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The Effect of Hydrostatic Pressure on Brittleness in Chromium

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ABSTRACT

Recrystallized chromium, which is normally brittle, shows high ductility at atmospheric pressure after subjection to a hydrostatic pressure of 10^4 atmospheres. The pressurization does not produce microscopically detectable deformation, but there is a marked drop in yield stress similar to that found in iron (Bullen *et al.* 1964); it is suggested that in each case the effect is due to the appearance of free dislocations during pressurization. It is argued that the stress at yield in pressurized material is insufficient to initiate cracks and that the stress required to initiate cracks is substantially increased by deformation. This accounts for the high ductility of pressurized specimens, the brittle appearance of their fracture even after ~60% strain and the observation that specimens pre-strained during or subsequent to pressurization remain ductile after ageing or in further straining at high strain rates.

§ 1. INTRODUCTION

DISLOCATION arrays (e.g. Meakin and Petch 1963), twins (e.g. Hull 1963) and segregates at grain boundaries (e.g. Low 1963) can act as stress concentrators to initiate brittle cracks. Whatever the mechanism involved, there is abundant evidence (Low 1963) that yielding is a necessary condition for brittle fracture. Hence solute locking, which increases both the magnitude of the yield stress and the inhomogeneity of yielding, will favour high local stresses and promote crack initiation. If the yield stress is sufficiently high, cracks once formed will propagate and lead to fracture. Since yielding is determined mainly by the *shear* components of the applied stress, whereas crack propagation is strongly dependent on the *tensile* stress components, the addition of a hydrostatic pressure should favour ductile behaviour by reducing the tensile stress components. Thus it is well known that many brittle materials may show ductility when tested in an environment of high hydrostatic pressure (Bridgman 1952) and this effect has been demonstrated in chromium (Asai and Hayes 1957).

The present paper reports another effect of hydrostatic pressure on brittleness. Brittle chromium is not only ductile while *under* hydrostatic

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pressure, but ductility can be retained at atmospheric pressure *after* an application of hydrostatic pressure during which no additional loads have been applied to the specimen. Parallel experiments have shown that the yield point in iron can be eliminated by such a cycle of hydrostatic pressure (Bullen *et al.* 1964). Thus, in both chromium and iron the pressurization has depressed the yield stress; in chromium the reduction is to a value below the stress necessary for brittle fracture.

§ 2. Experimental Details

Chromium rods were produced from arc-cast ingots by extruding and swaging. Nitrogen and oxygen were the main impurities and varied within the limits 0·0008–0·005 and 0·015–0·03 wt. % respectively. Tensile specimens of 1 in. gauge length and 0·14 in. diameter were ground from swaged rod, electropolished, and annealed *in vacuo* at 1250°C for 1 hour. X-ray diffraction photographs obtained with a micro-focus source showed complete recrystallization. Specimens for each series of tests were made from a single rod. The results from different series are not quantitatively comparable because of slight differences in purity and structure between rods.

The high-pressure apparatus used for most of the experiments has been described elsewhere (Paterson 1964). Essentially, it consists of a working chamber in which the pressure can be raised to any value up to 10^4 atmospheres, using an external intensifier and pumps. When straining under pressure is required, an additional axial load can be applied to specimens by means of a piston which enters the pressure chamber. Later experiments involving pressurization only were done with a simple pressure vessel in which the pressure is raised by pushing a piston into it with an hydraulic testing machine. In both cases, synthetic rubber O-ring piston seals have been used. The pressure fluid was either petroleum ether or kerosene.

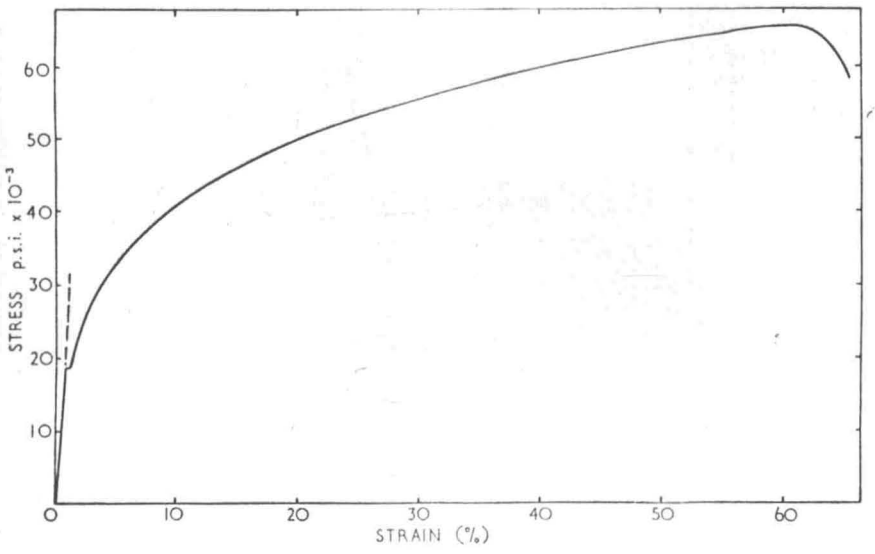
Specimens were not mechanically constrained during pressurization unless they were to be pre-strained under pressure. The pressure was applied slowly, held for 5 min (except when straining under pressure) and slowly released. After removal from the pressure vessel, specimens were stored in solid CO_2 until tested in an Instron testing machine at a strain rate of order 10^{-3} per min.

§ 3. Experimental Observations

3.1. *Effect of Hydrostatic Pressure on Brittleness*

At room temperature and pressure, the recrystallized chromium fractured without detectable plastic deformation. After pressurization at 10^4 atmospheres, strains of around 60% were commonly reached before fracture in subsequent testing at atmospheric pressure (fig. 1). However, the fracture of pressurized chromium had the characteristics of a ' brittle ' fracture, viz. fracture occurred suddenly at a given load and nearly every grain in the fracture surface contained cleavage facets. Figure 2 shows

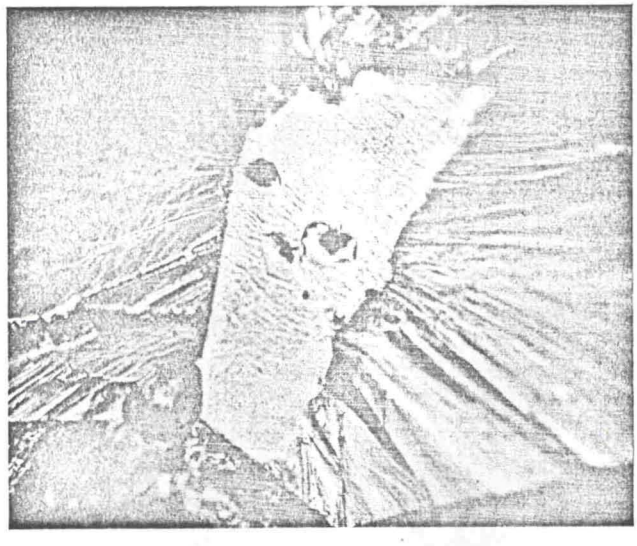
Fig. 1



Stress/strain curves for recrystallized chromium (dotted curve) and chromium after pressurization at 10^4 atmospheres (full curve). The stress has been corrected for the change in cross-sectional area with deformation; non-uniform deformation (necking) is responsible for the apparent decrease in strain hardening at large strains.

Note that the yield stress of pressurized chromium is approximately half the brittle fracture stress of recrystallized chromium.

Fig. 2

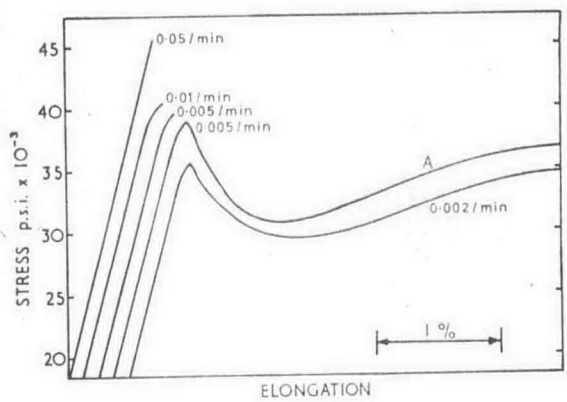


Typical source of fracture in a specimen of chromium pressurized at 10^4 atmospheres and fractured at 60% elongation (×750).

the origin of the fracture in a pressurized specimen; the crack appears to have formed at intergranular particles, as has been observed previously in brittle, recrystallized chromium (Hook and Adair 1963). The effectiveness of the pressurization is independent of whether kerosene or petroleum ether is used as the pressure fluid. This indicates that the effect is due purely to applied hydrostatic pressure and not to shearing by viscous forces in the fluid; the latter forces would be negligible in petroleum ether if not in kerosene.

Pressurized chromium yields at about half the fracture stress of recrystallized chromium (fig. 1). This is highly significant in view of the suggested close link between yield stress and brittleness (e.g. Stroh 1957, Cottrell 1958) and in view of the influence of pressurization on yielding in iron (Bullen *et al.* 1964). Further similarities exist between the effects of pressure on iron and chromium. After pressurization, both metals show characteristic rounded yield curves (fig. 3) and load drops at yield which depend on thermal activation as shown by varying the temperature for iron and strain rate for chromium (fig. 3). The brittleness of pressurized chromium at the higher strain rates (and hence at higher yield stress) also suggests that pressurization reduces brittleness by decreasing the yield stress. Furthermore pressurized specimens become brittle after ageing at temperatures of 450°C or above at which solute atoms can diffuse to lock free dislocations.

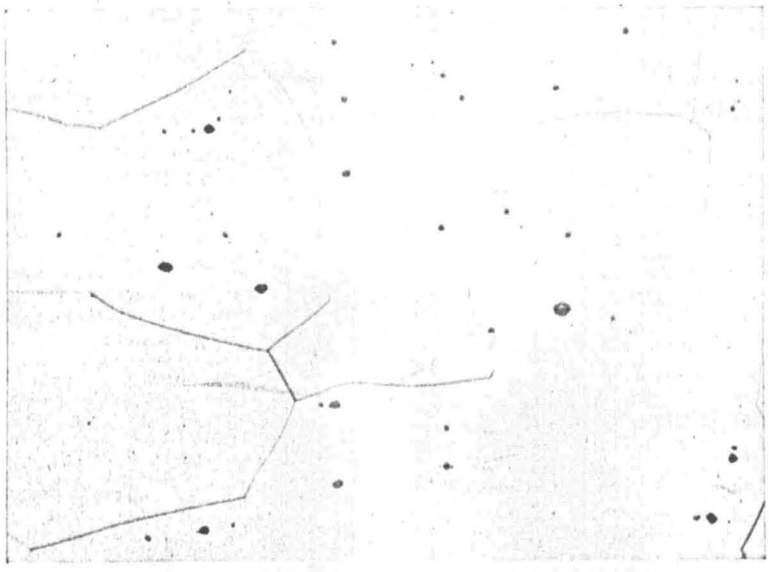
Fig. 3



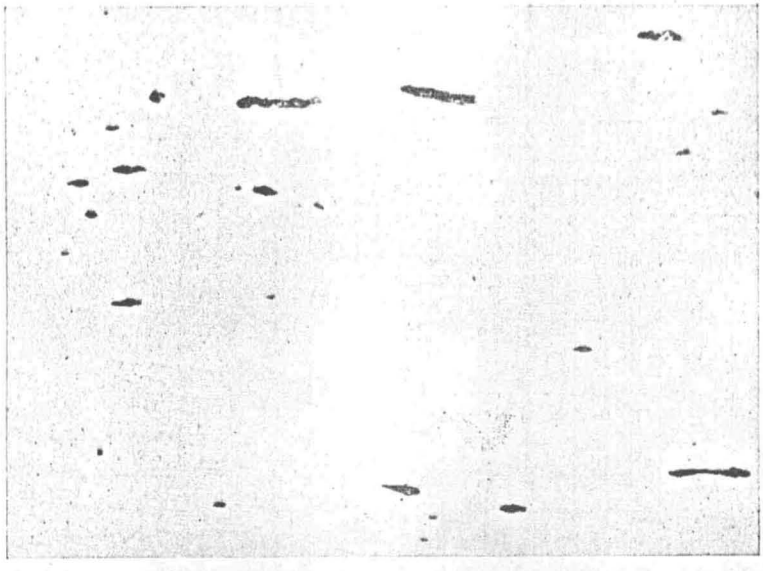
Stress/strain curves at the strain rates shown for chromium specimens pressurized at 10^4 atmospheres. Specimen A was ductile at a strain rate of 0·005/min; a similar specimen gave a slightly higher yield stress at the same strain rate and fractured at yield.

An extremely sharp transition in strain to fracture exists; specimens either failed at barely-detectable plastic strains or at strains in excess of 50% (fig. 3). The transition to the ductile range is associated with a marked increase in (true) fracture stress. Specimens just on the ductile side of the transition (e.g. A in fig. 3) were examined metallographically

Fig. 4

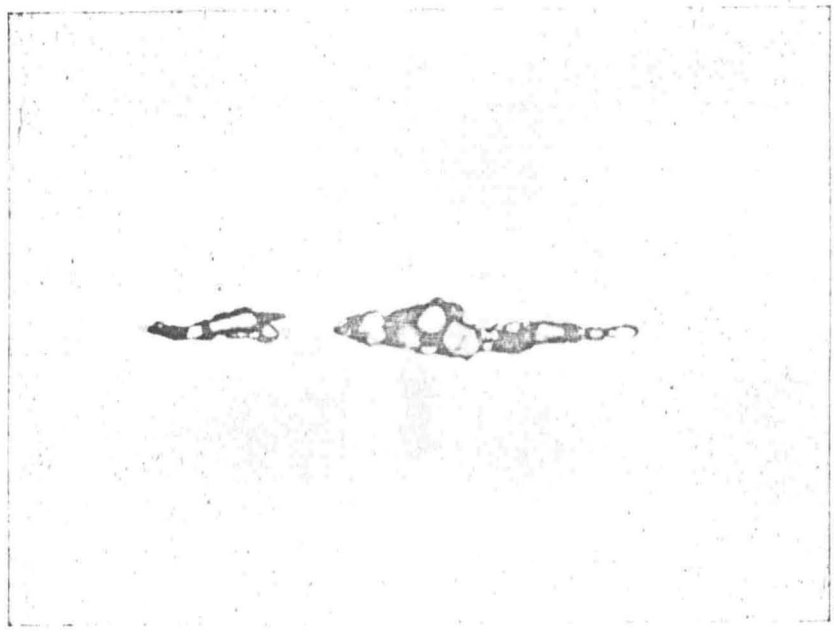


(*a*)



(*b*)

Fig. 4 (*continued*)



(*c*)

Longitudinal sections of pressurized chromium specimen deformed 50% in tension. (*a*) Undeformed shoulder, ×300. (*b*) Gauge length, ×300. (*c*) Gauge length, ×1000. ↔ Direction of applied stress.

after fracture. No cracks other than branches of the crack responsible for the fracture were detected, but marked ' tearing ' around inclusions was observed in longitudinal sections (fig. 4).

Repeated pressurization (five applications of 10^4 atmospheres) and prolonged pressurization (10^4 atmospheres for 1 hour) produced the same results as the normal pressurization.

Finally, chromium of the lowest nitrogen content (which was also the finest grained) remained brittle after pressurization at 10^4 atmospheres. Apparently pressurization did not decrease the yield stress sufficiently to induce ductility. This result is analogous to the effect in iron (Bullen *et al.* 1964) in which the yield point was removed more readily the lower the purity and the coarser the grain size. Further work is required to establish the threshold pressure for achieving ducility at room pressure by pressurization. It is expected that this threshold value will be a function of purity, grain size and subsequent initial strain rate.

3.2. *Examination of Pressurized Specimens*

The following are the results of various attempts to observe changes produced by pressurization:

(i) No surface deformation markings were detected by phase-contrast microscopy.

(ii) No misorientation or residual stress was revealed by x-ray diffraction.

(iii) No change in x-ray line broadening was found with a Geiger-counter diffractometer. Thus there appeared to be no change in the stacking faults although they need not have the same density of packing as the matrix in body-centred cubic crystals.

(iv) No change in bulk density was detected (sensitivity of measurement 0·001 g cm^{-3}).

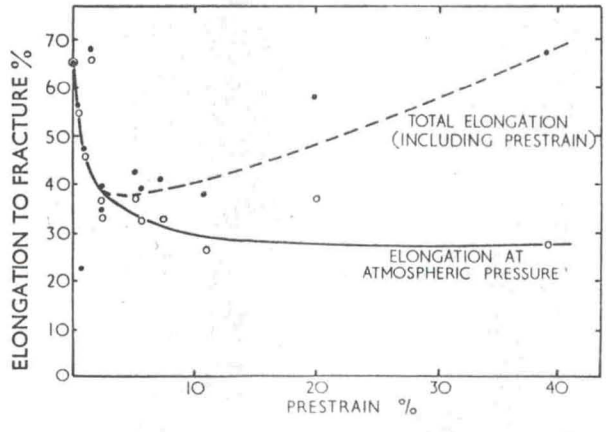
(v) Dislocations in recrystallized chromium foils, observed by transmission electron microscopy, are normally immobile. Free dislocations were observed in one pressurized foil, but in many others examined all dislocations were stationary. Hence any free dislocations produced by pressurization must be distributed very inhomogeneously.

We conclude that any changes during pressurization are extremely localized and therefore difficult to detect.

3.3. *Effect of Pre-strain during Pressurization*

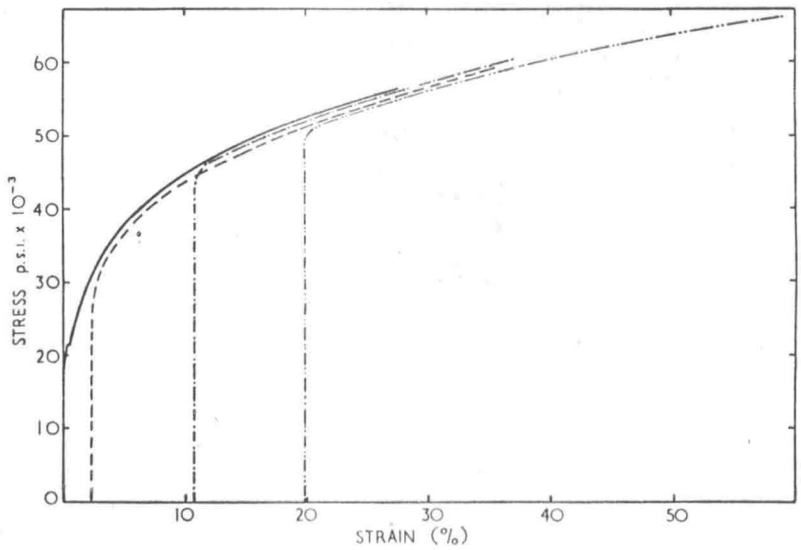
Recrystallized chromium could be deformed plastically to large strains while *under* pressure if the pressure was not less than a value somewhat below 2×10^3 atmospheres, depending on the purity of the chromium. At pressures below about 10^3 atmospheres, the specimens were brittle. Most of these tests under pressure were done at a strain rate of 0·02 per min. At lower strain rates, ductility was shown under slightly lower pressures. A pronounced yield point effect was shown in tests under pressure and the stress/strain curves were similar in magnitude to those obtained at room pressure.

Fig. 5



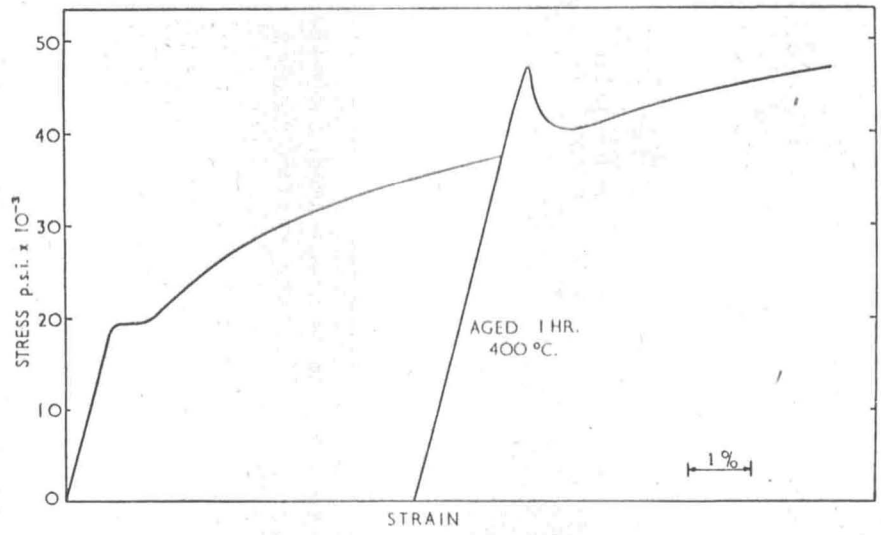
The effect of pre-strain under 10^4 atmospheres pressure on fracture at atmospheric pressure. The solid points and dotted lines show the total elongation to fracture (including the pre-strain) as a function of the amount of pre-strain; the open points and solid line show the variation of elongation at atmospheric pressure with pre-strain.

Fig. 6



Stress/strain curves for specimens pressurized at 10^4 atmospheres and pre-strained under pressure by the amounts shown. Pre-strain under pressure did not significantly affect the strain-hardening.

Fig. 7



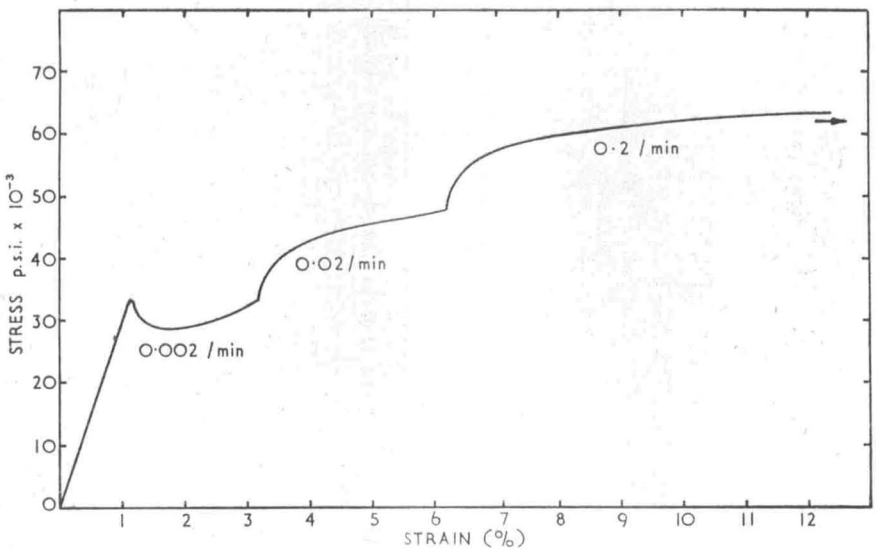
The effect of strain-ageing on pressurized specimens: Curve (*a*): Pressurized at 10^4 atmospheres. Curve (*b*): Deformed 5·8%, aged 1 hour at 400°C.

The influence of pre-strain under pressure on ductility in subsequent tests at room pressure was investigated (fig. 5). Pressurization without pre-strain gave the greatest elongation to fracture. Pre-strain up to 5% reduced the ductility, which then became insensitive to greater pre-strain. Thus the elongation to fracture (including the pre-strain) increased after a minimum at 5% pre-strain. Pre-strain had little effect on the stress/strain relationships at atmospheric pressure (fig. 6).

3.4. *Effects of Ageing and Strain Rate on Pre-strained Specimens*

Specimens were deformed various amounts either during or after pressurization and then aged before testing at atmospheric pressure. Pressurized specimens which had not been pre-strained became brittle on ageing at 450°C (§ 3.1). Specimens pre-strained even a few per cent were aged up to 1250°C without loss of ductility; recovery occurred at the higher temperatures and recrystallization at 1300°C. Large yields occurred after ageing at temperatures as low as 400°C (fig. 7), suggesting that sufficient solute was present to lock the dislocations. Provided no recovery occurred, ageing had little influence on fracture stress or elongation to fracture of pressurized specimens.

Fig. 8



Illustrates that pressurized chromium can be deformed at high strain rates after preliminary slower deformation. Pressurized chromium is brittle at initial strain rates greater than 0·005/min (fig. 3).

The effect of strain rate was investigated on pressurized specimens. After pre-strains of 1–2% at the standard testing rate at atmospheric pressure, specimens could be deformed plastically at rates far higher than that at which pressurized specimens (without pre-strain) became brittle

(figs. 8 and 3). Fracture stresses and elongations to fracture could not be measured at the high strain rates because the large flow stresses induced failure at the specimen grips.

§ 4. Discussion

4.1. *Effect of Pressurization*

Pressurized chromium yields at stresses much lower than the brittle fracture stress of recrystallized chromium (fig. 1). The yield point in iron is also affected by pressurization (Bullen *et al.* 1964) and pressurized iron and chromium show similar yield phenomena (§ 3.1). Hence we conclude that, as in iron, pressurization modifies the properties of chromium through the formation of free dislocations at elastic inhomogeneities. The present work adds little to this interpretation; the remainder of the discussion will deal with fracture in pressurized chromium.

Several authors (e.g. Cottrell 1958, Petch 1959) have emphasized the close association between yield points and brittleness. The condition for brittleness is that the yield stress must be sufficient both to initiate and to propagate cracks; solute locking promotes brittleness by raising the yield stress. Hence pressurization induces ductility by reducing the yield stress; conversely pressurized chromium is embrittled if the yield stress is raised by ageing or by testing at a high strain rate.

4.2. *Effect of Yield Stress on the Fracture Process*

The above general explanation suggests that pressurization favours ductility by lowering the yield stress. To explain other observations, e.g. the similarity in appearance between the fractures at large strains and brittle fractures, or the effects of pre-strain (§ 3.4), we need to understand how fracture is prevented during deformation.

The transition from brittleness to ductility in recrystallized body-centred cubic metals almost certainly occurs when the applied stress can no longer propagate cracks against the increasing plastic relaxation. Metallographic examination of iron and steel tested near the transition shows that micro-cracks form but do not propagate, and that the fracture surface becomes increasingly fibrous with increasing strain to fracture (e.g. Hahn *et al.* 1959). On the brittle side of the transition, the yield stress is sufficient for both initiation and propagation of cracks so that there is no information on the relative difficulties of these processes. Pressurization affords a unique opportunity to obtain such information since it provides a means of reducing the yield stress, and thereby obtaining ductility, without drastically affecting the crystal structure or changing the testing conditions. The structural change is so slight that it can only be detected by the change in yield point and it is unlikely that pressurization affects the flow stress beyond the yield point (Bullen *et al.* 1964).

The main difference between fracture in pressurized and recrystallized chromium is that the stress is initially high for recrystallized chromium

when the dislocation density is relatively low, and fracture commonly occurs at yield; after pressurization, similar stresses are not reached until the dislocation density has risen by several orders of magnitude. Since a metal is ductile only if cracks are not initiated or if cracks which have initiated are unable to propagate, the problem is whether the increased density of dislocations affects initiation or propagation.

The answer to this problem can be obtained by considering the case of propagation. The metallographic observations on pressurized specimens are the antithesis of those found under conditions where plastic relaxation damps out crack propagation; non-propagating micro-cracks have not been detected and the final fracture surfaces show almost complete cleavage even after 60% strain. The increase in fracture stress at the brittle/ductile transition is also relevant since it compares the stresses for fracture at low and high densities of dislocations. The fracture stress on the ductile side of the transition in pressurized chromium (fig. 3) is $\sim 2\frac{1}{4}$ times the value on the brittle side. This increase is considerably greater than those for recrystallized chromium ($\sim 1\frac{1}{2}$–2, Weaver 1961) and recrystallized iron ($\sim 1\frac{1}{2}$, Hahn *et al.* 1959); but it can hardly be attributed to greater plastic relaxation around cracks in pressurized chromium for the following reasons. The data for recrystallized metals refer to the transition from cleavage to ductile fracture; no comparable change in mode of fracture occurs at the transition in pressurized chromium (fig. 2). The low value (~ 7) of the exponent in the dislocation-velocity/driving-stress relationship for chromium at room temperature also suggests that free dislocations will not greatly affect crack propagation (Hahn and Jaffee 1963).

These considerations, which suggest that the increase in fracture stress at the transition is greater than could result from damping-out of crack propagation, and the lack of metallographic evidence that crack propagation is damped out, lead to the conclusion that the high ductility of pressurized chromium is not due to the difficulty of propagating cracks. Hence the brittle to ductile transition in pressurized chromium must be due to failure to initiate cracks in contrast to the transition in recrystallized chromium in which crack propagation is the limiting criterion. Stroh (1957) has predicted separate transitions due to crack initiation and propagation; usually the transition due to propagation occurs first and is the only one detected.

4.3. *Crack Initiation in Pressurized Specimens*

Since initiation is more difficult than propagation, it follows that the fracture stress is a measure of the stress for crack initiation. Pressurized chromium becomes brittle when the yield stress is slightly increased by ageing or by testing at higher strain rate, so that the stress to initiate cracks at yield is not much above the yield stress under our standard testing conditions. After small pre-strains, however, the flow stress can be increased by much larger amounts by ageing or by increasing the

strain rate without causing brittle fracture. Thus pre-strain has considerably increased the difficulty of initiating cracks. Observations on the effect of pre-strain at elevated temperatures on ductility at room temperature have also led Hook and Adair (1963) to the conclusion that cracks are not readily initiated in macroscopically deformed chromium.

We can estimate the relative difficulty of initiating cracks at yield and thereafter from the increase in fracture stress at the brittle/ductile transition in pressurized chromium, viz. $\sim 2\frac{1}{4}$ times. However, even this value may be an underestimate because the cracks responsible for the final fracture of ductile specimens probably form by a 'ductile' mechanism. Final fracture is preceded by 'necking' (fig. 1); at this stage wide voids form around oxide particles in chromium deformed at 400°C (Weaver 1961) and even in ductile metals such as copper (Rogers 1959). Voids can be detected when crack propagation cannot occur, i.e. at elevated temperatures or when the dimension of the tear transverse to the applied stress is small. However, at low temperatures the voids will initiate brittle cracks when their transverse dimension increases, i.e. at the onset of necking. The observation that the final fractures frequently form at inclusions supports this interpretation.

Dislocation locking cannot be the only reason for the comparative ease of crack initiation at yield. Specimens aged after pre-strain (e.g. fig. 7) show large yields but no loss of ductility; a similar effect has been found by Hook and Adair (1963). The most powerful influence is probably the increase in dislocation density with pre-strain. Cottrell (1963) has pointed out that the limiting value of the local stresses around stress concentrators during yielding depends on the dislocation density. When no dislocations are close to the stress concentrator, the local stress can rise even to the theoretical shear strength before plastic relaxation occurs. At higher densities of dislocations, the local stresses will be relaxed upon reaching the value required to unpin dislocations. Since the theoretical shear strength and the theoretical cohesive strength are of similar magnitude, which is considerably higher than the unpinning stress, crack initiation is far more likely at low densities of dislocations.

It is frequently found, e.g. in iron at low temperatures (Hahn *et al.* 1959), that cracks are continuously generated during deformation. This is not so for chromium deformed at room temperature. When cracks are prevented from forming during yielding, high ductility is observed even under conditions where cracks can propagate readily.

§ 5. Conclusions

1. Recrystallized chromium, normally brittle at room temperature, is highly ductile ($\sim 60\%$ strain) after pressurization at 10^4 atmospheres.

2. Pressurization reduces the 'yield stress' of recrystallized chromium considerably, probably by the creation of free dislocations at elastic inhomogeneities.

3. Pressurized chromium becomes brittle if the yield stress is raised by ageing or by increasing the rate of testing. This shows that the reduction in yield stress is directly responsible for the ductility of pressurized specimens.

4. Specimens pre-strained during or after pressurization do not become brittle on ageing or on testing at much higher strain rates than that required to embrittle pressurized chromium.

5. Even after 60% strain the fractures in pressurized chromium have the same appearance as a brittle fracture.

6. The final fracture and the effect of pre-strain on pressurized chromium are explained on the basis that crack initiation, which is the limiting condition for fracture under our test conditions, only occurs readily at yield or during necking.

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