JOURNAL OF MATERIALS SCIENCE **36** (2001) 2009–2012

Interaction between a dislocation and various divalent impurity in KCl single crystals for the Fleischer's model taking account of the Friedel relation

Y. KOHZUKI, T. OHGAKU
Faculty of Engineering, Kanazawa University, Kodatsuno 2-40-20, Kanazawa 920-8667, Japan

The interaction between a dislocation and the impurity in KCl : Mg^{2+} (0.035 mol% in the melt), KCl : Ca^{2+} (0.035 and 0.065 mol% in the melt) and KCl : Ba^{2+} (0.050 and 0.065 mol% in the melt) was investigated from the strain-rate cycling test during the Blaha effect measurement. This was carried out at 77–254 K. As a result, it was found that the Fleischer's model taking account of the Friedel relation seems to be suitable for KCl : Ca^{2+} and KCl : Ba^{2+}. However, it was not appropriate for KCl : Mg^{2+}. Furthermore, the values of T_c, $\Delta H(T_c)$ and ΔG_0 were obtained for the specimens. T_c is the critical temperature at which effective stress is zero. $\Delta H(T_c)$ and ΔG_0 are the enthalpy and the Gibbs free energy of activation for the breakaway of the dislocation from the impurity, respectively. $\Delta H(T_c)$ was almost the same for the specimens except KCl : Mg^{2+}. ΔG_0 increased with increasing the divalent cation size. In addition, the tetragonality around the divalent ion-positive ion vacancy pair was estimated on the basis of ΔG_0 for the each specimen. © *2001 Kluwer Academic Publishers*

1. Introduction

The strain-rate cycling test during the Blaha effect measurement was previously carried out for four kinds of single crystals: KCl doped with Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} [1]. The measurement of strain-rate sensitivity under application of ultrasonic oscillatory stress during plastic deformation gave useful information on dislocation motion. It is imaged that the dislocation moves on the slip plane containing many impurities and a few forest dislocations [2, 3]. The study was undertaken on the assumption that the interaction between a dislocation and the impurity can be approximated to the Fleischer's model [4]. Then, we did not discuss whether the Friedel relation [5] can be taken into the Fleischer's model. Recently, it was confirmed for KCl : Sr^{2+} (0.035, 0.050, 0.065 mol% in the melt) [6] that the Friedel relation can be taken into the Fleischer's model. This model is hereafter termed the F–F. In this study, we examine whether the F–F is appropriate to the interaction between a dislocation and the impurity for the other three kinds of specimens, namely, KCl : Mg^{2+}, KCl : Ca^{2+} and KCl : Ba^{2+}. Furthermore, activation energy for breakaway of the dislocation from the impurity is obtained for the each specimen.

2. Experimental procedure

Three kinds of single crystals, which are KCl doped with Mg^{2+} (0.035 mol% in the melt), Ca^{2+} (0.035 and 0.065 mol% in the melt) or Ba^{2+} (0.050 and 0.065 mol% in the melt), were deformed by compression along the $\langle 100\rangle$ axis at 77–254 K. Furthermore, the ultrasonic oscillatory stress was applied by a resonator in the same direction as the compression. The stress drop due to superposition of oscillatory stress during plastic deformation is $\Delta\tau$. When the strain-rate cycling is carried out keeping the stress amplitude constant, the stress change due to the strain-rate cycling is $\Delta\tau'$. $\Delta\tau'/\Delta \ln\dot{\varepsilon}$ was obtained as the strain-rate sensitivity. The resonant frequency was 20 kHz and the size of the specimens was about $5 \times 5 \times 15\ \mathrm{mm}^3$. The strain-rate cycling tests were carried out between the crosshead speeds of 20 and 100 μm min^{-1}. The preparation for the specimens and the strain-rate cycling test during the Blaha effect measurement are already described in the papers [3, 7].

3. Results and discussion

3.1. Relation between effective stress and temperature

If the interaction between a dislocation and the impurity can be approximated to the F–F, the relative formula of the effective stress, τ_{p1}, and temperature is expressed by [6]

$$(\tau_{p1}/\tau_{p0})^{1/3} = 1 - (T/T_c)^{1/2} \tag{1}$$

where τ_{p0} is the effective stress due to the impurity without thermal activation and T_c is the critical temperature at which τ_{p1} is zero. τ_{p1} is considered to represent the effective stress due to only one type of the impurities which lie on the dislocation when the dislocation moves forward with the help of oscillation [3]. τ_{p0} is obtained

0022–2461

TABLE I Values of τ_{p0} for the F–F

Specimen (mol%)		τ_{p0} (MPa)
KCl : Mg^{2+}	(0.035)	17.91
KCl : Ca^{2+}	(0.035)	15.34
	(0.065)	14.11
KCl : Ba^{2+}	(0.050)	5.34
	(0.065)	7.27

TABLE II Values of T_c for the F–F

Specimen	T_c (K)
KCl : Mg^{2+}	199
KCl : Ca^{2+}	278
KCl : Sr^{2+}	289 [6]
KCl : Ba^{2+}	370

by extrapolating linear relationship between $\tau_{p1}^{1/3}$ and $T^{1/2}$ to 0 K. Then, the values of τ_{p0} for the three kinds of specimens are given in Table I. The result agrees with Equation 1 is shown in Fig. 1a–c. From the value at which the line intersects the abscissa, T_c can be determined as shown in Table II. T_c tends to increase with increasing the divalent cation size.

We investigate whether the Friedel relation can be taken into the Fleischer's model for the interaction between a dislocation and the impurity in the each specimen. This is examined from the bending angle, ϕ_0, at which the dislocation embraces the impurities under τ_{p0} as the following [6]

$$\phi_0/2 = \cos^{-1}\{\tau_{p0} L_0 b/(2E)\}^{2/3} \tag{2}$$

where L_0 is the average spacing of impurities on the slip plane and b is the magnitude of the Burgers vector. In addition, E is the line tension of the dislocations and is calculated by μb^2. The shear modulus, μ, for [110] direction is assumed to be 1.01×10^{10} Pa at 0 K [8]. The average spacing of impurities on the slip plane is given by [4, 9]

$$L_0 = b \Big/ \left(\frac{4c}{3}\right)^{1/2} \tag{3}$$

where c is the concentration of the impurities. The values of c and ϕ_0 are given in Table III. The result shows that the F–F is supposed to be suitable for the interaction between a dislocation and the impurity in KCl : Ca^{2+} (0.035, 0.065 mol% in the melt) and KCl : Ba^{2+} (0.050, 0.065 mol% in the melt), because the values of ϕ_0 for

TABLE III Values of c and ϕ_0

Specimen (mol%)		c (p.p.m.)[a]	ϕ_0 (degrees)
KCl : Mg^{2+}	(0.035)	7.9	130
KCl : Ca^{2+}	(0.035)	43.1	155
	(0.065)	43.5	157
KCl : Ba^{2+}	(0.050)	9.2	159
	(0.065)	28.3	163

[a] The concentration of the impurities is obtained from dielectric loss measurement.

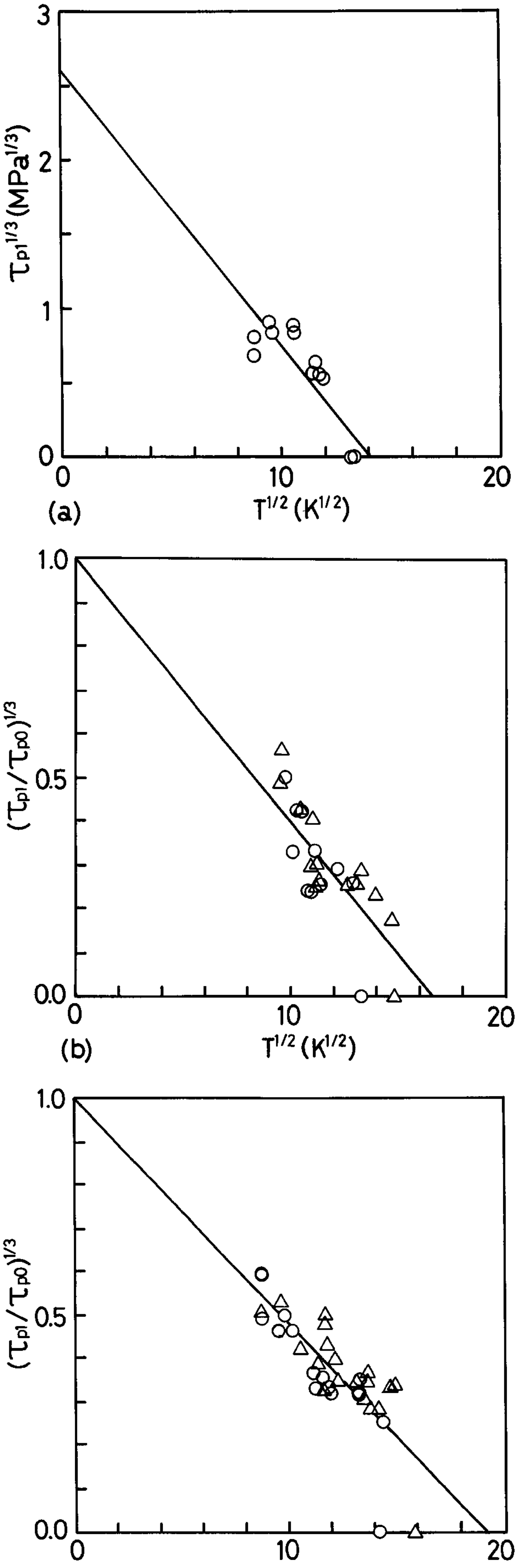

Figure 1 Relationship between the effective stress and the temperature at the F–F for (a) KCl : Mg^{2+} (○) 0.035 mol% (b) KCl : Ca^{2+} (○) 0.035 mol% and (△) 0.065 mol% and (c) KCl : Ba^{2+} (○) 0.050 mol% and (△) 0.065 mol%.

the specimens exceed about 140 degrees [10]. However, it is seemed not to be appropriate for KCl : Mg^{2+} (0.035 mol% in the melt), since the ϕ_0 is below 140 degrees.

3.2. The enthalpy and the Gibbs free energy of activation

When a dislocation overcomes the impurity with the aid of thermal fluctuation, activation enthalpy, ΔH, for the F–F is obtained from the following equation [6]

$$\Delta H = -kT^2(\Delta \ln \dot{\varepsilon}/\Delta \tau')_p\{-3\tau_{p0}/(2T_c)\} \times (T_c/T)^{1/2}\{1-(T/T_c)^{1/2}\}^2 \qquad (4)$$

where kT has the usual meaning. The $(\Delta\tau'/\Delta \ln \dot{\varepsilon})_p$ is assumed to be the strain-rate sensitivity due to the impurities and is given by the difference between strain-rate sensitivity at first plateau region and at second one on the relative curve of strain-rate sensitivity and stress decrement [1, 7, 11]. On the other hand, ΔH for the Fleischer's model is given by [1, 11]

$$\Delta H = -kT^2(\Delta \ln \dot{\varepsilon}/\Delta \tau')_p\{1-(T/T_c)^{-1/2}\}\tau_{p0}/T_c \qquad (5)$$

The activation enthalpy derived from Equation 4 is shown as a function of temperature in Fig. 2b for KCl : Ca^{2+} and c for KCl : Ba^{2+}. That from Equation 5 is shown in Fig. 2a for KCl : Mg^{2+}. The Gibbs free energy, ΔG_0, for the breakaway of the dislocation from the impurity is calculated from the equation [6]

$$\partial \ln \dot{\varepsilon}/\partial\tau = \{2\Delta G_0/(3kT\tau_{p0})\}\{1-(T/T_c)^{1/2}\}^{-2} \times (T/T_c)^{1/2} + \partial \ln \dot{\varepsilon}_0/\partial\tau \qquad (6)$$

where $\dot{\varepsilon}_0$ is a frequency factor. The result of Equation 6 for the F–F is shown in Fig. 3a and b. The values of ΔG_0 obtained from the slope of the line and $\Delta H(T_c)$ are given in Table IV. ΔG_0 and $\Delta H(T_c)$ correspond to the Gibbs free energy and the activation enthalpy for overcoming the impurity by a dislocation at 0 K respectively. ΔG_0 for KCl : Mg^{2+} could not be obtained. This will be examined in a subsequent paper. When the interaction between a dislocation and the impurity in KCl doped with the divalent cation is approximated to the Fleischer's model, $\Delta H(T_c)$ increased with increasing divalent cation size [1]. However, the value of $\Delta H(T_c)$ for the F–F is almost the same for KCl : Ca^{2+}, KCl : Sr^{2+} and KCl : Ba^{2+} except KCl : Mg^{2+}. $\Delta H(T_c)$ for KCl : Sr^{2+} is obtained from Equation 4 [6]. ΔG_0 tends to increase with increasing the divalent cation size in Table IV. Therefore the tetragonality, $\Delta\varepsilon$, produced around the divalent ion-positive ion vacancy pair seems

TABLE IV Values of $\Delta H(T_c)$, ΔG_0 and $\Delta\varepsilon$

Specimen	$\Delta H(T_c)$ (eV)	ΔG_0 (eV)	$\Delta\varepsilon$
KCl : Mg^{2+}	0.65	——	——
KCl : Ca^{2+}	0.76	0.29	0.20
KCl : Sr^{2+}	0.79 [6]	0.39 [6]	0.27
KCl : Ba^{2+}	0.75	0.48	0.33

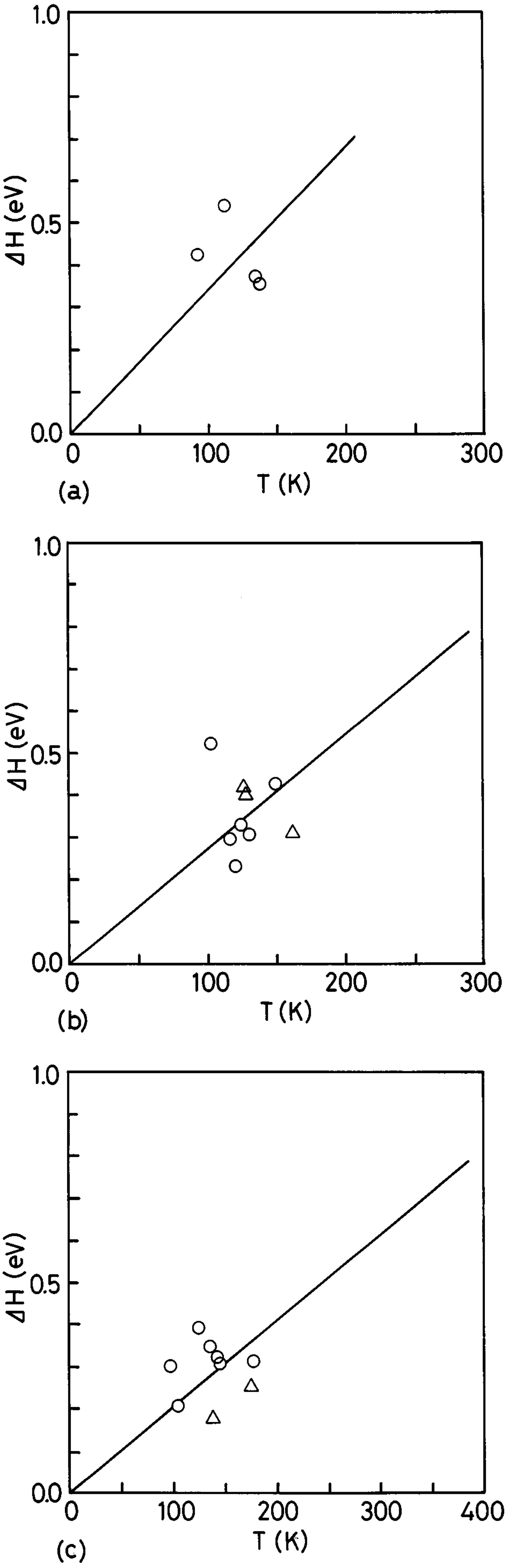

Figure 2 Relationship between the temperature and the activation enthalpy for the interaction between a dislocation and the impurity for (a) KCl : Mg^{2+} (○) 0.035 mol%, (b) KCl : Ca^{2+} (○) 0.035 mol% and (△) 0.065 mol% and (c) KCl : Ba^{2+} (○) 0.050 mol% and (△) 0.065 mol%.

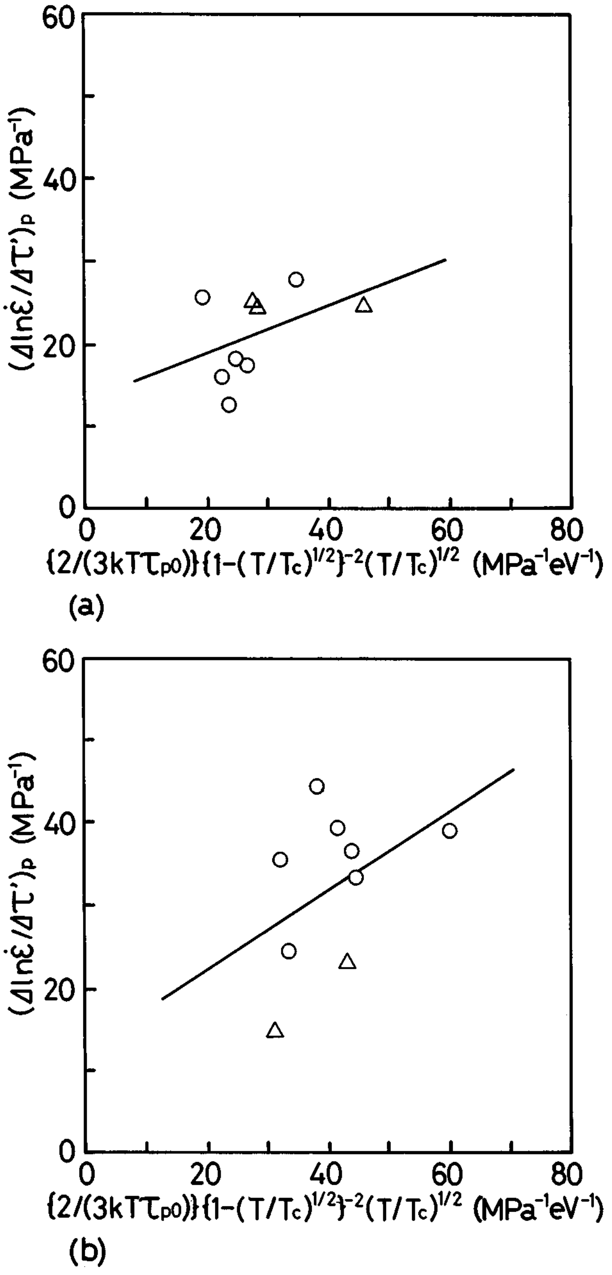

Figure 3 Linear plots of Equation 6 for (a) KCl : Ca^{2+} (○) 0.035 mol% and (△) 0.065 mol% and (b) KCl : Ba^{2+} (○) 0.050 mol% and (△) 0.065 mol%.

to increase from the Fleischer's model as suggested in the previous paper [1] when the divalent cation size approaches to the K^+ ionic size. We estimate the $\Delta\varepsilon$ for KCl : Ca^{2+}, KCl : Sr^{2+} and KCl : Ba^{2+}. The force acted on the dislocation at 0 K is expressed as [4, 12]

$$F_0 = bL_0\mu\Delta\varepsilon c^{1/2}/3.3 \qquad (7)$$

The $\Delta\varepsilon$ is calculated from the substitutional equation of Equation 3 in Equation 7, namely

$$\Delta\varepsilon = 3.81\Delta G_0/(b^3\mu) \quad (\Delta G_0 = F_0 b) \qquad (8)$$

The values of $\Delta\varepsilon$ derived from Equation 8 is given in Table IV.

4. Conclusions

1. If the interaction between a dislocation and the impurity can be approximated to the F–F, T_c tends to increase with increasing the divalent cation size.

2. From the values of ϕ_0 for the three kinds of specimens, the F–F seems to be suitable for the interaction between a dislocation and the impurity in KCl : Ca^{2+} (0.035, 0.065 mol% in the melt) and KCl : Ba^{2+} (0.050, 0.065 mol% in the melt). However, it is seemed that the F–F is not appropriate for KCl : Mg^{2+} (0.035 mol% in the melt).

3. The value of $\Delta H(T_c)$ which is obtained from Equation 4 for the F–F is almost the same for KCl : Ca^{2+}, KCl : Sr^{2+} and KCl : Ba^{2+}. However, ΔG_0 increases with increasing the divalent cation size.

4. The value of $\Delta\varepsilon$ is obtained by substituting the value of ΔG_0 in Equation 8. The $\Delta\varepsilon$ for the each specimen is given in Table IV.

References

1. Y. Kohzuki, T. Ohgaku and N. Takeuchi, *J. Mater. Sci.* **30** (1995) 101.
2. T. Ohgaku and N. Takeuchi, *Phys. Status Solidi (a)* **134** (1992) 397.
3. Y. Kohzuki, T. Ohgaku and N. Takeuchi, *J. Mater. Sci.* **28** (1993) 3612.
4. R. L. Fleischer, *J. Appl. Phys.* **33** (1962) 3504.
5. J. Friedel, "Dislocations" (Pergamon Press, Oxford, 1964) p. 224.
6. Y. Kohzuki, *J. Mater. Sci.* **35** (2000) 3397.
7. *Idem, ibid.* **33** (1998) 5613.
8. S. Hart, *Brit. J. Appl. Phys. (J. Phys. D) ser. 2* **1** (1968) 1285.
9. M. T. Sprackling, "The Plastic Deformation of Simple Ionic Crystals," edited by A. M. Alper, J. L. Margrave and A. S. Nowick (Academic Press, London, 1976) p. 141.
10. A. J. E. Foreman and M. J. Makin, *Phil. Mag.* **14** (1966) 911.
11. Y. Kohzuki, T. Ohgaku and N. Takeuchi, *J. Mater. Sci.* **28** (1993) 6329.
12. D. J. Lloyd and K. Tangri, *Phil. Mag.* **26** (1972) 665.

Received 4 January
and accepted 9 August 2000