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Analysis of observations on solid-solution hardening in KBr–KCl single crystals

Ali Asif · Muhammad Zakria Butt

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Abstract Available data on the temperature and concentration dependences of the critical resolved shear stress (CRSS) of KBr–KCl solid-solution crystals containing 8–41 mol% KCl in the temperature range 77–230 K have been analysed within the frame work of the kink-pair nucleation model of plastic flow in solid-solution crystals. It is found that CRSS τ decreases with the increase in temperature T in accord with the model relation $\ln \tau = A–BT$, where A and B are positive constants. The CRSS τ at a given temperature depends on solute concentration c as $\tau \propto c^p$, where exponent p has a value between 0.5 and 1 depending on the temperature at which deformation is carried out. The model parameter W_o, i.e. binding energy between the edge-dislocation segment involved in the unit activation process and the solute atoms close to it ($T \rightarrow 0$ K), which is inversely proportional to B, increases with solute concentration c monotonically in accord with the model prediction $W_o \propto c^{1/4}$ upto a critical value $c_m = 35$ mol% KCl. However, W_o decreases with increase in c beyond c_m, which indicates somewhat ordered distribution of solute in the host lattice of concentrated solid-solutions with $c > c_m$.

Introduction

Investigations of yielding behaviour of metallic solid-solution crystals have been carried out extensively in the past. Since 1948 many theories [e.g. 1–14] have been proposed to account for the observations regarding temperature and concentration dependences of the critical resolved shear stress (CRSS) and of the activation volume. Among these, kink-pair nucleation (KPN) model of plastic flow [11–14] has been found to correlate well with the experimental results in the case of face-centred cubic (FCC), body-centred cubic (BCC) and hexagonal close-packed (HCP) metallic solid-solutions [15–20]. The main objective of the present work was to explore whether the KPN model can also adequately explain the salient features of the deformation behaviour of ionic solid-solutions or not. We shall examine the experimental data appertaining to KBr–KCl <100> oriented solid-solution single crystals with solute concentration 8, 20, 34 and 41 mol% KCl deformed in compression by Sakamoto and Yamada [21] at a strain rate of 8.3×10^{-5} s^{-1} at various temperatures between 77 and 230 K, where diffusional recovery processes do not occur in the crystal.

The kink-pair nucleation model

In the KPN model of plastic flow in solid-solution crystals [11–14], yielding is visualized to occur as a consequence of the breakaway of edge-dislocation segments from short rows of closely spaced solute-atom pinning points in a manner analogous to the kink-pair mode of escape of screw dislocations from Peierls barriers in BCC metals [22, 23]. The maximum displacement nb of a dislocation segment of length L, after unpinning, must be adequate to remove most of the freed arc from the short range stress field of the

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A. Asif · M. Z. Butt (✉)
Department of Physics, Government College University,
Lahore 54000, Pakistan
e-mail: mzbutt49@yahoo.com

initial pinning points. Here b is the length of the Burgers vector, and n the number of interatomic spacings by which a dislocation bordered by a kink pair would advance in a stress-assisted, thermally activated jump. The model predicts a relationship between τ and T as under [11, 12]:

$$\ln \tau = A - BT \tag{1}$$

with $A = \ln \tau_o$, $B = mk/W_o$, $\tau_o = Uc^{1/2}/nb^3$ and $W_o = n(Uc^{1/2}Gb^3)^{1/2}$. Here τ_o is the CRSS at $T \rightarrow 0$ K, m is a constant equal to 25, k is Boltzmann constant, W_o is the binding energy between the edge-dislocation segment L_o involved in the unit activation process ($T \rightarrow 0$ K) and solute atoms close to it, U is the mean binding energy between a solute atom and the edge dislocation, c is solute concentration expressed in atomic fraction and G is shear modulus,

The microscopic parameters of slip envisaged in the model are given by the following formulae [13]:

$$n^3 = (W_o/Gb^3)^2[4G/\tau_o] \tag{2}$$

$$U = W_o^2/n^2Gb^3c^{1/2} \tag{3}$$

$$L_o = (4Gn/\tau_o)^{1/2}b \tag{4}$$

$$v_o = (1/4)nL_ob^2 \tag{5}$$

Here v_o is activation volume associated with τ_o.

Data analysis

We shall now analyse the temperature and concentration dependences of the CRSS of KBr–KCl single crystals [21] within the framework of KPN model. It should be noted that CRSS was obtained from the measured compressive stress by resolving the latter on the {110} <110> slip system. Figure 1 depicts in semi-logarithmic representation the CRSS data, denoted by points, as a function of temperature T at which deformation of KBr–KCl crystals was carried out. The lines drawn through data points for a given alloy by least-squares fit method are encompassed by the model Eq. (1) with the values of constants A and B given in Table 1.The value of correlation factor r (Table 1) in each case shows excellent linear relationship between ln τ and T. The intercept made by the ln τ–T line at stress axis ($T \rightarrow 0$ K) is equal to A (=lnτ_o) which gives τ_o value, while the magnitude of slope B (=mk/W_o) of the line yields W_o . The values of τ_o and W_o for each alloy are given in Table 2. These together with appropriate values of G, b and c, when substituted in Eqs. (2)–(5), provide the values of microscopic parameters n, U, L_o and v_o (Table 2).

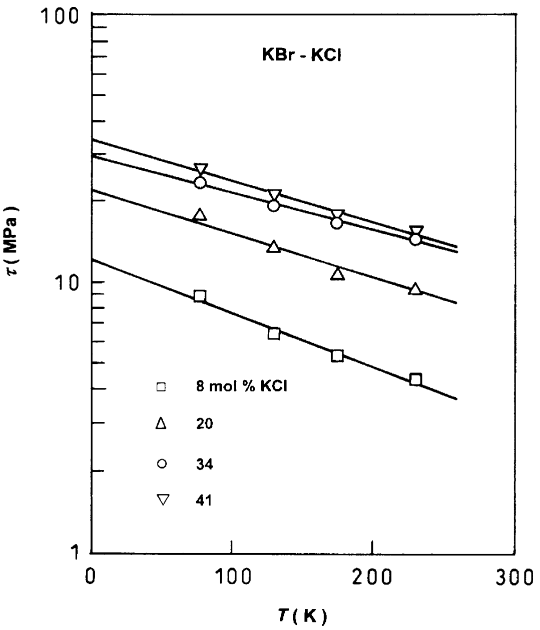

Fig. 1 Relationship between CRSS τ and temperature T in log-linear coordinates

Table 1 Numerical values of constants A and B in Eq. (1) correlating ln τ and T, along with correlation factor r, for a range of solute concentration in KBr–KCl single crystals

c (mol%KCl)	A	B (10^{-3} K^{-1})	r
8	2.483	4.496	–0.990
20	3.093	3.682	–0.998
34	3.375	3.127	–0.995
41	3.511	3.495	–0.992

Table 2 Numerical values of various parameters of KPN model of plastic flow in solid-solution crystals derived from the experimental temperature dependence of the CRSS of KBr single crystals alloyed with KCl

c (mol%KCl)	τ_o (MPa)	W_o (eV)	n	U (meV)	L_o (b)	v_o (b^3)
8	12.0	0.479	2.36	15.7	108.0	63.7
20	22.0	0.585	2.20	17.0	77.0	42.4
34	29.2	0.689	2.23	17.6	67.2	37.5
41	33.5	0.616	1.98	16.2	59.2	29.3

$G = 1.48 \times 10^4$ MPa, $b = 0.4653$ nm and $Gb^3 = 9.3$ eV in all cases

Figure 2 illustrates in logarithmic coordinates the concentration dependence of CRSS τ of KBr–KCl single crystals at different temperatures in the range 0–230 K. The lines drawn through data points for a given

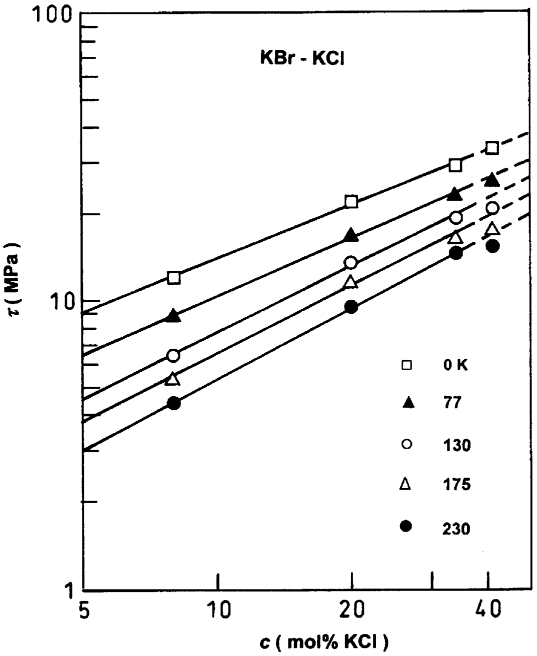

Fig. 2 Relationship between CRSS τ and solute concentration c at different temperatures in logarithmic coordinates

temperature, excluding one for 41 mol% KCl, by least-squares fit method comply with the mathematical expression:

$$\ln \tau = C + D \ln c, \qquad (6)$$

with the values of constants C and D given in Table 3. Again the values of correlation factor r (Table 3) being close to one in all the five cases show excellent linear relationship between ln τ and ln c. One can readily note that the value of the slope of ln τ – ln c line increase from 0.62 to 0.83 as temperature T rises from 0 to 230 K. Thus $\tau \propto c^p$, where p = 0.62–0.83 for T = 0–230 K. This is in accord with the model prediction, i.e. exponent p progressively increases from 0.5 to 1 as temperature T is increased from 0 K to rather high values [14].

Similarly Figs. 3–7 manifest in logarithmic coordinates the concentration dependence of parameters W_o, n, U, L_o and v_o for KBr–KCl system. Points denote the

Table 3 Numerical values of constants C and D in Eq. (6) for a linear relationship between ln τ and ln c, along with correlation factor r, for KBr–KCl single crystal at different temperatures

T (K)	C	D	r
0	4.07	0.62	0.998
77	3.90	0.68	0.999
130	3.81	0.77	0.999
175	3.69	0.80	0.998
230	3.58	0.83	0.999

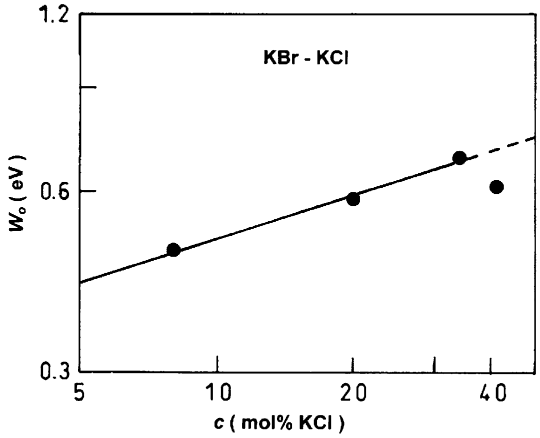

Fig. 3 Relationship between parameter W_o and solute concentration c in logarithmic coordinates

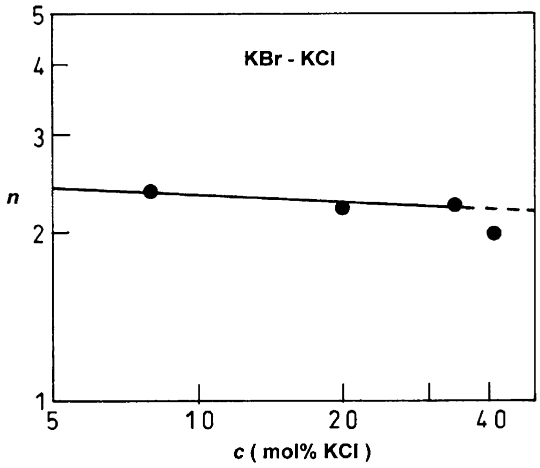

Fig. 4 Relationship between parameter n and solute concentration c in logarithmic coordinates

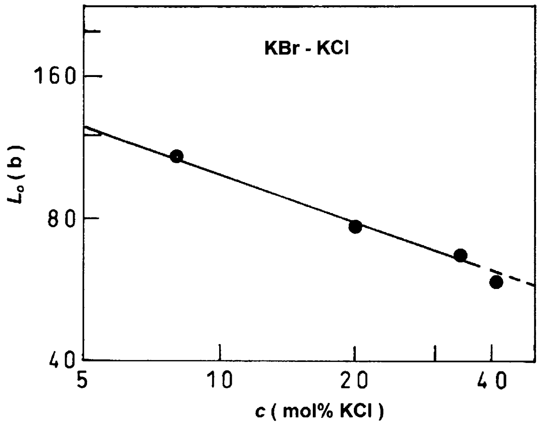

Fig. 5 Relationship between edge-dislocation segment L_o and solute concentration c in logarithmic coordinates

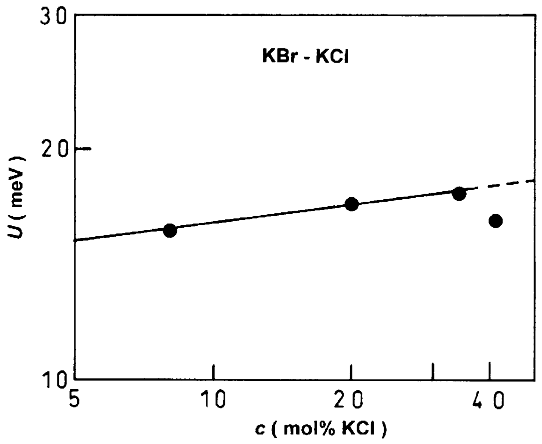

Fig. 6 Relationship between parameter U and solute concentration c in logarithmic coordinates

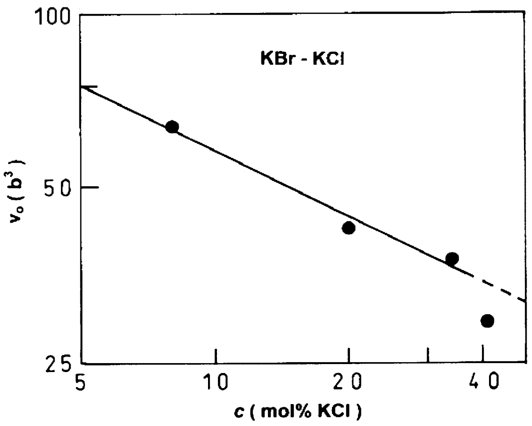

Fig. 7 Relationship between activation volume v_o and solute concentration c in logarithmic coordinates

values of these parameters listed in Table 2, while lines drawn through the data points, excluding one for 41 mol% KCl, by least-squares fit method are represented by:

$$\ln W_o = -0.12 + 0.249 \ln c, \tag{7}$$

$$\ln n = 0.740 - 0.044 \ln c, \tag{8}$$

$$\ln U = 2.96 + 0.080 \ln c, \tag{9}$$

$$\ln L_o = 3.83 - 0.332 \ln c, \tag{10}$$

$$\ln v_o = 3.19 - 0.377 \ln c, \tag{11}$$

with correlation factors r = 0.996, –0.847, 0.998, –0.996 and –0.989, respectively. It is apparent from Eq. (7) that W_o depends on solute concentration c as $W_o \propto c^{0.249}$, which is in excellent agreement with the prediction of KPN model i.e. $W_o \propto c^{1/4}$. Also Eqs. (8)–(11) show that dependence of n and U on solute concentration c is rather weak ($n \propto c^{-0.044}$, $U \propto c^{0.080}$) whereas that of L_o and v_o is moderately strong ($L_o \propto c^{-0.332}$, $v_o \propto c^{-0.377}$). This can also be accounted for in terms of model Eqs. (2)–(5) as follows. Assuming G and b rather independent of solute concentration c, one can note from Eq. (2) that since $W_o \propto c^{1/4}$ and $\tau_o \propto c^{1/2}$, then n should be independent of c. Similarly one can gather from Eq. (3) that as $W_o \propto c^{1/4}$, therefore n and U should be independent of c. This is confirmed by rather weak c—dependence of n and U depicted by Eqs. (8) and (9), respectively. Moreover, Eq. (4) indicates that as $\tau_o \propto c^{1/2}$, then L_o should be proportional to $c^{-1/4}$, and hence from Eq. (5) one also gets $v_o \propto c^{-1/4}$. This is borne out by Eqs. (10) and (11) which show c-dependence of L_o and v_o close to the prediction of the KPN model.

It will be pertinent to mention here that a common feature of the KPN model [11–14] and computer simulation results used by Sakamoto and Yamada [21] to account for the observed temperature and concentration dependences of the CRSS in KBr–KCl solid solution crystals at rather low temperatures (T < 300 K) where no diffusional recovery processes occur in the crystal is thermally activated motion of an edge dislocation overcoming several randomly distributed solute atom simultaneously. However their computer simulation study leads to $\tau \propto c(1-c)$ independent of temperature T at which deformation is carried out while the KPN model predicts temperature sensitive c-dependence of τ as illustrated and discussed above.

Finally, we shall discuss deviations observed in the concentration dependence of macroscopic (Fig. 2) and microscopic (Figs. 3–7) parameters in the case of KBr–41 mol% KCl with special reference to the nature of solute distribution in the slip plane of KBr–KCl solid-solution single crystals. This can be explored from the variation of W_o with solute concentration c (Fig. 8) within the frame work of the KPN model. In Fig. 8 the value of W_o for pure KBr single crystal has been taken from [24], while those for KBr–KCl alloys are from Table 1. One can see that W_o increases monotonically as c increases from 0 to 34 mol% KCl in accord with the model prediction ($W_o \propto c^{1/4}$). However after c_m = 35 mol% KCl, W_o decreases as c increases, which indicates that some deviation from random distribution of solute, e.g. local ordering, whether clustering or short range order, occurs beyond a critical concentration c_m corresponding to a maximum in the W_o–c curve. The change in c– dependence of τ_o, W_o, n, U, L_o and v_o beyond c_m is also evident for KBr–41 mol% KCl crystal in Figs. 2–7. Similar observations have also

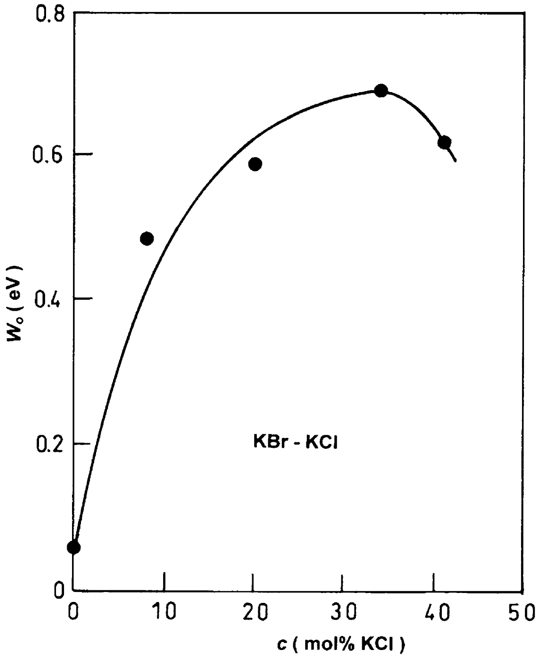

Fig. 8 Relationship between parameter W_o and solute concentration c

been made in case of metallic solid-solutions based on Cu [17], Ni [19] and Al [20]. The yield stress of concentrated solid-solutions is in fact sensitive to heat treatment and/or natural aging [e.g. 25, 26] even though second phase precipitates are not expected and are not observed by TEM techniques. The nature of solute distribution, whether random or non-random, also has a marked effect on the strain-rate sensitivity of flow stress in metallic solid-solutions [27].

Conclusions

1. The CRSS τ of KBr–KCl single crystals measured by Sakamoto and Yamada [21] between 77 and 230 K is found to decrease with the increase in temperature T in accord with the KPN model relation : $\ln \tau = A–BT$, where A and B are positive constants.
2. The observed concentration dependence of the CRSS $\tau \propto c^p$, with $p = 0.62$ to 0.83 in the range 0–230 K, is accounted for by the KPN model in which p increases with T between the limits 0.5 and 1.
3. The binding energy W_o of edge-dislocation segment L_o involved in the unit activation process ($T \rightarrow 0$ K) with solute atoms close to it depends on solute concentration c as $W_o \propto c^{1/4}$ up to a critical value $c_m = 35$ mol% KCl, which is in excellent agreement with the prediction of the KPN model.
4. Measured value of parameter W_o however decreases with further increase in c beyond $c_m = 35$ mol% KCl. Maximum corresponding to c_m in the W_o–c correlation indicates that distribution of solute in the host lattice is random for $c < c_m$, as assumed in the KPN model, and non-random in rather more concentrated solid-solutions with $c > c_m$.

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