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Effect of surface imperfections on the ductility of pure chromium

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The fracture behaviour of high-purity polycrystalline chromium was investigated using bend tests at room temperature in air. It was found that plasticity was dependent largely on surface imperfections. For example, brittle fracture took place in a roughly polished specimen containing a large number of small cracks on the surface. However, once the specimen was polished finely or electropolished, it was able to be bent by more than 90° without showing any brittle fracture. Such a surface effect on the fracture mode is very similar to the observations in glasses and in alkali halide crystals (for example, NaCl and LiF).

1. Introduction

Chromium and its alloys exhibit an excellent combination of low density, high creep strength and good oxidation resistance at high temperatures [1]. However, there is still a large barrier to practical use because of the poor ductility at room temperature. The ductility of chromium is known to be influenced by impurities, surface imperfections, and also metallurgical structures [2, 3]. In other words, the ductile-to-brittle transition temperature varies largely with these factors. For example, the transition temperature increases from 213 to 533 K as nitrogen content increases from 0.026 to 1 mass% [2]. The transition temperature also increases with decreasing grain size, and a large single crystal shows a transition temperature well below 200 K [4]. The recrystallization of a cold-rolled specimen increases the transition temperature by about 400 K [2]. But if the specimen is deformed slightly during cooling after recrystallization, the transition temperature is reduced to a similar level of the cold-rolled specimen [2, 5]. These results imply that the existence of mobile dislocations improves the ductility significantly [6].

It is also reported that surface filing produces a distinct but minor embrittlement [2], even though any detailed explanation has not been given on this observation. For example, it is still unclear whether notching or the work-hardened layer is the prime cause of this premature fracture [2, 3].

The purpose of the present paper is to show the results of bend tests for pure chromium. The importance of surface imperfections was proved firmly to the understanding of the fracture mode for chromium.

2. Experimental procedure

2.1. Specimen

High purity chromium powders prepared by the electrolytic method were used as the starting materials for this investigation. These powders were sintered in a hydrogen atmosphere at about 1500 K, and then rolled into a plate of about 3 mm thickness in the temperature range of 873 to 1173 K. The density of the specimen after consolidation was about 96% of the bulk one. The chemical composition of the specimen is shown in Table I. The nitrogen and oxygen contents were 0.005 and 0.011 mass%, respectively. Grains of about 100 μm were a little elongated along the rolling direction, but a marked preferred orientation was not normally developed in the structure, which is in agreement with a previous report [3]. The thickness of the plate specimen was reduced by 1 mm by grinding, and various surface treatments were applied to the specimen for bend tests.

Also, for comparison, the plate of the sintered specimen was remelted using a tri-arc furnace under a purified argon gas atmosphere. The button-shaped specimen was cut into shape for bend tests and then heat treated at 1273 K for 3.6 ks and air cooled. The

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TABLE I Chemical composition of chromium (mass %)

C	H	O	N	S	P	Si	Al	Pb	Cu	Fe	Cr
0.008	0.0003	0.011	0.005	0.001	0.0008	0.018	0.020	0.0001	0.0004	0.006	Balance

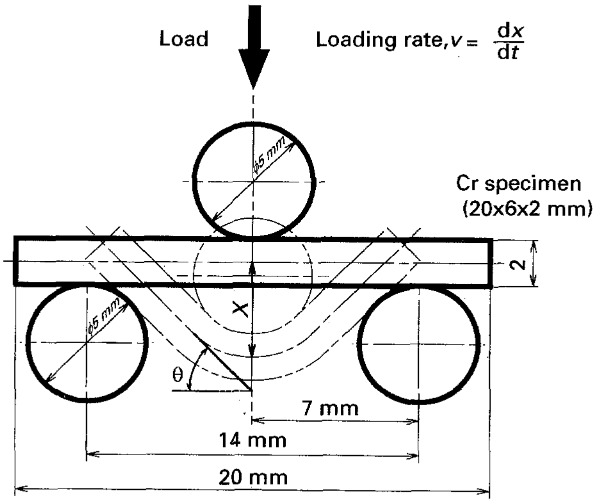

Figure 1 Schematic drawing of a three point bend test.

effect of fabrication methods on the ductility was examined with this arc-melted specimen and the sintered specimen as well.

2.2. Bend tests

The bend test was made at room temperature on a three-point loading rig as shown in Fig. 1. The specimen size was approximately $20 \times 6 \times 2$ mm. The loading rate, i.e. the crosshead speed, v, was varied from 0.002 to 0.100 mm s^{-1}. Surface treatment of the specimen was performed by either coarse, intermediate, or fine polishing using the corresponding abrasive paper (No. 200, 400, 1500) or a buff, dripping a solution of 0.06 mm Al_2O_3 powders in water on it. Also, in some cases electropolishing was further applied to the finely polished specimen in order to remove a work-hardened layer on the abrasive surface.

The surface roughness was measured by a conventional method. The results are shown in Fig. 2a–d. The depth of surface irregularities, R_{max}, was found to be about 2.5 μm for the coarse polishing shown in Fig. 2a, 0.5 μm for the intermediate polishing shown in Fig. 2b, 0.2 μm for the fine polishing shown in Fig. 2c, and 0.3 μm for the electropolishing shown in Fig. 2d. Thus, the surface of the electropolished specimen was a little rougher than that of the finely polished specimen, but still smoother and less vibrational in signals as compared to that of the intermediate polished specimen.

In addition, the surface oxidation effect on the ductility was investigated by making a thin oxide film of a few micron thickness on the surface of the finely polished specimen.

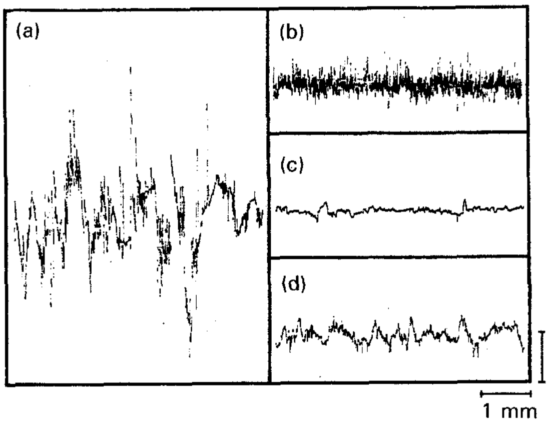

Figure 2 Surface roughness of the specimens prepared by (a) coarse polishing, (b) intermediate polishing, (c) fine polishing, and (d) electropolishing.

3. Results

3.1. Load–deflection curves

Load–deflection curves obtained at a constant loading rate of 0.005 mm s^{-1} are shown in Fig. 3 for the specimens prepared by three kinds of polishing treatments. The coarsely polished specimen shown in Fig. 3a fractured without showing any plastic deflection. On the other hand, the finely polished specimen shown in Fig. 3c was unbroken even at a deflection of 6.5 mm, which is the maximum travel distance of the plunger of the machine, and this corresponds to bending of the specimen by more than 90° 2θ (see Fig. 1). The upper and lower yield points were not seen clearly in the curve. The yield strength was estimated to be about 600 MPa from a standard equation for the three-point bend test [2]. This value for the sintered specimen was, however, significantly larger than the reported values, 300–450 MPa [3, 7, 8]. Also, work-hardening occurred after yielding.

Also as might be expected, the specimen prepared by intermediate polishing deformed plastically by a small amount before fracture, as shown in Fig. 3b. These results agreed with previous studies [2, 3], even though the filing effect has been tested using specimens with surface roughness as large as 24–35 μm [2]. The present results indicate clearly the importance of surface imperfections in a submicron scale on the fracture of chromium.

3.2. Appearance of specimens after bend tests

Further study was continued by changing both the surface condition of the specimens and the loading rate for bend tests.

The appearance of eight specimens after bend tests is shown in Fig. 4. As shown in Fig. 4a, b, the coarsely

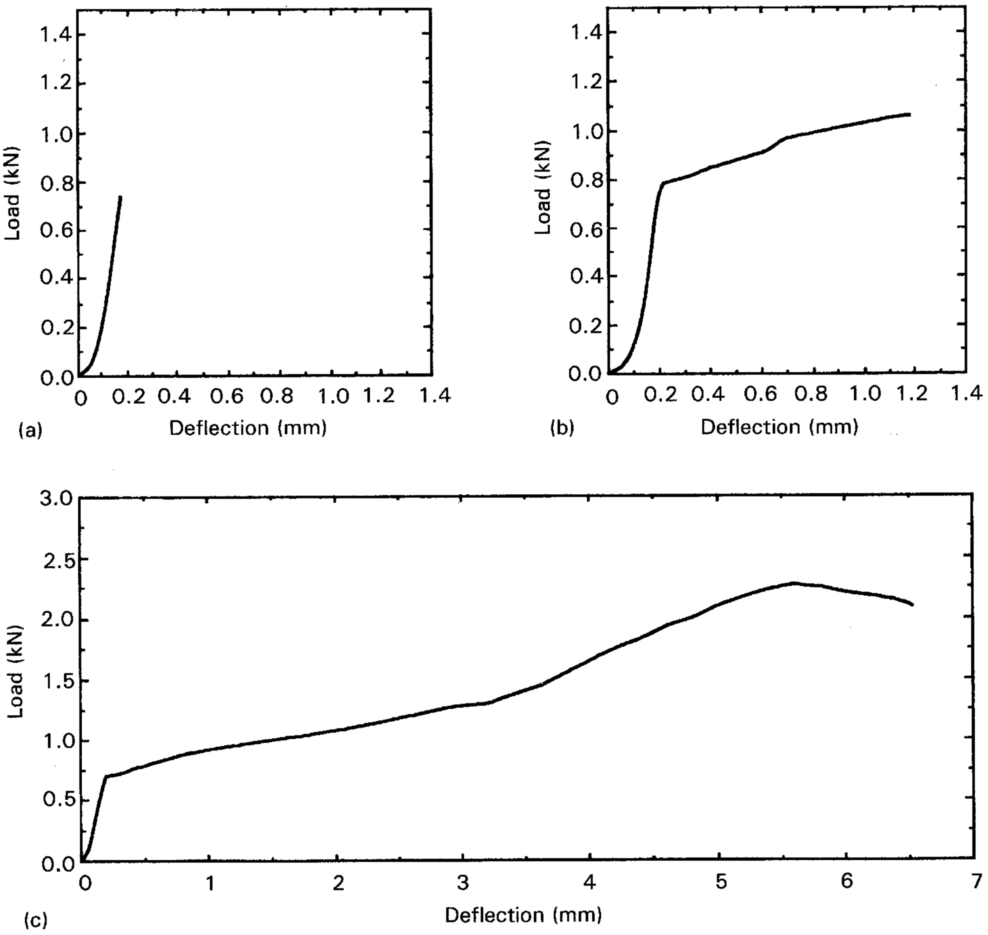

Figure 3 Load–deflection curves for the specimens prepared by (a) coarse polishing, (b) intermediate polishing, and (c) fine polishing; the loading rate was 0.005 mm s^{-1}.

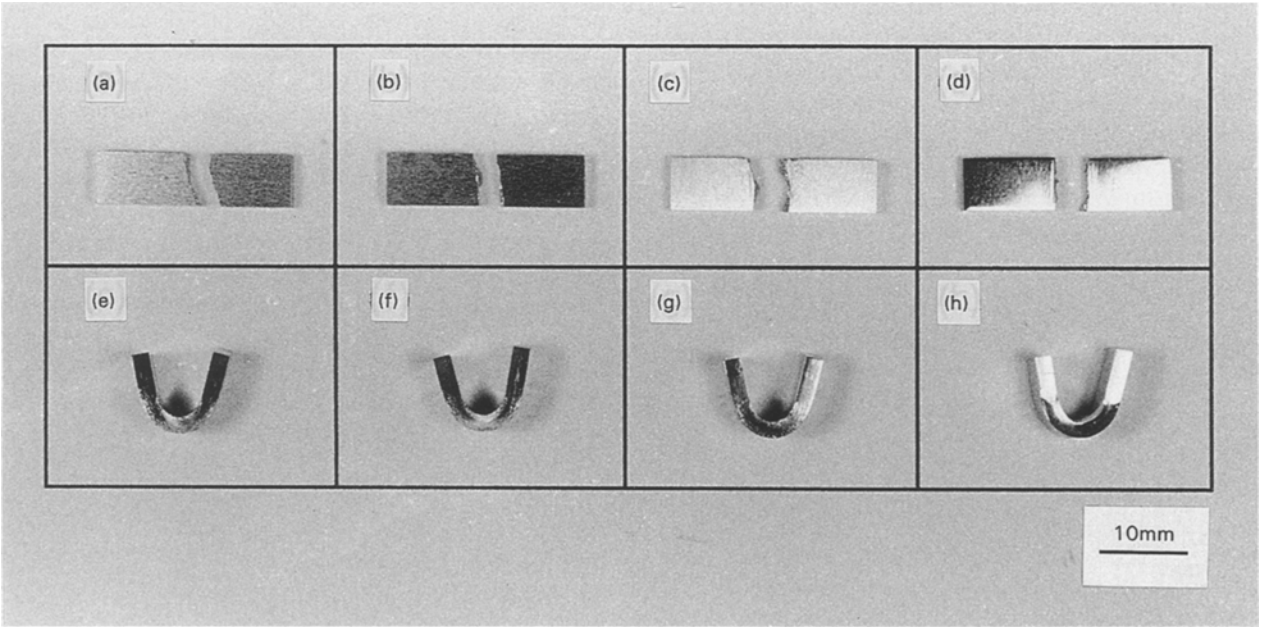

Figure 4 Appearance of the specimens after bend tests: (a) coarse polishing, loading rate, $v = 0.100$ mm s^{-1}; (b) coarse polishing, $v = 0.005$ mm s^{-1}; (c) intermediate polishing, $v = 0.005$ mm s^{-1}; (d) surface oxidation, $v = 0.005$ mm s^{-1}; (e) fine polishing, $v = 0.080$ mm s^{-1}; (f) fine polishing, $v = 0.005$ mm s^{-1}; (g) electropolishing, $v = 0.040$ mm s^{-1}; and (h) arc-melting and then fine polishing, $v = 0.005$ mm s^{-1}.

polished specimens fractured in a brittle manner, irrespective of the loading rate. Also as explained in the preceding section, intermediate polishing could yield a small plastic deflection as shown in Fig. 4c, but still the deformation was limited. In addition as shown in Fig. 4d, the existence of a surface oxide layer made the specimen very brittle, despite bending at an extremely low loading rate of 0.005 mm s^{-1}. This result indicates that the oxide is more susceptible to surface imperfections than chromium.

On the other hand, the finely polished specimen was not broken even at the measuring limit of the machine, and a largely deformed U-shaped specimen was obtained as shown in Fig. 4e, f. This occurred at a loading rate of either 0.005 or 0.080 mm s^{-1}. Such large deformation was also observed for the electropolished specimen tested at a loading rate of 0.040 mm s^{-1} as shown in Fig. 4g. This was seen not only in the sintered specimen, but also in the arc-melted specimen as shown in Fig. 4h, indicating that the ductility of chromium is independent of the fabrication methods. The measured yield strength for the arc-melted specimen was about 350 MPa, much smaller than the value of 600 MPa for the sintered specimen. This difference may be partially due to the very larger grain size (2–3 mm) of the arc-melted specimen compared to that of the sintered specimen (about 100 μm).

3.3. Changes in bend angles with loading rates

The bend angles of the specimens depended on the loading rate, as is shown in Fig. 5. The vertical arrow in the figure indicates that the bend angle was more than 90° and the specimen was bent into a U-shape as shown in Fig 4e–h.

Here, it is noted that for the electropolished specimen bend angles decreased with increasing loading rate, and brittle fracture will be expected to take place at a loading rate of more than 0.4 mm s^{-1}. The load–deflection curves for these electropolished specimens are shown in Fig. 6. There is an apparent increase of the yield stress with the loading rate in the curves. This is explained in terms of the magnitude of shear stress which must be applied before dislocations move through the crystal at any given velocity [9]. In general, such a shear stress is high in body centred cubic metals, and it further increases with increasing dislocation velocities [10]. This trend is reflected in a straightforward way by the observed increase of the yield stress with loading rates. Needless to say, if the shear stress necessary for dislocations to move at a high velocity, exceeds an endurance stress limit for cleavage fracture, the specimen will break in a brittle manner.

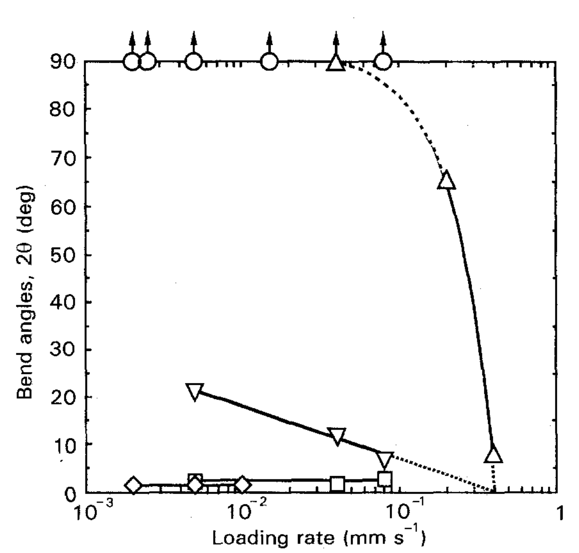

Figure 5 Changes in the bend angles of specimens with loading rates: (◇) coarse polishing, (▽) intermediate polishing; (○) fine polishing; (△) electropolishing, and (□) surface oxidation.

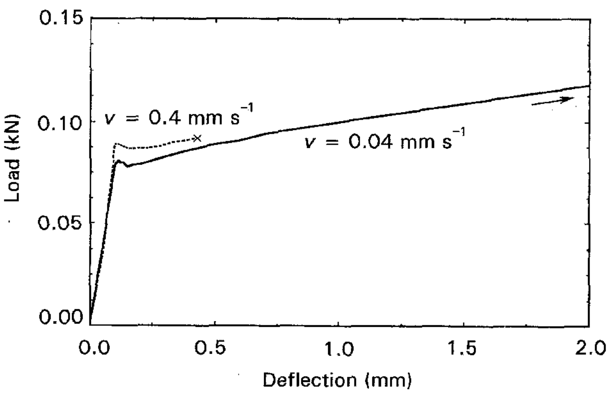

Figure 6 Load–deflection curves for the electropolished specimens tested under two different loading rates (v).

For the intermediate polished specimen there was a similar trend in the decrease of the bend angles with loading rates, as is shown in Fig. 5. Thus, there is indeed a certain threshold in the loading rate above which plastic deformation never occurs at room temperature in chromium. A slight deterioration in ductility on increasing the loading rate is also reported by other workers [5, 11].

4. Discussion

4.1. Surface imperfections

It was found from the present investigation that fracture of pure chromium is susceptible to surface imperfections, irrespective of the loading rate. This is similar to the fracture observed in glassy materials, alkali halides and many dense crystalline ceramics [12]. For example, for the NaCl crystal, it is well known that fracture originates from flaws in the surface. In these materials once microcracks are formed, the stress builds up at their tips until the strength of the solid is exceeded, and finally fracture takes place in a brittle manner [12]. In other words, the stress field cannot be relieved by plastic deformation in the crystal. On the contrary, for ductile materials the stress field induces plastic deformation near the crack tip, which results in stress relief, and hence in limited crack growth in the material.

4.2. Grain boundary effect

Single crystal chromium is ductile at room temperature, but polycrystalline chromium becomes more brittle as the grain size decreases [4]. Thus, it is apparent that the grain boundary provides a crack initiation site. As shown in Fig. 6, fracture takes place after yielding, even in deformation at a high loading rate of 0.4 mm s^{-1}. This result may support the model of slip induced grain boundary rupture proposed by Gilbert *et al.* [4]. Any cracks formed on grain boundaries by the slip mechanism will act as a sort of surface imperfection, and hence will be immediately followed by breaking in a brittle manner. Thus, high susceptibility of surface imperfections is substantial even to grain boundary fracture.

4.3. Surface energy and shear modulus

High susceptibility of surface imperfections to fracture implies that once cracks are formed, propagation can occur easily in chromium [4]. Some physical characteristics of chromium may be related to this phenomenon. Obviously crack propagation will be enhanced when the surface energy, γ, for the $\{1\,0\,0\}$ cleavage plane is low, as is found in NaCl-type alkali halides (for example, NaCl and LiF [12]). In this case, because of the low surface energy, the free crystal surface will extend readily to the inside of the specimen from original cracks on the surface. Although there are no experimental data on the surface energy of solid chromium, the measured surface energy of liquid chromium is comparable to or slightly lower than that of other 3d transition metals, despite its high melting temperature. For example, the measured value is about 1.70 $\mathrm{J\,m^{-2}}$ for Cr, which is smaller than 1.88 $\mathrm{J\,m^{-2}}$ for Fe, 1.95 $\mathrm{J\,m^{-2}}$ for V, 1.88 $\mathrm{J\,m^{-2}}$ for Co and 1.82 $\mathrm{J\,m^{-2}}$ for Ni, and it is comparable to 1.65 $\mathrm{J\,m^{-2}}$ for Ti [13].

Furthermore, it is interesting to note that dislocation energies are higher in chromium than in other ductile metals. Namely, elastic strain energy of dislocations increases proportionally to the shear modulus of the metal [14]. Following the Voigt and Reuss averages, the shear modulus, G, was calculated from single crystal elastic stiffnesses, C_{ij}, or elastic compliances, S_{ij}. The results are shown in Fig. 7 [15]. Chromium has the highest G value among the 3d metals. Mo, Ru (4d metals) and W, Re, Ir (5d metals) also have high shear moduli. Among these metals it is known that Mo and W are brittle at low temperature, as is Cr [16]. Also, Ru, Re and Ir are not base centred cubic metals like Cr, but they may be brittle at low temperature even though available data are limited on these metals at the moment. Such relatively high dislocation energies may make a certain barrier to dislocation formation in the crystal, resulting in further acceleration of brittle fracture in chromium. This may be supported by the experimental result that the cold-rolled specimen containing mobile dislocations is somewhat ductile, but removal of such dislocations from the specimen by complete recrystallization makes it very brittle and raises the ductile-to-brittle transition temperatures remarkably [2, 3].

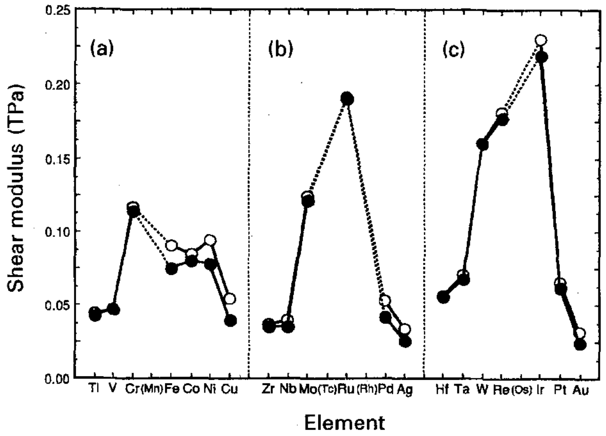

Figure 7 Calculated shear moduli for (a) 3d, (b) 4d and (c) 5d transition metals [15]: (○) Voigt average, and (●) Reuss average.

Thus, both low surface energy and high dislocation energy may cause high sensitivity to surface imperfections in chromium. In other words, as the ratio of shear modulus to surface energy increases, the sensitivity is supposed to increase. This has also been pointed out by Rice and Thomson [17]. So, this ratio was calculated for several materials as shown in Table II. Here, experimental data of surface energies were taken from [12] and [13]. Also, shear moduli used were the Voigt averaged ones [13, 15]. It is evident from this table that the calculated ratio is indeed high for every brittle and notch-sensitive material. Thus, this ratio is indeed a good indication of the brittleness of materials. The ratio will also vary with the presence of impurities or other constituent elements in the material. Improvement of the ductility of chromium may be achievable by reducing this ratio by alloying.

4.4. Effect of surface polishing on the ductile-to-brittle transition

The ductile-to-brittle transition has been discussed extensively in terms of dislocation nucleation and motion near the crack tip [17–20]. For example, the

TABLE II Comparison of the ratio of shear modulus to surface energy between the materials

Material	Test temperature (K)	Surface energy, γ ($\mathrm{J\,m^{-2}}$)	Shear modulus, G ($\times 10^{-1}$ TPa)	G/γ ($\times 10^{10}\ \mathrm{m^{-1}}$)
Ag	1198	1.130	0.196	1.73
Cu	1273	1.730	0.354	2.05
Sn	488	0.685	0.143	2.09
Ni	1273	2.000	0.649	3.25
W	2000	2.900	1.259	4.34
NaCl	298	0.300	0.149	4.97
CaF_2	298	0.450	0.441	9.80
MgO	298	1.000	1.332	13.32
LiF	298	0.340	0.516	15.18
Zn	77	0.105	0.508	48.38

transition temperature, T_c, is shown to be dependent largely on the ease with which dislocations nucleate at the crack tip [18, 19]. It is said that a sharp ductile-to-brittle transition arises from the need to nucleate a high density of crack tip sources, which emit dislocations which rapidly shield the crack [19]. Also, according to Warren's experiment using a precracked Si crystal [20], T_c increases when parts of the mobile dislocations are eliminated by removing the plastic zone region around a precrack from the surface. But T_c decreases inversely when mobile dislocations are introduced into the specimen by abrading it using 6 μm diamond paste. In addition, the strain rate dependence of T_c is known to be controlled by the activation energy for dislocation velocity [18]. Furthermore, it is reported that T_c decreases as the dislocation density is increased in body centred cubic metals where there is high lattice resistance to the dislocation motion [21]. In other words, in body centred cubic metals with high dislocation densities, dislocations lie close to a crack tip, and then the lattice resistance could be exceeded by the crack tip field, which causes enhancement of the dislocation motion and dislocation nucleation as well, resulting in blunting of the crack tip.

According to these dislocation approaches, the present results may be interpreted in the following way. As shown in Fig. 2, coarse polishing generates deep cracks, whereas fine polishing generates shallow cracks. Also, either polishing will introduce dislocation sources into the surface, as is similar to the case of precracked Si [20]. It is likely that such dislocation sources can shield the shallow cracks in some ways, but cannot shield the deep cracks. As a result, brittle fracture was observed in the coarsely polished specimen, irrespective of the loading rate. On the other hand, for fine polishing (or electropolishing) the loading rate dependence shown in Fig. 6 may arise from the need for dislocations to screen the crack tips before the critical stress intensity factor for brittle cleavage is reached. Therefore, fine polishing will make the Cr specimen ductile if the loading rate is slow, as is observed in the present experiment.

However, there still remains a problem in this interpretation. Recently, an environmental effect on the ductility of pure chromium [22] has been discovered. It becomes either brittle or ductile, depending on the test atmosphere, even for the use of the specimens prepared by the same polishing in those experiments. Further study is now under way in order to elucidate the ductile-to-brittle transition of pure chromium.

5. Conclusions

The surface imperfections were found to affect strongly the brittle or ductile nature of pure chromium at room temperature in air.

Acknowledgements

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