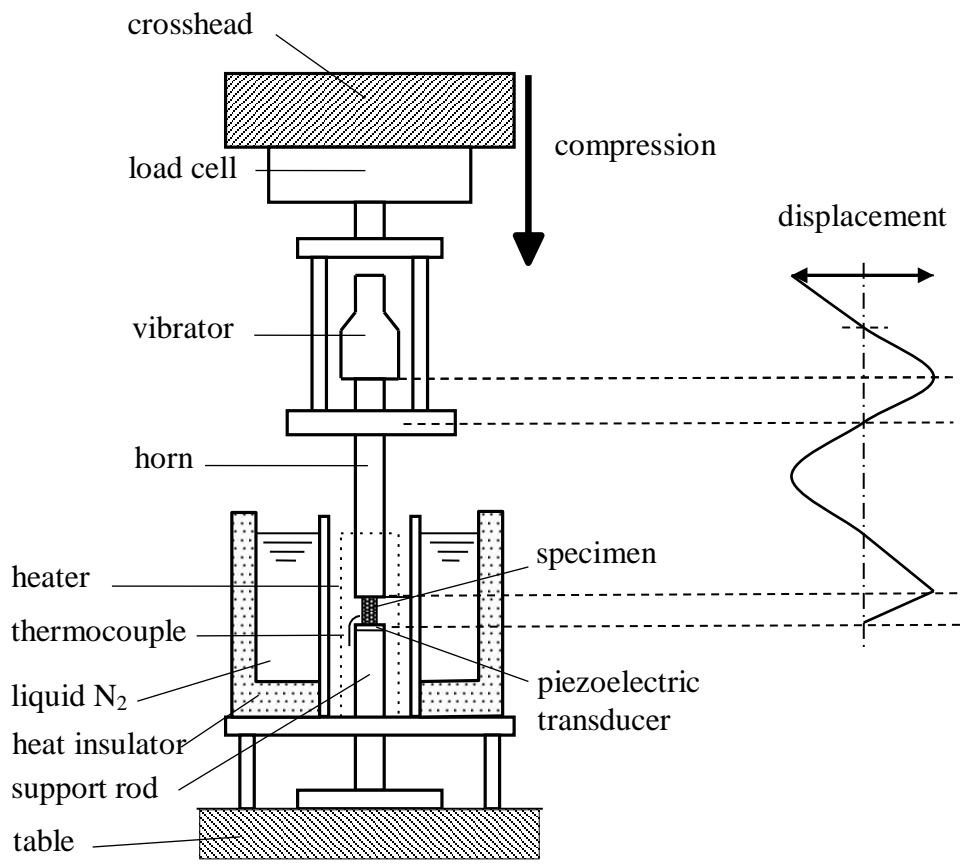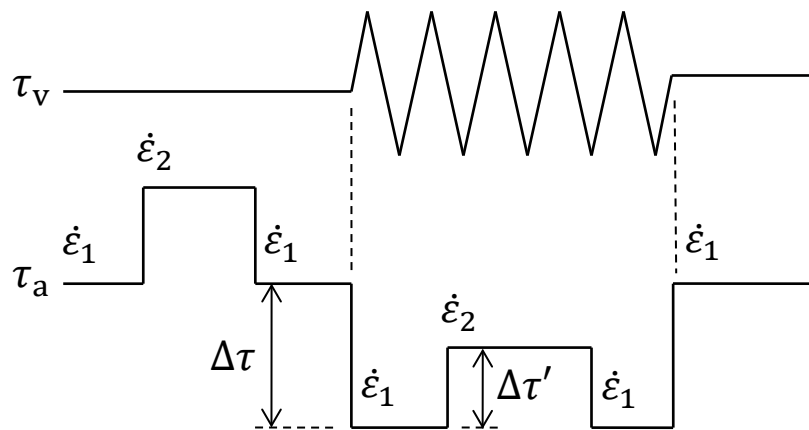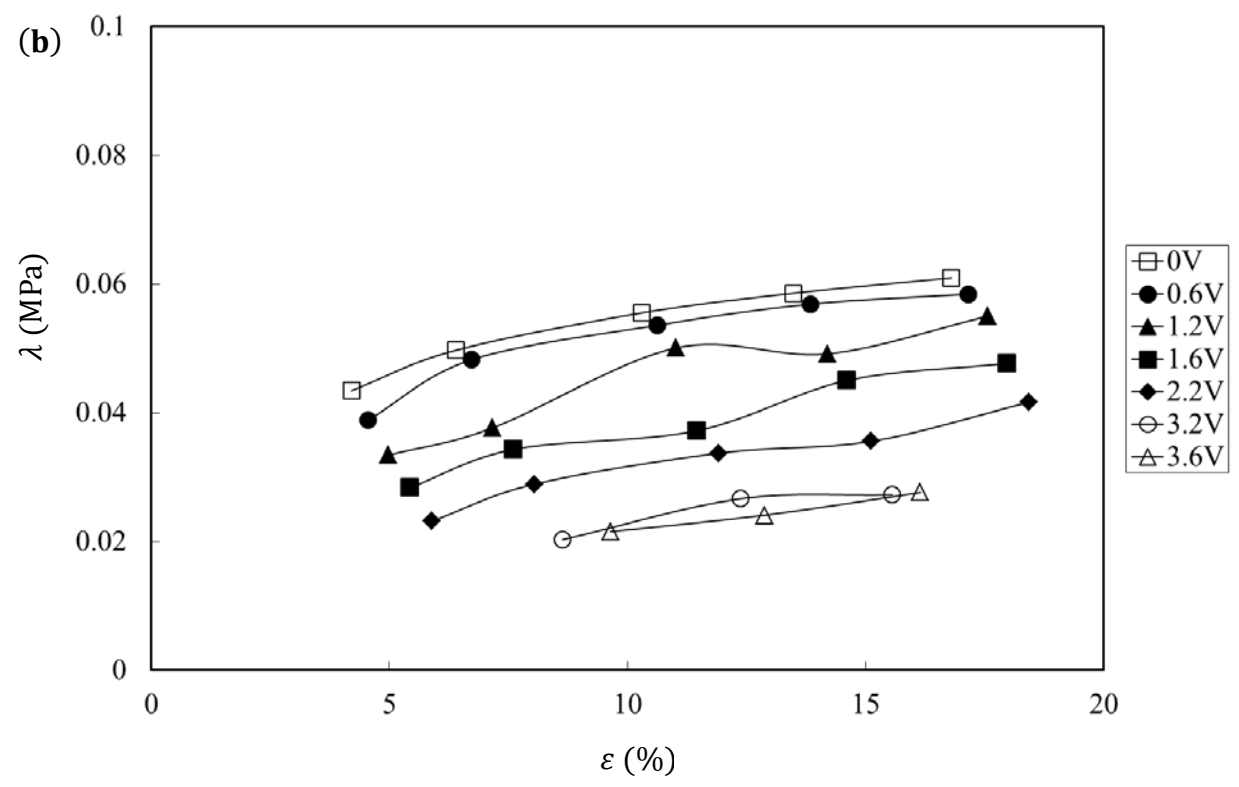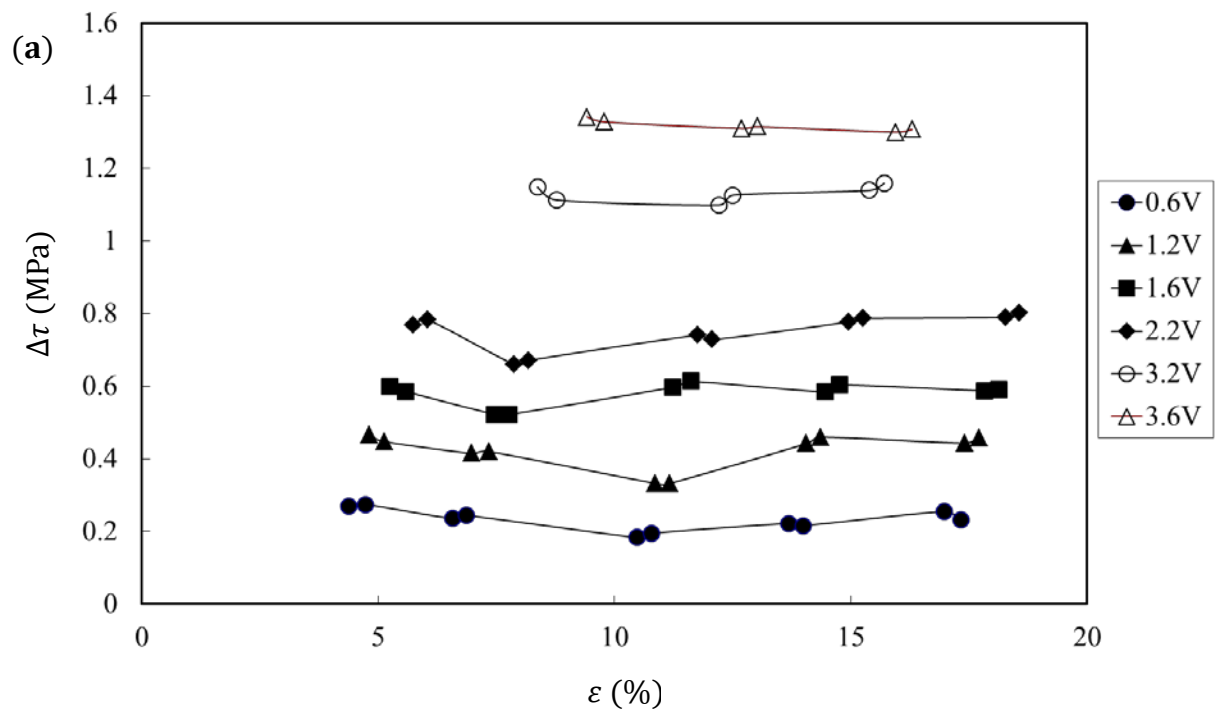
Fig. 1

Fig. 2

Fig. 3 (a), (b)

Fig. 4

Fig. 5

Fig. 6

(a)

(b)

Fig. 7 (a), (b)

(a)

(b)

Fig. 8 (a), (b)

(a)

(b)

Fig. 9 (a), (b)

(a)

Fig. 10 (a), (b)