

THE UNIVERSITY OF MANITOBA
DEFORMATION BEHAVIOUR IN SINGLE AND POLYCRYSTALLINE
MAGNESIUM OXIDE

by
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ABSTRACT

The yielding and flow behaviour of single and polycrystalline MgO containing ~ 100 p.p.m. of Fe as the major impurity has been investigated. Strain rate change and stress relaxation techniques have been used to investigate the rate-controlling deformation mechanism in single crystals. In the case of polycrystals a precise microstrain measurement technique together with etch pitting has been used to investigate the pre-fracture deformation behaviour.

In the air-quenched state, after annealing at 1250°C, the defects controlling deformation below 700°K in single crystals are recognized as 'elastic dipoles' consisting of Fe⁺³-ion-vacancy pairs located close to the slip plane (Fleischer interaction). Theoretical considerations employing the double kink mechanism of dislocation propagation do not account satisfactorily for the experimental observations. Also, since the thermal component of the flow stress and activation volume are independent of strain, the dislocation debris often resulting from deformation of ionic solids is not controlling the deformation in the present experiments.

The deformation kinetics obey the Johnston-Gilman empirical power law expression, $\bar{v} \propto (\sigma^*)^{m^*}$, with m^* between 38-5 in the temperature range of 77° - 673°K; and show that the dislocation dynamics and the rate theory approaches to deformation are equivalent in the present experiments, thus obviating any need to invoke entropy effects. Over the temperature range considered, the thermal component

of flow stress, σ^* , is independent of strain while the athermal stress, σ_i , is found to be the main contributor to work hardening.

To evaluate the effects of grain boundaries, the steps leading to the elastic-plastic transition preceeding dislocation-initiated fracture of a range of grain sizes in polycrystalline MgO were investigated. It is shown that when grown-in dislocations are pinned and the specimens are chemically polished, the initial dislocation activity occurs in the region of grain boundaries at a stress independent of grain size and below the microyield stress. The microyield stress corresponds to the stress necessary for propagating slip across the grains. The microyield stress obeys a Petch type of relationship with respect to grain size and this is attributed to the variation of dislocation density with grain size. The fracture stress-grain size relationship also follows the Petch equation but indicates that extensive work hardening has occurred prior to fracture.

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CONTENTS

<u>Chapter</u>	<u>Page</u>
1.0 INTRODUCTION AND OBJECTIVES	1
2.0 REVIEW OF PRIOR WORK	4
2.1 Single Crystal Deformation	4
2.1.1 Slip systems and dislocation intersections	6
2.1.2 Mechanisms of yielding in rock salt materials	12
2.1.2.1 Dislocation dynamics approach to plastic deformation	14
2.1.2.2 Rate theory approach to plastic deformation	19
2.1.3 The influence of heat treatment	32
2.2 Polycrystal Deformation	34
2.2.1 Role of grain boundaries	36
2.2.1.1 Grain boundaries as sources of dislocations	38
2.2.1.2 Compatibility at grain boundaries	39
2.2.2 The flow and fracture stress	43
2.2.3 Effect of grain size	45
2.2.3.1 The grain size dependence of flow and fracture stress	47
2.2.3.2 Correlation with experimental data	52
3.0 EXPERIMENTAL TECHNIQUES	56
3.1 Materials and Specimen Preparations	56
3.1.1 MgO Single crystals	56
3.1.2 Polycrystalline MgO	57
3.2 The Etch Pit Experiments	59
3.3 Mechanical Testing	61
3.3.1 Compression testing of MgO single crystals	61
3.3.2 Tensile testing of polycrystalline MgO	64
4.0 EXPERIMENTAL RESULTS	68
4.1 Compressive Deformation of MgO Single Crystals	68
4.1.1 General deformation characteristics	68
4.1.2 Temperature dependence of CRSS	68

<u>Chapter</u>	<u>Page</u>
4.1.3 The strain rate sensitivity of flow stress at various temperatures	71
4.1.4 Evaluation of the dislocation velocity-effective stress exponent, m^*	75
4.1.4.1 Stress relaxation technique	75
4.1.4.2 Extrapolation and other techniques	79
4.1.5 The Activation Volume	85
4.1.6 The Activation Energy	91
4.1.7 Work hardening in MgO single crystals	95
4.1.8 Etch-pit studies on the dislocation structures of MgO crystals	97
4.1.8.1 As-annealed structures	97
4.1.8.2 Distribution of slip in deformed specimens	97
4.2 Tensile Deformation of Polycrystalline MgO	102
4.2.1 Stress-strain results	
4.2.2 Grain size effect	106
4.2.3 Etch pit studies on polycrystalline MgO	111
5.0 DISCUSSION	121
5.1 Dislocation Dynamics and Thermally-activated Deformation of MgO Single Crystals	121
5.1.1 Considerations of a singly-activated mechanism	121
5.1.2 Evaluation of the rate-controlling deformation mechanism	123
5.1.3 Power law approach	137
5.2 Work hardening Behaviour of MgO Single Crystals	142
5.3 Microyielding and Fracture in Polycrystalline MgO	144
5.3.1 Slip initiation	145
5.3.2 Microyield	148
5.3.3 Fracture behaviour	153
6.0 SUMMARY AND CONCLUSIONS	157
6.1 Deformation of MgO Single Crystals	157
6.2 Deformation of Polycrystalline MgO	158
7.0 FURTHER RECOMMENDED RESEARCH	160
7.1 Single Crystals	160
7.2 Polycrystals	160
8.0 CITED LITERATURE	161

LIST OF FIGURES AND DIAGRAMS

	<u>Page</u>
Fig. 2.1: Diagram illustrating slip geometry in the rock salt structure.	8
Fig. 2.2: Illustration of the "oblique" dislocation reaction in the rock salt structure.	11
Fig. 2.3: A model of polycrystal deformation proposed by Ashby (ref. [133]).	40
Fig. 2.4: Schematic of the predicted mode of failure of a semi-brittle polycrystalline ceramic by dislocation mechanism.	46
Fig. 3.1: Compression testing jig used in the present investigation.	63
Fig. 3.2: Tensile testing jig used in the present investigation.	65
Fig. 3.3: Photograph of the device used for aligning the tensile specimen.	67
Fig. 4.1: Shear stress-shear strain curves for MgO single crystals.	69
Fig. 4.2: Temperature dependence of the CRSS for MgO crystals.	70
Fig. 4.3: Temperature dependence of the shear modulus for MgO.	72
Fig. 4.4: $\Delta\sigma$ vs. plastic strain for different temperatures.	73
Fig. 4.5: $\Delta\sigma$ vs. T at an equivalent plastic strain of 1.0%.	74
Fig. 4.6: Typical stress relaxation curves.	76
Fig. 4.7: Log (stress-rate) vs. log (time) plots.	77
Fig. 4.8: σ_A , σ^* and σ_i as a function of plastic strain.	80

	<u>Page</u>
Fig. 4.9: The variation of σ^* with temperature.	81
Fig. 4.10: m as a function of plastic strain.	83
Fig. 4.11: $(\text{strain})^{1/2}$ dependence of m for 77° , 208° and 293°K .	84
Fig. 4.12: m^* as a function of plastic strain.	86
Fig. 4.13: $\ln \dot{\epsilon}$ vs. $\ln \sigma$ plots for 773° , 873° and 973°K .	89
Fig. 4.14: The temperature dependence of m^* and m^*T .	90
Fig. 4.15: Plot of activation volume against effective stress.	92
Fig. 4.16: Activation volume as a function of plastic strain.	93
Fig. 4.17: Variation of activation volume with temperature.	94
Fig. 4.18: ΔH and H_0 against testing temperature.	96
Fig. 4.19: Work hardening rates as a function of temperature for MgO single crystals.	98
Fig. 4.20: As-annealed dislocation structures in MgO single crystals.	99
Fig. 4.21: Examples of slip initiation in MgO crystals.	101
Fig. 4.22: Reconstructed views of MgO crystals as observed by etch pitting after deforming at different temperatures in low strain regime.	103
Fig. 4.23: Applied stress against lattice and total strain, for room temperature tensile deformation of polycrystalline MgO.	105
Fig. 4.24: Applied stress vs. microplastic strain curves for different grain sizes.	108
Fig. 4.25: Stress-(grain size) $^{1/2}$ plots for the slip initiation stress, σ_d , microyield stress, σ_m , microflow stress at 3×10^{-5} plastic strain and fracture stress σ_F .	109

	<u>Page</u>
Fig. 4.26; Maximum plastic strain achieved before fracture for different grain sizes.	110
Fig. 4.27: Micrographs representing typical grown-in dislocation pits in polycrystalline MgO.	112
Fig. 4.28: Graph showing the variation of initial dislocation density with grain size.	113
Fig. 4.29: Examples of slip initiation from grain boundaries in MgO.	114
Fig. 4.30: Further supporting evidence for grain boundary dislocation generation in MgO.	116
Fig. 4.31: Slip bands activity about inclusions in polycrystalline MgO.	117
Fig. 4.32: Representative micrographs showing slip propagation up to the grain dimension.	118
Fig. 4.33: Slip activity at stresses approximately 80% of fracture stress.	119
Fig. 4.34: Spawning of secondary bands from the main glide bands.	120
Fig. 5.1: Thermally-activated components of the flow stress against activation energy in dimensionless units.	126
Fig. 5.2: Plot of σ_0^* against (concentration of Fe^{+3}) ^{1/2} .	128
Fig. 5.3: The relationships between $(\sigma^*)^{1/2}$ vs. $(T)^{1/2}$ and $(\sigma^*)^{1/2}$ vs. $(\Delta H)^{1/2}$.	131
Fig. 5.4: The stress dependence of the activation volume for slip in MgO crystals.	134
Fig. 5.5: σ^* versus T data (experimental) compared with the predictions of Fleischer's theory.	135
Fig. 5.6: σ^* versus ΔH data (experimental) compared with the predictions of Fleischer's theory.	136
Fig. 5.7: Plots of $1/m^*$ against temperature.	140

LIST OF TABLES

	<u>Page</u>
Table 2.1: Orientation dependence of CRSS in rock salt crystals.	7
Table 2.2: Dislocation reactions on the slip systems of the $\{110\} \langle 110 \rangle$ type.	7
Table 3.1: Chemical analysis of MgO single crystals.	58
Table 3.2: Chemical analysis of Polycrystalline MgO.	58
Table 3.3: Heat treatments, resultant grain sizes and dislocation density for polycrystalline MgO.	60
Table 4.1(a): Comparison of results for dislocation velocity-effective stress exponent, m^* , from different studies.	87
Table 4.1(b): m^* values of the present investigation obtained by different methods.	88
Table 4.2: Results of microyield stress measurements for polycrystalline MgO.	107

DEFORMATION BEHAVIOUR IN SINGLE AND POLYCRYSTALLINE MAGNESIUM

OXIDE

1.0 INTRODUCTION AND OBJECTIVES

The mechanical behaviour of ionic materials with the rock salt structure has been extensively studied in the past both in search of a high temperature, corrosion-resistant engineering material as well as for understanding the physical nature of plastic deformation and fracture phenomena. By virtue of the fact that the ionic materials contain a relatively low density of dislocations and a limited number of glide systems, these have been considered model systems for plasticity studies. Starting with the classic work of Johnston and Gilman in 1959 on LiF crystals, a vast amount of data on the characteristics of plasticity has emerged. In order to ascertain the mechanisms of yielding and strain hardening, the mobility of individual dislocations as a function of stress and temperature has been measured by stress pulse-etch pit technique for several metallic and non-metallic crystals. Most of the information on dislocation plasticity of non-metals has however, been obtained on softer alkali halides.

While magnesium oxide has been considered as a potential high temperature ceramic material which behaves similarly to NaCl and LiF, a detailed study of its deformation behaviour has been lacking. Despite the considerable effort devoted to the study of crack nucleation and fracture phenomena in MgO single crystals, only modest progress has

been made in understanding its yielding behaviour in terms of the dynamics of individual dislocations. Although previous studies on MgO crystals have been carried out to show that the nature, total content and state of the impurities has a substantial effect on its mechanical behaviour, the evaluation of the rate-controlling mechanism for plastic flow has received relatively little attention. Because of the necessity for the dislocations to overcome Columbic interactions that happens to be in this case for structural reasons, most workers believe that the Peierls energy in MgO is high. On the other hand, representative data on crystals of rock salt family, even in purest form, have failed to show convincing evidence that the Peierls stress is rate-controlling. Moreover, it appears that the aliovalent impurities play a dominant role in controlling dislocation mobility in all rock salt type materials.

The purpose of the present work on single crystals of MgO, thus consists in assessing the applicability of various models for thermally-activated dislocation motion to describe the plastic deformation processes at low temperatures, in obtaining values of the activation parameters characterizing dislocation motion in MgO and in studying the possible correlation between the dislocation dynamics and thermally-activated rate theory approaches to plastic deformation. Strain rate cycling and stress relaxation experiments have been performed to investigate the yielding behaviour and rate-controlling mechanism in MgO crystals deformed in cube orientation over the temperature range of 77° to 673°K .

For the polycrystalline ceramics, our knowledge of the deformation behaviour and fracture can be best described as empirical. In spite of the growing evidence for the role of plastic flow prior to fracture and similarity in the microstructure between metals and pure oxide ceramics, attempts to relate the behaviour of dislocations with general stress-strain characteristics has been rather meagre. Thus an important aspect namely; the mechanism and role of pre-fracture yielding and work hardening has been overlooked. Against the available background it thus became obvious that a proper understanding of the generation and multiplication behaviour of dislocations during loading is essential for developing some rationale for its fracture behaviour. As such, the microplastic behaviour of a series of polycrystalline MgO were investigated by means of a special microstrain measurement technique sensitive to $\pm 1 \times 10^{-6}$, together with the classical etch pit method for monitoring the generation and growth of individual glide bands. Furthermore, the experimental results on the microyielding and work hardening behaviour with respect to grain size have been considered in light of current theories of polycrystal deformation.

2.0 REVIEW OF PRIOR WORK

The main concern of this chapter is to review previous research on the deformation of rock salt type materials and in particular magnesium oxide. The materials which we shall mainly consider are NaCl, LiF and MgO. In the first half of the review, we consider the deformation of single crystals and the second half is devoted to polycrystalline behaviour. In this latter section the fundamental role of grain boundaries is examined, which has relevance to the problems of brittleness in ceramic materials.

2.1 Single Crystal Deformation

Much important information on the nature of plastic deformation in ceramic materials was first obtained in single crystals having rock salt structure, including the discovery of slip (in NaCl crystals) by Reusch in 1867 [1]. Prominent amongst the more recent work was the first experimental determination of the velocity of dislocations in LiF crystals by Johnston and Gilman [2] in 1959. There was also the demonstration by Gorum et al [3] and Stokes et al [4] (1958) that the apparent brittleness of MgO single crystals, its yield strength and subsequent work hardening characteristics could be understood in terms of the absence or abundance of mobile dislocations.

The mechanical behaviour of magnesium oxide single crystals

has been studied in greater detail than any other high melting point ceramic. MgO is cubic and has the NaCl structure. Its mechanical behaviour is characteristic of what one would normally expect for the other members of this structure type such as NaCl and LiF, except that in spite of the extensive dislocation mobility even at as low a temperature as 77°K and even when comparisons are made at the same homologous temperature (the room temperature corresponds to 0.28 T_m , 0.26 T_m and 0.098 T_m respectively for NaCl, LiF and MgO where T_m is the melting point in °K), MgO differs from other materials in several ways:

- (i) Higher shear stresses and higher temperatures are required to initiate plastic flow;
- (ii) The density and distribution of surface dislocation sources are much more important in controlling yield and fracture behaviour, and therefore often requires extreme precautions in specimen preparation, handling, etc;
- (iii) The work hardening rate commonly observed in MgO is much higher than that observed for NaCl and LiF (160 kg/mm² compared to 11.7 kg/mm² for NaCl and 21.7 kg/mm² for LiF [5]);
- (iv) The density of dislocations and hence the amount of strain in a glide band in MgO crystals is much higher than that in the softer crystal (e.g. NaCl) even when comparisons are made at the same level of plastic strain.

2.1.1 Slip systems and dislocation intersections

Ionic rock salt type materials primarily deform by slip on $\{110\}$ $\langle 110 \rangle$ family of slip systems. The direction of slip $\langle 110 \rangle$ is the shortest translation vector of this crystal structure. Translation in a $\langle 110 \rangle$ direction does not require any nearest-neighbour ions of the same polarity to become juxtaposed during the process of gliding. Thus no large electrostatic repulsive forces develop when slip occurs in this direction. $\{100\}$ $\langle 110 \rangle$ and $\{111\}$ $\langle 110 \rangle$ slip dominates either at higher temperatures (when the electrostatic binding is somewhat weakened) or for tests along $\langle 111 \rangle$ axis, where the $\{110\}$ $\langle 110 \rangle$ systems has no resolved shear stress (see e.g. Table 2.1). For uniaxial tests along $\langle 001 \rangle$, out of six unique $\{110\}$ slip planes depicted in fig. 2.1, the four slip systems, $(011) [\bar{0}\bar{1}1]$, $(0\bar{1}1) [011]$, $(101) [\bar{1}01]$ and $(\bar{1}01) [101]$ all sustain equal resolved shear stress. The reason why $\{100\}$ planes are not the primary glide plane is probably that gliding on them is accompanied by electrostatic faulting. MgO crystals of different orientations have been tested by many workers and the results have been summarized by Pask and Copley [6]. It has been found that the stress to promote slip on $\{100\}$ systems for MgO at room temperature is about 100 times higher than to cause slip on $\{110\}$ system. This difference is reduced to about a factor of 10 at $\sim 1000^\circ\text{C}$, equivalent to the situation in LiF and NaCl at room temperature.

It is apparent from fig. 2.1 that slip planes of the

TABLE 2.1 Orientation Dependence of CRSS in Rock Salt Crystals			
Loading axis → CRSS on ↓	< 100 >	< 110 >	< 111 >
{ 110 } < 110 >	0.5σ	0.25σ	0
{ 100 } < 110 >	0	0.310σ	0.469σ
{ 111 } < 110 >	0.415σ	0.405σ	0.28σ
σ = applied stress			

TABLE 2.2 Dislocation reactions on the slip systems of the { 110 } < 110 > type			
$b_1 + b_2 \rightarrow b_3$	$b_1^2 + b_2^2$	b_3^2	reaction
(1) $\frac{a}{2}[\bar{1}\bar{1}0] + \frac{a}{2}[\bar{1}10] \rightarrow a[\bar{1}00]$	a^2	a^2	Orthogonal (90°)
(2) $\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[10\bar{1}] \rightarrow \frac{a}{2}[\bar{1}\bar{1}0]$	a^2	$a^2/2$	Oblique (120°)
(3) $\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[\bar{1}01] \rightarrow \frac{a}{2}[\bar{1}\bar{1}2]$	a^2	$\frac{3a^2}{2}$	Oblique (60°)

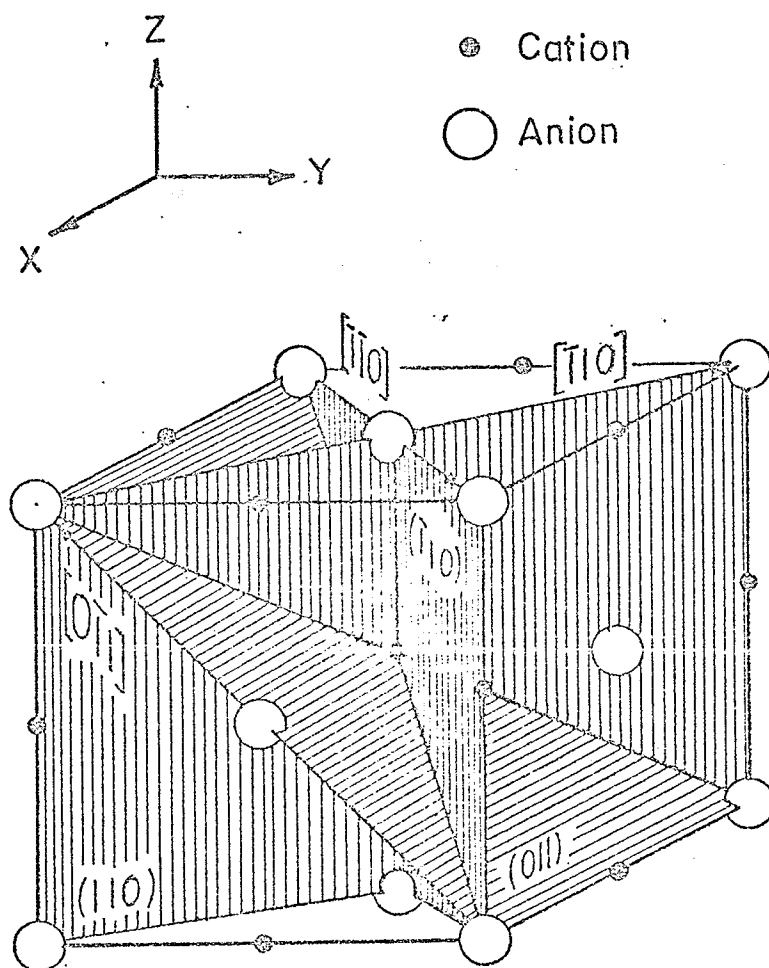


FIGURE 2.1: Diagram illustrating slip geometry in the rock salt structure.

{ 110 } < 110 > type can intersect at either 90° (orthogonal) or 120° (oblique). The reaction between dislocations on these intersection planes have been discussed by Kear et al [7]. The three possibilities that arise are listed in Table 2.2. It is seen that in reaction (1), the elastic energy is not changed because the sum of the energies of the unreacted dislocations is just equal to the energy of the dislocation that results from the reaction. Also, since a displacement of the crystal in the direction of b_3 creates an electrostatic fault, this reaction is not normally expected to occur. Some support for this is believed to come from the experimental finding that piling up of dislocations according to reaction (1) has been often found to result in the formation of cleavage cracks on { 100 } [8,9].

Reaction (3) is unlikely to occur since $b_3^2 > b_1^2 + b_2^2$, which means that the elastic energy of the dislocation is increased by the reaction.

Reaction (2) is the most favourable to occur; since for this reaction there is a net decrease in the elastic energy of the dislocations. This reaction is illustrated in more detail in fig. 2.2. Considering that the slip occurs by the motion of dislocation half loops on two obliquely intersecting (011) and (101) slip planes, the edge and screw components of the individual dislocations can be written as:

$$\frac{a}{2}[0\bar{1}1] = \frac{a}{6}[2\bar{1}1]_{\text{edge}} + \frac{a}{3}[\bar{1}\bar{1}1]_{\text{screw}}$$

$$\frac{a}{2}[10\bar{1}] = \frac{a}{6}[1\bar{2}\bar{1}]_{\text{edge}} + \frac{a}{3}[11\bar{1}]_{\text{screw}}$$

As shown in fig. 2.2(a), the two screw components cancel each other and the edge components combine together; so the resulting reactions become

$$\frac{a}{6}[2\bar{1}\bar{1}] + \frac{a}{6}[1\bar{2}\bar{1}] = \frac{a}{2}[1\bar{1}0]$$

$$\frac{a}{3}[\bar{1}\bar{1}\bar{1}] + \frac{a}{3}[11\bar{1}] = 0$$

The resultant dislocation line has a vector $a/2[1\bar{1}0]$ and lies on the (112) plane as shown in fig. 2.2(b). Because (112) plane is not the glide plane, the dislocation is immobile. Its role in the plastic deformation of LiF and MgO crystals has been discussed by several workers [7,10-13].

Since in the above oblique type of reaction there is reduction in the energy of the resultant product, this should be spontaneous in all of the NaCl type materials. However, the further interpenetration of dislocations forming 120° glide bands should be more difficult because of the fact that the resultant dislocation lie on { 112 } plane which is not the glide plane at low temperatures. Direct observations of 90° and 120° dislocation intersections in deformed crystals by transmission electron microscopy [11,14] and etch pit studies [15-17] supports this. In the case of magnesium oxide, it has been observed that when a crystal is strained in the

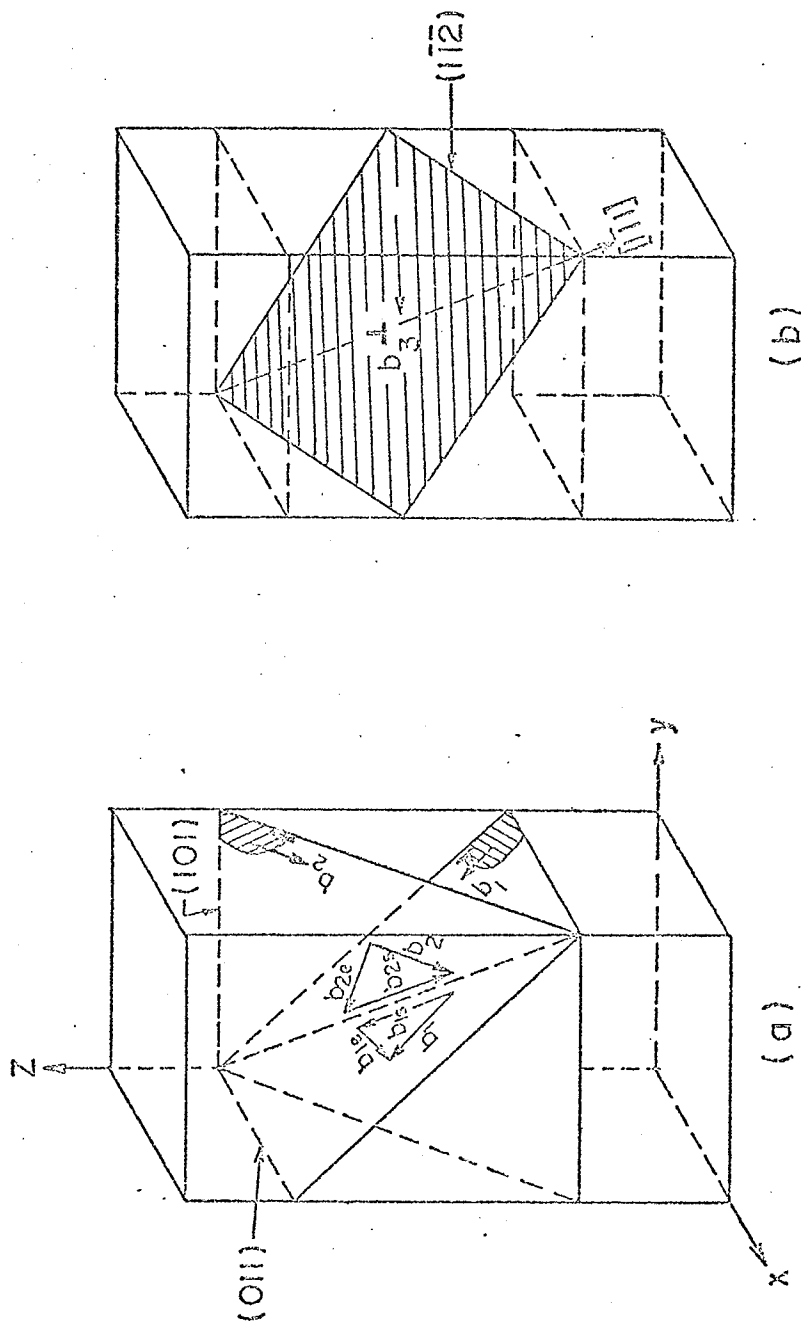


FIGURE 2.2: Illustration of the "oblique" dislocation reaction in the rock salt structure.

$\langle 100 \rangle$ direction at room temperature, the slip is usually confined to only one of the two pairs of orthogonal $\{ 110 \}$ $\langle 110 \rangle$ slip systems that are equally favourably stressed, and the rate of work hardening associated with this slip is relatively low. However, when slip occurs on the oblique systems, the hardening rate is relatively higher [18-22]. Although a statistical analysis of these reactions has not been attempted for any of the rock salt material, it is likely to throw more light on the strain hardening and its temperature dependence for various rock salt materials. Indications that such an approach can be attractive is apparent in the preliminary work reported by Smirnov and Efinov [23].

2.1.2 Mechanisms of yielding in rock salt materials

Most of our present understanding of the mechanism of yielding and deformation of rock salt materials comes from the extensive studies of Gilman and Johnston on LiF crystals (see e.g. ref. 24 for a review of their work). Significant progress has since been made in correlating the plastic properties of ionic materials with the velocity and number of mobile dislocations present. Some of the more significant findings common to rock salt materials can be summarized as follows:

- (i) When a stress is applied, slip usually starts by nucleation of 'fresh' dislocation half-loops at the most severe surface stress concentration. In nominally pure crystals,

'old' or 'grown-in' dislocations accumulate sufficient chemical impurity to immobilize (pin) them for any reasonable level of applied stress (examples for MgO have been provided in ref. 25-27).

- (ii) The macroscopic yield stress is, in fact, a result of the stress required to move dislocations at some moderate velocity in the crystal.
- (iii) In most of these materials edge dislocations move faster than screws, leading to long lengths of pure screw dislocations ideally oriented for double cross slip. Cross slip of screw dislocations can occur only by slip on a plane other than a $\{110\}$ plane since only one $\langle 110 \rangle$ direction is contained in a given $\{110\}$ plane. The multiple cross-slip which then proceeds, forms the basis for dislocation multiplication and the slip band formation with increasing deformation.
- (iv) Double cross slip of a screw as well as its interaction with another dislocation on an oblique slip plane produces jogs of short segments of edge dislocations joining the two screw components lying on two parallel planes. Depending upon the distance between the parallel planes, dragging of jogs can produce vacancies/interstitial and/or dipoles. Extensive dipole formation has been observed in deformed MgO crystals by transmission electron microscopy [28-31]. Hence these obstacles become

important in the sense that they can resist dislocation motion resulting in an increase in hardening, which will further increase with attendant dislocation multiplication and debris formation [32,33]. A good account of the previous work on the strain hardening in ionic materials has been reviewed by Frank and Seeger [34].

Two approaches have been used in the deformation theory: the dislocation dynamics approach of Gilman [35] and the thermally-activated rate equation approach which is based on Eyring's rate theory. While the rate equation has some fundamental basis, dislocation dynamics approach is largely empirical. The studies devoted for an understanding of these are reviewed in the following utilizing data available on the rock salt type materials.

2.1.2.1 Dislocation dynamics approach to plastic deformation

The microdynamical theory of plastic deformation is due to Gilman [35], who was amongst the first to recognize Orowan's assertion [36] that plastic yield should be interpreted in terms of the dynamics of individual dislocations. The basis equation relating the macroscopic quantity, $\dot{\epsilon}_p$ (plastic strain rate), to dislocation velocity, $\bar{v}$ is [36]:

$$\dot{\epsilon}_p = \phi b \rho_m \bar{v} \quad (2.1)$$

where ϕ is an orientation factor, b is the Burgers vector, ρ_m is the mobile dislocation density and $\bar{v}$ is the average velocity of dislocations.

Experimental results [37] have suggested that dislocation velocity depends primarily on stress and at a given temperature can be represented by an empirical equation of the form:

$$\bar{v} = A(\sigma^*)^{m^*} \quad (2.2)$$

where, σ^* is the average effective stress acting on the dislocations which in course of deformation is reduced by the development of an internal or back stress, σ_i , acting in opposition to the applied stress, σ , formally described by:

$$\sigma = \sigma^* + \sigma_i \quad (2.3)$$

and A and m^* are temperature (and possibly purity) dependent constants designated respectively as the dislocation velocity at unit effective shear stress and dislocation velocity-effective stress exponent.

Substitution of (2.2) into (2.1) gives,

$$\dot{\epsilon}_p = \phi b \rho_m A (\sigma^*)^{m^*} \quad (2.4a)$$

or, if ρ_m is assumed constant

$$\dot{\epsilon}_p = B (\sigma^*)^{m^*} \quad (2.4b)$$

Besides the original studies of Johnston and Gilman [37] on LiF crystals (with 75 p.p.m. of Mg^{++}), the dislocation mobility experiments have so far been carried out on several metallic as well as ceramic crystals. For ceramic crystals possessing rock salt structure, examples are: on NaCl [38-40] (with less than 1 to a maximum of 100 p.p.m. of impurities), KBr [41,42] (with 200 p.p.m. of impurity), LiF [43,44,45] (with unspecified impurity) and MgO [46,47]. All of these studies show a large stress sensitivity of dislocation velocity. This sensitivity further increases in going from softer alkali halides (e.g. KBr) to harder crystals such as MgO. In some cases it has been found that dislocation velocity vs shear stress data show a transition (S-shaped curve) at very low and very high stress regions (e.g. KBr data in ref. 41 and 42) and in view of this different forms of eqn. (2.2) have been suggested. They are; in exponential form

$$\bar{v} = \bar{v}_c \exp(A\sigma) \quad (2.2a)$$

or in inverse exponential form

$$\bar{v} = \bar{v}_c \exp[-D/\sigma] \quad (2.2b)$$

($\bar{v}_c$ = appropriate sonic speed)

D = a constant

Consequently the form of the stress dependence is somewhat variable and there are limiting conditions on the stress-velocity relation which must

be specified. At intermediate stresses, where a linear relation is observed in the $(\bar{v} - \sigma)$ log plots, eqn. (2.2) is found to explain satisfactorily the majority of the existing experimental data below a dislocation velocity of $\sim 10^2$ cm/sec.

Besides the stress-pulse-etch pit technique or its variation [48] for correlating dislocation behaviour with stress, techniques have also been devised to obtain the same information by taking advantage of eqn. (2.4b). Provided, ρ_m , and the 'dislocation structure' is assumed constant, the exponent, m^* appearing in eqn. (2.4b) can also be evaluated using strain rate cycling and/or stress relaxation techniques (known as 'indirect' techniques). These have the added advantage that they enable the effective (thermal) and internal (athermal) components of the applied stress to be determined and are much simpler to perform than the stress pulse-etch pit techniques. These techniques have been reviewed by many workers [49-51]. Evans [52] has discussed these with regard to ceramic materials.

The use of the parameter, m^* , in the Johnston-Gilman empirical power law expression, eqn. (2.2), and its physical significance for the description of a mechanism of plastic deformation has been a controversial subject in recent years. A number of papers have recently appeared in the literature [53-57] mainly on this aspect. A very thorough and up-to-date survey [58] however, indicates that the majority of published results are in agreement with eqn. (2.2). In view of this and the fact that 'power law' approach originated from the experiments on ionic crystals which contained moderate amounts of impurities in solid solution,

Argon [59] and Nix and Menezes [58] envisage that the power law is useful, but probably works well only with similarly impure materials and with low initial dislocation density. Although it is doubtful that a complete interpretation of deformation result solely on the basis of the parameter, m^* , is unambiguous, its use in conjunction with the basic parameters of thermally-activated deformation studies may provide some further insight into the deformation mechanisms in some circumstances [60,61].

Apart from the difficulties in assigning some physical meaning to the dislocation velocity-effective stress exponent, m^* , difficulties have also been encountered in obtaining the same value of m^* by different techniques on one material. Consequently, suggestions were made to recognize the important differences in the various experimental means of obtaining the parameter, m^* [49,63]. It was pointed out that in all these experiments, the internal back stress, σ_i , the mobile dislocation density, ρ_m , and the actual plastic strain rate, $\dot{\epsilon}_p$, with which specimens deform; are the three important parameters one has to consider. While in some cases the assumptions regarding the constancy of ρ_m has been partially and indirectly confirmed [49,62,63] during strain rate changes, discrepancy continues to exist in many other cases. One example of this is the recent work by Srinivasan [64]. However, when strain rate sensitivity experiments are in agreement with directly measured velocities, such techniques as strain rate change and stress relaxation have been shown to be very useful in extending our understanding of the relation between dislocation dynamics

and plastic deformation. Examples are: Johnston and Stein's work on Si-Fe and LiF [65], Gupta and Li on NaCl, LiF [66] and b.c.c. metals [67].

2.1.2.2 Rate theory approach to plastic deformation

A description of how the intrinsic mechanisms govern the dislocation velocity and hence cause a change in the flow stress with respect to temperature, involves a determination of the rate-controlling process for slip. This can be accomplished by determining the activation parameters such as the activation energy and the activation volume of slip. The experimentally determined parameters can then be compared with those predicted for specific mechanisms.

Because the rate theory of plastic deformation is now well founded, many good reviews can be found in the literature. Among the best are those by Guyot and Dorn [68], Conrad [69] and Dorn et al [70]. Evans [52] has reviewed the works on ceramic materials.

Before a discussion of the activation parameters is presented it is necessary to consider the components of the flow stress.

Components of the flow stress:

It is often convenient to separate the yield or flow stress, σ , in general into two components: a thermal (or effective) component, σ^* , which depends sensitively on temperature, T , and strain rate, $\dot{\gamma}$; and an athermal (or internal) component, σ_i , which is dependent on temperature only through the shear modulus, μ ; thus

$$\sigma = \sigma^*(T, \dot{\gamma}) + \sigma_i(\mu) \quad (2.5)$$

The thermal component is presumed to be associated with short range barrier or stress field ($< 10\text{\AA}$) opposing the dislocation motion and thermal fluctuations can assist applied stress in overcoming them. Examples of such barriers are the Peierls-Nabarro stress, forest dislocations, resistance to the motion of small jogs and cross-slip and impurity atom. The athermal component is presumed to represent long-range obstacles in which case thermal fluctuations cannot assist the external stress in helping the dislocations to overcome the barrier. The exact significance of grain size effect is a controversial subject, but studies have indicated that the thermal and athermal contribution to the flow stress can be separated by studying the variation of flow stress with grain size. This is discussed in the second part of this review.

The activation parameters:

The starting point in the treatment of thermally-activated dislocation motion is the rate equation, which in an explicit form gives for the plastic strain rate

$$\dot{\epsilon}_p = \phi b A' N v \exp\left(\frac{S}{k}\right) \exp\left(-\frac{H_0 - V^* \sigma^*}{kT}\right) \quad (2.6)$$

where, A' is the average area swept out by a dislocation per successful event, N is the number of sites/unit volume where thermally-activated events can occur, v is a frequency factor, S is the entropy of activation,

H_0 is the activation enthalpy, V^* is the apparent activation volume, k is the Boltzmann constant, T is the temperature in $^{\circ}\text{K}$ and other terms are as previously defined.

Equation (2.6) contains a number of assumptions:

- (i) In treating dislocation jumps over the short range barriers, the possibility of thermal activation in the opposite direction to applied stress has been neglected (see e.g. ref. 71 for a treatment of this aspect),
- (ii) The strain-rate expression, eqn. (2.6), is valid only when a single mechanism is operating over a given range of stress and temperature considered. In a typical material there can be more than one process operating [72];
- (iii) If the temperature is in the vicinity of 0°K , the mechanism may not be completely the thermally-activated surmounting of barriers [73].

If all the terms up to the first bracket in eqn. (2.6) are assumed constant to a first approximation, the expression for strain rate in the simplest form becomes:

$$\dot{\epsilon}_p = \dot{\epsilon}_0 \exp(-\Delta G/kT) \quad (2.7)$$

where $\dot{\epsilon}_0$ is called the 'pre-exponential' factor and ΔG is the activation

free energy required to overcome the barrier, such that $\Delta G = \Delta H - T\Delta S$. The 'pre-exponential' term, $\dot{\epsilon}_0$, is unfortunately one of the most uncertain quantities as far as precise analysis of experimental data is concerned, and in a way is similar to the parameter, ρ_m , in the dislocation dynamics treatment of the preceeding section.

The basic problem in the thermal activation analysis is therefore to determine the activation free energy for dislocation movement past the obstacle. This is usually accomplished by calculating the reversible work needed to move dislocations from a position of equilibrium to the saddle point configuration. There have been two approaches for formulating the actual expressions for various parameters: one is based on taking the applied stress [74-77], σ , as the appropriate thermodynamic quantity and the other which is based on the thermal stress, σ^* [78-80]. More recently Hirth and Nix [81] have shown that while the (σ^*, T) and the (σ, T) formulations are mathematically equivalent and as such no controversy arises; (σ^*, T) formulations are more justified and meaningful than the (σ, T) approach. In the present work on magnesium oxide crystals, we have followed the (σ^*, T) convention throughout. Since some of the expression from this formulation have been used quite often in the work reported in this dissertation, it is advantageous to present a brief account of the derivations and their interrelations.

Conrad and Weiderisch [78] were responsible for one of the first, straight-forward derivations for the activation parameters in a quite general manner. With the starting condition that

$\Delta H - T\Delta S = \Delta G$ and $\sigma = \sigma^* + \sigma_i$, they obtained for activation energy,

$$\Delta H(\sigma^*, T) = -kT^2 \left(\frac{\partial \ln \dot{\epsilon} p}{\partial \sigma^*} \right)_T \left(\frac{\partial \sigma}{\partial T} \right)_\epsilon \quad (2.8)$$

and since activation volume by definition is a stress-derivative of the activation energy, we have

$$V^* = -\frac{\partial \Delta H}{\partial \sigma^*} = kT \left(\frac{\partial \ln \dot{\epsilon} p}{\partial \sigma^*} \right)_T \quad (2.9)$$

One of the main assumptions is the use of ΔH in the above equations which in fact should be taken as ΔG , unless the entropy term $\left(\frac{\Delta S}{k} \right)$ is calculated or shown experimentally to be negligible. This problem has been discussed by Li [49,82] who postulated on the basis of the third law of thermodynamics that the entropy of activation should be zero at 0°K . The usual test for a positive activation entropy involves an examination of the temperature dependence of the activation energy.

From the basic thermodynamic relation

$$\left(\frac{\partial \Delta H}{\partial T} \right)_{P, \sigma^*} = T \left(\frac{\partial \Delta S}{\partial T} \right)_{P, \sigma^*} \quad (2.10)$$

and if V^* is defined as

$$V^* = -\left(\frac{\partial \Delta G}{\partial \sigma^*} \right)_T = -kT \left(\frac{\partial \ln \dot{\gamma}}{\partial \sigma^*} \right)_T, \quad (\dot{\epsilon}_0 = \text{constant})$$

$$\text{we have, } \left(\frac{\partial \Delta S}{\partial \sigma^*} \right)_T = \left(\frac{\partial V^*}{\partial T} \right)_{\sigma^*} \quad (2.11)$$

Examination of the above relationships reveals two important points. Firstly, ΔH should be a linear function (due to its stress dependence) of T at a constant strain rate, to indicate constant ΔS (so a constant pre-exponential factor) over the range of temperature considered as found in some experiments [83-85]. If ΔH is not solely a function of temperature, a plot of ΔH vs T will not be a straight line but will have a positive curvature as shown by Arsenault and Li [85], provided that $\sigma_i \neq 0$. Non-linearity in ΔH vs T plot can also indicate several other factors, such as:

- (i) More than one mechanism operating,
- (ii) Entropy varying with temperature (but not necessarily zero), and
- (iii) Variation in 'pre-exponential' term, $\dot{\epsilon}_0$.

Li [49] and Balasubramaniam [53,54] have pointed out that the condition $\Delta S \neq 0$ requires (m^*T) to be temperature dependent. They conclude that in cases where $(m^*T) \neq \text{constant}$, ΔS will have some non-zero value (see also ref. 55-57).

Secondly, from eqn. (2.11), if the change in ΔS above 0°K does not remain constant (i.e. at a constant temperature if V^* were not a function of σ^*), then a straight line would be obtained in the $V^*-\sigma^*$ plot. But experimental results show that V^* is a function of σ^* ; the curve has an increasing curvature with decreasing σ^* such that $V^* \propto 1/\sigma^*$ is obtained. When written in relation to that of the parameter, m^* , one finds that

$$m^* \equiv \frac{V^* \sigma^*}{kT} \quad (2.12)$$

Therefore if eqn. (2.12) is obeyed, it can be concluded that the power law and the rate theory approaches to deformation are equivalent and that there is no need to invoke entropy effects.

Another aspect of the activation parameters that should be examined is their temperature and effective stress dependence. Most of all it is important to recognize that the basic premise of strain rate expression concerning the identification of the number of mechanisms operating over a given range of temperature in question is fulfilled. Since the total activation enthalpy, H_0 (ΔH at $\sigma^* = 0$), is expressed as:

$$H_0 = \Delta H + \int_0^{\sigma^*} V^*(\sigma^*) d\sigma^* \quad (2.13)$$

if there is a single rate-controlling mechanism operating over the whole range of temperature and stress considered, H_0 should be independent of temperature and effective stress.

The proposed rate-controlling mechanisms:

Mainly two classes of mechanisms are discussed in the literature to account for the temperature dependence of yield stress in crystalline solids: the Peierls-Nabarro (lattice resistance) mechanism and the dislocation-impurity atom interaction mechanism. Experimental investigations which have been made and discussed on the basis of these mechanisms indicate that while Peierls-mechanism is

probably rate-controlling in b.c.c. metals [68], the yield stress-temperature relationships for rock salt type materials show agreement with the mechanism based on impurity-interactions [52,87-89].

Although the original treatment of the Peierls-Nabarro stress did not deal explicitly with the directionality of bonding, it was implicit in the development. Since that time many experiments have shown that the Peierls stress is very slight in crystals for which the bonding is non-directional, such as in the case of f.c.c. metals and ionic crystals [41,42,90-93]. On the other hand, covalent crystals [94] and some b.c.c. metals (being partly covalent in character) are believed to exhibit large Peierls stress. That the directionality of bonding is important can be understood by noting that when a dislocation moves, the atoms in the core slide past each other and causes severe bond-angle distortions in the process. Thus the energies and forces needed for dislocation movement depend sensitively on the directionality of the bonding forces. According to Cottrell, the theoretical tensile strength, σ_t , is related to the dislocation width, w , as

$$w = \mu/2\pi(1-\nu)\sigma_t \quad (2.14)$$

where ν is Poisson's ratio. Thus materials with wide dislocations have relatively low yield strengths and are regarded as intrinsically soft. In ionic solids however, the dislocations are narrow because the operative slip systems are the ones which avoid bringing ions of like charges together.

The other class of mechanisms are those which deal with the role of impurity as being the major barriers to dislocation movement. Fleischer [95] considered the interaction of the stress field of dislocations with the point defects and pointed out that the effect on flow stress is much greater when the stress field of the defect is tetragonal rather than isotropic. Treating the impurity-vacancy dipole occurring in rock salt type crystals [87] (where it is now well known that the aliovalent impurity becomes associated with a cationic vacancy to maintain the charge neutrality, thus forming a 'non-symmetrical' defect), he was able to satisfactorily explain the results of Johnston [96] on air-cooled LiF crystals containing Mg^{++} (75 p.p.m.) impurities both with respect to the form and slope of the flow stress curve as a function of temperature. The crucial problem that has been solved for tetragonal defects by Fleischer is the calculation of F_{max} (maximum interaction force) for cubic crystals-metals as well as ionic - and therefore its applicability in describing a wide variety of problems associated with point defect hardening. As pointed out by Ono [97] and recently by Barnett and Nix [98] (after a re-examination of Fleischer's force-distance relation) that despite some unjustified assumptions concerning a stress independent obstacle spacing, the tetragonal defect model of Fleischer is more useful since the functions used therein have been based on descriptions of an actual obstacle-dislocation interaction. The intuitive selection of the force-distance relationship also appears close to the physical situation, especially in rock salt cubic crystals, for the 'rigid' impurity-

vacancy dipole that exists in impure materials.

Another feature which ought to be of specific significance to ionic crystals is the hardening caused by electrostatic interactions. The possibility of the alternating charges on the composite extra half-plane interacting with a charged imperfection must also be considered. Akimoto and Sibley [99] first examined this problem and using a simple electrostatic model found that the increase in flow stress caused by interaction between a dislocation line and a stationary charged defect is of the same order of magnitude as the hardening effect produced by a tetragonal defect. Therefore, even though one might expect the tetragonal hardening mechanism of Fleischer to be applicable due to the presence of aliovalent impurities in ionic crystals, contribution of electrostatic interactions between dislocations and charged defects may not be negligible under some circumstances.

The usual comparison between theories dealing with either Peierls-Nabarro stress [100] or impurity-interaction [87] with experimental results are based on the following criteria:

- (i) A discrimination between possible mechanisms is possible by comparison based on activation volume, V^* . A Peierls mechanism is found to operate if V^* is independent of strain and about $10 - 20 b^3$ in magnitude. It should be noted however, that Hirth [101] has recently pointed out that activation volumes as

usually derived may be misleading since the stress dependence of the pre-exponential term ($\dot{\epsilon}_0$, in eqn. 2.7) in strain rate expression is ignored. According to Dorn-Rajnak model [100], the activation volume depends only on σ^* (increasing with decreasing σ^*), the line energy, Γ_0 , and very insignificantly on the shape of the Peierls hills. In contrast, although the magnitude of V^* for impurity atom-dislocation interaction mechanism might fall in the same range as for the Peierls mechanism (only with one concentration of impurity), it is proportional to $1/\sqrt{C}$, where C is the effective concentration of impurity.

- (ii) σ_0^* (σ^* at 0°K) for the Peierls mechanism must remain independent of plastic strain (and hence dislocation density) and concentration of impurity; which increases with $\sqrt{C}$ in the case of impurity mechanism.
- (iii) Within the permissible variations due to changes in the shape of the Peierls hills, the relationships between σ^*/σ_0^* and T/T_0 plotted in non-dimensional form (T_0 is critical temperature where $\sigma^* = 0$) must be obeyed as predicted by the theory. It should be pointed out however, that the magnitude of either σ_0^* or T_0 may remain unknown in the absolute theoretical sense.
- (iv) The most important check of the Peierls mechanism (after Dorn-Rajnak treatment) is that the line energy,

Γ_0 , deduced from the experimentally determined σ_0^* and kink energy, U_K , should approximate roughly Nabarro's estimate of $\approx \mu b^2/2$, where μ = shear modulus.

- (v) Another possible check concerns the correct range of the pre-exponential term in the strain rate expression. This issue however, cannot be taken as critical in view of a large number of undetermined parameters appearing in the pre-exponential term.

Frank [88,89] has modified the Fleischer theory using a smooth-topped force-distance curve instead of the sharp cusp considered by Fleischer. In this theory the flow stress-temperature relationship is

$$x(\sigma^*) = [\Delta G_0 - kT \ln(\frac{\rho_m b^2 v}{\dot{\epsilon}})] \frac{C_{eff}}{b^2 d} \quad (2.15)$$

The temperature dependence of σ^* is implicitly given through the relation;

$$T = A - Bx(\sigma^*) \quad (2.16)$$

where

$$x(\sigma^*) = \sigma^* \left(\frac{C}{\sqrt{\sigma^*}} - 1 \right)$$

and A, B and C are constants having the following meanings:

$$\left. \begin{aligned} A &= \Delta G_o / k \ln \left(\frac{\rho_m b^2 v}{\epsilon} \right) \\ B &= b^3 d / \sqrt{C_{\text{eff}}} k \ln \left(\frac{\rho_m b^2 v}{\epsilon} \right), \text{ and} \\ C &= 2.846 \sqrt{\Delta G_o / C_{\text{eff}}} / b^3 d \end{aligned} \right\} \quad (2.17)$$

with C_{eff} = effective concentration of the impurity, d = distance of the center of the dipole from the slip plane. Frank's theory has been applied recently to explain the temperature dependence of yield stress in many b.c.c. metals [102,103] and also in the case of polycrystalline AgCl [104] and LiF [109] crystals. Although it was possible to obtain reasonable fit with eqn. (2.16) by suitably choosing the constants in the theory, but in most cases C_{eff} is not known so a full test of the theory is not possible.

Another mechanism of dislocation-impurity atom interaction in ionic crystals deserves mention. Pratt et al. [105] and Chang and Graham [106] have suggested that interaction between dislocations moving past cation impurity-vacancy complexes can cause the dipoles to reorientate in the dislocation strain fields of both edge and screw dislocations in such a way as to lower the elastic energy of the system. Their calculations indicate that the energy involved is not negligible and may contribute significantly to the flow stress.

2.1.3 The influence of heat treatment

In spite of the extensive evidence in the literature that impurities dominate the low temperature deformation behaviour of NaCl type materials, one particular area of research in which the form and state of the dispersed impurities play an important role seems to have received little attention. Because of the arbitrary selection of materials, almost all previous studies have had varying amounts of impurities content and quite different heat treatments; and as a result it has often been difficult to decide about the operating rate-controlling mechanisms.

Johnston and Gilman [2] found that in their experiments with LiF crystals containing 75 p.p.m. of Mg^{++} as the major divalent impurity, the dislocation velocity and yield stress was dependent on the cooling rate employed, such that the air-cooled crystals were always softer than slowly-cooled ones which contained precipitates. Similar effects have been noted in NaCl [107] (containing Ca^{++} impurities) and other alkali halide crystals [108]. More recently, Rappich [109] has systematically investigated the effect of Mg^{++} (from 1 p.p.m. to 1110 p.p.m.) and cooling rates (from $1^{\circ}C/min$ to $50^{\circ}C/min$) on the CRSS of LiF. The well-known quench-softening effect was found only in specimens with 'medium' impurity concentrations. An analogous effect of the state of dispersion of impurities has also been observed in NaCl crystals by Gutmanas and Nadgorni [93]. These authors also studied the dynamics of dislocations with respect to heat treatment.

It was shown that an increase in dislocation velocity-stress exponent, m^* , occurs with increasing impurity concentrations and particularly with annealed state of the crystals prepared by slow cooling. It was also shown that under slow cooling conditions agglomerates of complexes (impurity ion-cationic vacancy) are formed, while under fast-cooling conditions no such agglomerates occur. Thus both the quantity and the state of impurities considerably influence the dislocation mobility.

The effect of heat treatment on the deformation behaviour of MgO crystals has also been studied by a number of investigators [110-114]. Moon and Pratt [113] have studied the effect of Fe^{+3} concentration (10 - 130 p.p.m.) on activation volume and found a sharp decrease in V^*/b^3 with increasing Fe^{+3} concentrations. Their paper does not mention about the cooling rate etc. used during the preparation of specimens. Kumar [114] however, using MgO crystals with fixed Fe^{+3} content (75 p.p.m.) observed the activation volume to be strongly dependent on the state of dispersion of impurity which was deliberately changed by rapid and slow cooling after annealing. Furthermore, V^* was found to be constant with strain up to 6% of plastic strain. Since according to the Peierls mechanism, the magnitude of activation volume is independent of state of dispersion of impurity, the author concluded that the results were in agreement with the Fleischer model. Other mechanisms such as the dislocation intersection or debris were also ruled out since activation volume was independent of plastic strain.

A parallel attempt to study the effect of the state of

dispersion of ions on the rate-controlling mechanism has been made by Gaiduchenya et al. [115] on LiF crystals. It was found that irrespective of the impurity content (from a total cation impurity of 5×10^{-3} at % to 0.1 at %) and prior heat treatment (that is, whether 'quenched' or 'annealed'), the thermal activation parameters such as V^* , σ^* and ΔH showed comparable behaviour expected with Fleischer's theory of tetragonal distortion. These studies therefore indicate that by examining the influence of prior heat treatment and testing atmosphere on various thermal activation parameters one can indirectly determine the nature of the strengthening mechanisms involved.

2.2 Polycrystal Deformation

Whilst the preceeding sections show that the plasticity and dislocation mechanism of yielding in ionic single crystals has been the subject of extensive study in the past, there is relatively little information in the literature on the dislocation behaviour of bi- and polycrystals. For example, no explicit study has been conducted on any of the polycrystalline rock salt materials to examine the role played by dislocations in the fracture of these semi-brittle ceramics. Most of the available data on polycrystals are limited to fracture strength measurements. Consequently, the overall picture of yielding and its connection with fracture in these materials has remained unclear. The question whether final cracking proceeds catastrophically from inherent flaws, or whether cracks form following plastic deformation

is still unanswered irrespective of the fact that equivalent crystals show extensive plastic flow by dislocation movement and multiplication.

A vital factor in the normal brittleness of polycrystalline ceramics having rock salt structure is generally thought to be the failure of $\{110\} \langle 110 \rangle$ slip to provide five independent slip systems required by the von Mises-Taylor criteria for ductility. This has been the basis for general interpretation for a lack of ductility in these materials, most of which possess less than five independent operating slip systems at low temperatures [11]. Because deformation may not be accommodated from one grain to the next, grain boundaries act as strong barriers to slip and potent sites for crack nucleation. In recent years however, there has been growing interest to further understand the limited ductility from the view point of dislocation mobility. Ductility has been observed only at temperatures above which slip lines are wavy indicating perhaps the role of enhanced cross-slip and easy interpenetration of the slip on different planes. It has also been shown that even when five independent systems are available, brittleness may be encountered in polycrystals due to local strain incompatibility at barriers to plastic flow. Moreover, when the actual heterogeneity of deformation from grain to grain or within grains is taken into account, the von Mises-Taylor criteria is found to be 'necessary but insufficient' condition for ductility and other conditions may also have to be satisfied to avoid catastrophic propagation of cracks.

Besides the consequences of limited flexibility in glide,

most of the polycrystalline ceramic materials either processed commercially or made in laboratories contain a wide range of microstructures with residual porosity, a variety of phases and quite different surface conditions. Several of these factors may contribute to the stress-strain behaviour at any one time and therefore it is not surprising that a vast majority of research effort in the past have dealt mainly with the role of these variables. However, recent attempts to make pure and fully-dense materials having rock salt structure such as LiF and MgO have been quite successful and some renewed efforts to understand their limited ductility are being made. The central problem for understanding the behaviour of polycrystalline ceramics at present appears to be a general lack of information about the structure and properties of grain boundaries. The work done to-date towards this has been reviewed in the following first section. The subject of flow and fracture strength measurements is considered next. Finally, the relationship between grain size and the yield, flow or fracture stress is discussed.

2.2.1 Role of grain boundaries

Previous work on the role of a single grain boundary and its orientation with respect to applied stress and slip direction can be found in ref. (116). In most of these studies the role of a grain boundary has been studied from crack nucleation aspects rather than its effect on the stress-strain behaviour. There is now considerable

experimental evidence for the production of cracks at grain boundaries in MgO [117-120], LiF [121] and NaCl [122]. MgO crystals with either one or two grain boundaries have been chosen by all investigators for this purpose and etch pitting has been used to advantage in all experiments to identify the glide band interactions with the grain boundary.

Johnston et al. [120] have investigated the role of edge vs screw dislocation bands against increasing misorientation across the boundary. It was found that the probability of crack formation at the point of impingement of an edge slip band upon the boundary increased with increasing misorientation. At boundaries of small misorientation, blocked slip bands nucleated slip on the opposite side of the boundary. Transgranular cracks formed at boundaries of medium misorientation, whereas intergranular cracks were nucleated at boundaries of large misorientation.

The role of cross-slip in relieving stress concentrations at the grain boundary (where slip bands intersect) was further studied by Stokes and Li [123] on NaCl and MgO bicrystals. The slight ductility exhibited by NaCl bicrystals at room temperature and by MgO bicrystals at 450°C was postulated to arise from the enhanced cross-slip at these temperatures. It was hoped by these authors that further information about stress relief by cross-slip might be obtained by studying the crack nucleation as a function of orientation and temperature. But such a study has not yet been reported.

Ku and Johnston [124] have studied the stress necessary to

form a crack at the intersection of a slip band and a grain boundary in MgO in a rather elegant way. Slip bands were initiated at microhardness indentations on the surfaces of bicrystals which were extensively polished to remove all other dislocation sources. It was found that the crack nucleation stress of the bi-crystals obeyed the well-known Hall-Petch relation:

$$\sigma_F = \sigma_0 + Kd^{-1/2} \quad (2.18)$$

where in this case, 'd' was equal to the distance from the microhardness indentation to the grain boundary. The constant, σ_0 , was considered to be the stress for dislocation multiplication rather than the minimum stress to move dislocations, whereas the constant, K, was correlated with the cohesive strength of the boundary. The detailed description of eqn. (2.18) is made further in the last section.

2.2.1.1 Grain boundaries as sources of dislocations

It is interesting to note that while in almost all of the previous studies on bi-crystals of MgO and NaCl, the sources of mobile dislocations were invariably dependent on the presence of artificial indentations on the crystal surface or arising from the mechanical contacts (such as from grips used in the loading device); very little attention has been paid to the role of grain boundaries per se as sources of dislocations. Perhaps the earliest evidence that grain

boundaries themselves may act as dislocation sources in ceramics (as in metals) comes from the micrographs in the work of Whitworth [125] (see his fig. 5(b)) on NaCl crystals containing sub-boundaries, Westwood [117] on MgO bi-crystals and Scott and Pask [126] on polycrystalline LiF. More recent examples of grain boundary dislocation generation can be cited from the work on polycrystalline NaCl by Evans et al. [127]. Similarly there is evidence that in MgO [128] and LiF [129] precipitate particles serves to nucleate dislocations internally by acting as shear stress raisers.

2.2.1.2 Compatibility at grain boundaries

As pointed out before, a key factor which inhibits the macroscopic flow in most of the polycrystalline ionic materials is the general compatibility conditions originating from the criteria due to Von Mises and Taylor for arbitrary and uniform deformation of a grain. If each grain in a rigid polycrystalline matrix undergoes uniform strain, there would be a tendency for overlap of material in some places, and void appearance in others. This is shown in fig. 2.3 from the paper by Ashby [133]. As suggested by Ashby, the occurrence of overlaps and voids in fig. 2.3(b) can be corrected by introducing 'geometrically-necessary' dislocations, as shown at (c) and (d). Since contiguity is equivalent to establishing gradients of plastic deformation within the grain (in order to avoid the formation of voids or regions of overlaps at the grain boundaries), the required strain

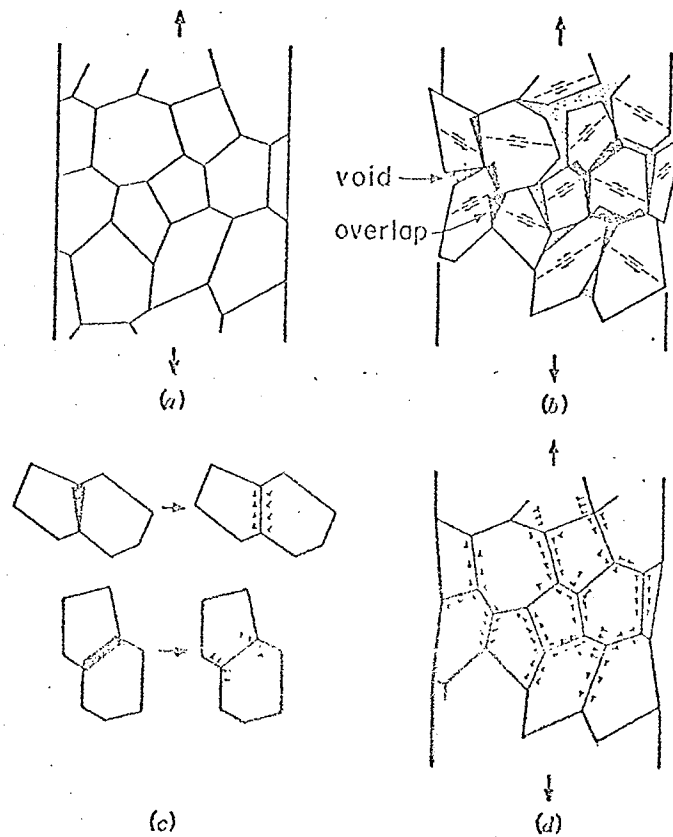


FIGURE 2.3: A recent model of polycrystal deformation proposed by Ashby [133]. If each grain of a polycrystal, shown at (a), deforms in a uniform manner, overlap and void appear as indicated in (b). These can be corrected by introducing geometrically-necessary dislocations, as shown at (c) and (d).

gradients can be described in terms of the density of additional dislocations which must be stored in the system. In the case of polycrystalline rock salt materials, where contiguity requirements are vital throughout the deformation, it might seem appropriate to consider in future the above concept in more detail. It is also evident that there is a need to further understand the differences between dislocation behaviour in grain boundary regions and in regions remote from the boundary. Since fracture occurs through crack nucleation where a slip band impinges on grain boundary, this concept in the macroscopic sense would require that for material to flow, either accommodating slip should take place or the accompanying elastic strains be released through crack formation in the adjoining grains.

Chung and Buessem [130] have shown that most materials, including most cubic structured ones, are elastically anisotropic. Hasselman [131] has shown that such elastic anisotropy can lead to local increases in stress of 5-15% for equiaxed grains, which further increases as the shape of the grains also becomes anisotropic. More recently Tangri et al. [132] have specifically analyzed the incompatibility stresses for the situations where it leads to stress concentrations at interfaces such as grain boundaries. Although a similar detailed analysis has not been attempted for ionic polycrystals, it appears interesting to compare some of the available results at least on a qualitative basis with those for metallic materials.

- (i) The most important effect that arises from elastic

anisotropy and plastic incompatibility (von Mises-Taylor Criteria) conditions for the deformation of a rigid polycrystalline body is the development of a strain gradient in the grain boundary regions. As suggested by Ashby [133], it is conceptually possible then to distinguish between the dislocations which are required near the grain boundary region to maintain continuity of the polycrystal and those accumulated in the grain interior. Since in the grain boundary region a different behaviour is expected (because of the presence of grain boundary), it is likely that the dislocations required to maintain continuity may be provided via nucleation of dislocations from grain boundaries to compensate for the local strain gradient. The results to-date on numerous b.c.c. [134-139], f.c.c. [140-141] metals as well as on rock salt ionic materials [115,125-127] where in the early stages of deformation, dislocation generation is found mainly from the grain boundaries appears to be consistent with this view.

(ii) The requirement for plastic compatibility discussed above can also lead to the operation of secondary slip systems at the grain boundaries and at resolved shear stresses far less than the critical value, as has been found in Fe-Si bicrystals [142]. This feature again resembles the observations on polycrystalline LiF by Scott and Pask [126], where local slip near grain boundaries was seen on the secondary $\{100\} \langle 110 \rangle$ systems apart from the normal room temperature $\{110\} \langle 110 \rangle$ slip, so the effect was caused by plastic incompatibility. The value of m (Schmid factor) were as low as 0.22 on secondary slip systems operating near the boundary.

(iii) As a consequence of stress concentration due to elastic anisotropy and notch effect of boundary ledges, it has been demonstrated that while theoretical estimates for dislocation generation (from grain boundaries) in metals range from $G/2\pi$ to $G/30$, the observed values are far lower than this [132]. Judging from the studies of Scott and Pask [126] on polycrystalline LiF and of the present results on polycrystalline MgO, similar conclusions can be drawn in these materials.

From these examples it seems quite likely therefore, that even in the absence of a well-founded theory of grain boundary structure in ionic materials (although Carlignia [143] has recently proposed a grain boundary model analogous to that of metals), the results suggested by compatibility effects agree at least qualitatively with those of the metallic polycrystals.

2.2.2 The flow and fracture stress

Apart from great many other variables influencing the flow and fracture stress of ceramic polycrystals, one other single factor that has been discussed widely in the literature is perhaps the influence of various testing techniques. Although many useful standards for mechanical testing in general as well as for some specific purposes are available, the property variation on account of using various techniques are either too wide or sometimes the testing technique itself undesirable to suit the purpose. Often the

understanding of plasticity from the viewpoint of dislocation motion demands the research to be conducted under uniaxial loading conditions whereby a comparison with the properties of single crystal material can be made.

Ceramics have been and are almost invariably being tested under a simple three - or four point - loading system: this is obviously a sort of 'guarded' tensile test. Direct tensile testing with uniaxial stressing is difficult, but not impossible; while keeping other factors constant, compression test should in principle yield identical information like that of tensile test at least in the beginning of deformation characterizing dislocation motion. However, because of the fact that cracks are far less stable in tension than in compression, the final fracture stress even for one given material turns out to be quite different depending upon the mode of testing.

Irrespective of the mode of testing, for the case of materials in which the final fracture is controlled by movement and multiplication of dislocations, rather than 'pre-existing cracks'; to characterize different portions of a stress-strain curve with various degrees of refinement, one may enumerate:

(i) A dislocation initiation stress, σ_d , which is the minimum stress at which etch pitting shows dislocation generation from grain boundaries,

(ii) A 'microscopic' flow stress, σ_m , which can be measured with the help of a microstrain measurement technique involving strain

measuring capabilities of 10^{-6} or less [144] corresponding to a plastic strain of 5×10^{-6} (or better, if feasible); which is well below the conventional yield stress; and

(iii) A 'macroscopic' flow (or yield) stress, σ_y , for general flow, representing the conventional flow stress at a plastic strain of 10^{-2} .

The steps leading to dislocation-initiated fracture is shown schematically in fig. 2.4. For polycrystalline NaCl and LiF which show some macroscopic ductility at room temperature, the scheme can well be as shown in this figure. In the case of polycrystalline MgO however, the fracture stress, σ_F , will closely correspond to the microscopic yield stress, σ_m ; unless tested either at higher temperature or under confining pressure, which can extend the range of σ_y by suppressing the crack growth stage. Recent work by Paterson and Weaver [145] on polycrystalline MgO deformed under confining pressure can be cited as an example.

2.2.3 Effect of grain size

The effect of grain size on the mechanical behaviour of polycrystalline ceramics is another important topic and has received more attention than any other variable [116]. In most of the studies reported however, interest has been limited to fracture stress determination. While grain size has been found to produce significant effect on the fracture strength, an detailed interpretation of yielding

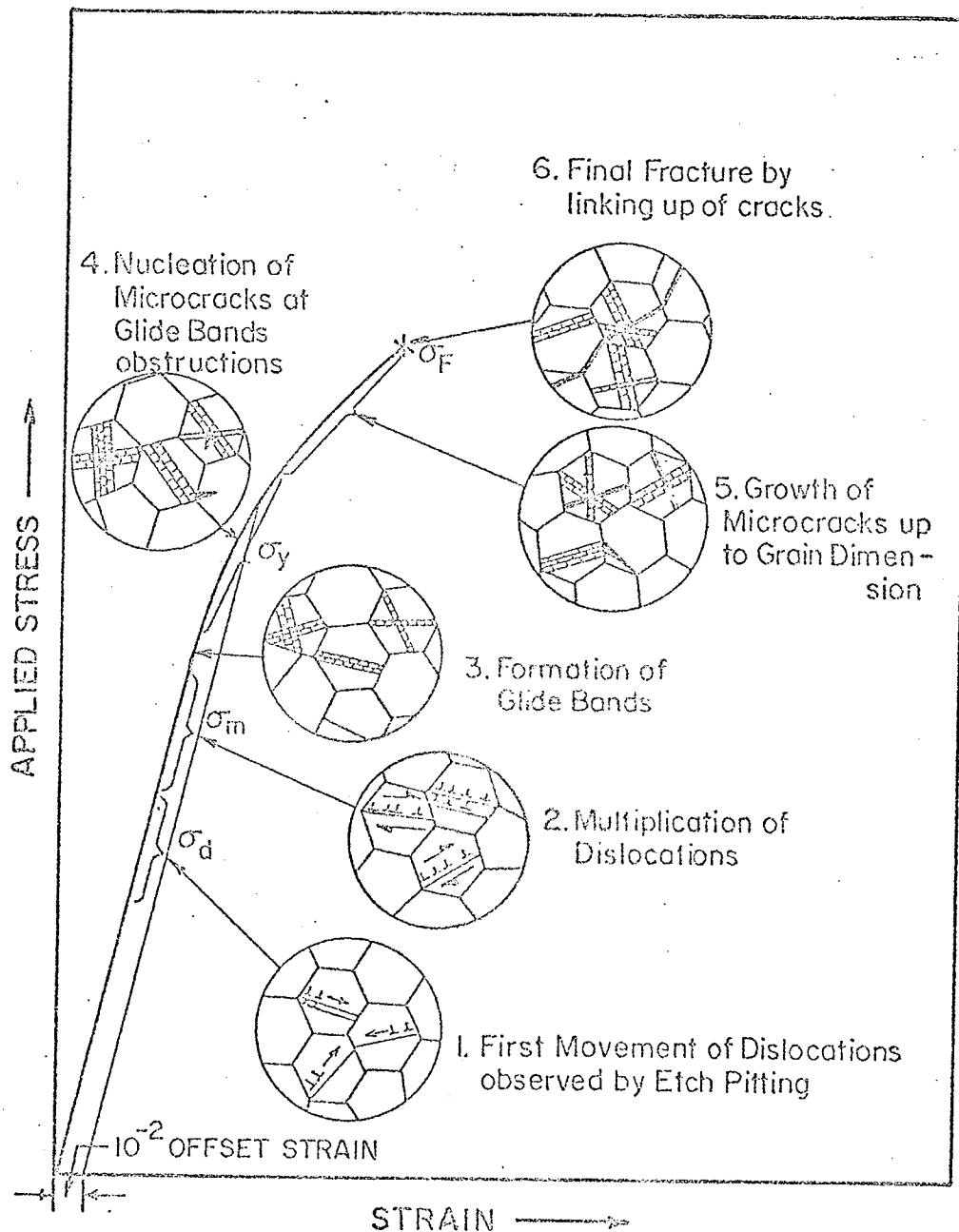


FIGURE 2.4: Schematic of the predicted mode of failure of a semi-brittle polycrystalline ceramic by dislocation mechanism. σ_d = dislocation initiation stress, σ_m = microscopic flow stress, σ_y = macroscopic yield stress, and σ_F = fracture stress.

behaviour and its dependence on grain size is not available. For polycrystalline magnesium oxide at low temperatures, the occurrence of dislocation motion prior to fracture has been variously reported, but we do not have any information on the nature and mechanism of hardening resulting from this. Even if grain boundaries are well-accepted as the sole potential obstacles to slip, giving rise to cracking; its role in the microyield deformation is completely unexplored.

2.2.3.1 The grain size dependence of flow and fracture stress

An examination of the results on the grain size dependence of fracture stress of polycrystalline rock salt materials show that similar to metals, the data are in accord [146,147] with the well-known ' $d^{-1/2}$ ' law, often given by the so-called Hall-Petch relation:

$$\sigma_F = \sigma_{OF} + K_F d^{-1/2} \quad (2.18a)$$

where, σ_F = fracture stress, d = grain size and σ_{OF} and K_F are constants for the fracture criteria as denoted by the subscript, F.

Several authors [145-151] have discussed the applicability of the Hall-Petch relation in explaining the grain size dependence of fracture stress. In many other cases, variation of strength due to grain sizes have also been treated according to Griffith-Orowan [152] approach based on the surface energy criteria. While a satisfactory

explanation of the strength of other (non-cubic) polycrystalline ceramics is still not available, the role of plastic flow in rock salt type polycrystals appears to be widely accepted through the Hall-Petch relation. Carlignia [147] and Rice [150] have discussed the Petch behaviour from the point of view of influence of plastic flow in the fracture. Although no specific suggestion was made about the mechanism of yielding, Carlignia [147] chose to interpret Petch type of behaviour in terms of a model for the grain boundary structure which he adapted from Mott's fit-misfit model. He assumed that the fact that the fracture stress lay above that given by the Griffith-Orowan criterion resulted from the fact that the initial cracks propagated through the grain, but that the grain boundary structure permitted blunting of the crack tips [143]. It was also pointed out that deformation of grain boundaries (where the atomic arrangement is irregular and electrostatic faulting is high) could be possible which may help in identifying the σ_0 term in eqn. (2.18a). In the following we review the various rationalizations that are available for explaining the ' $d^{-1/2}$ ' behaviour. Correlation with the available experimental results on NaCl, LiF and MgO will be provided in a later section.

Theoretical explanations for the effect of grain size on strength are principally of three types: (i) the dislocation pile up model [153-155], (ii) the work hardening model [156-157], and (iii) the dislocation accumulation model [133].

(i) In the pile-up model, the effect of grain size arises from the number, n , of dislocations piled up against a grain boundary and in turn from the stress concentrations at the head of the pile-up. If we assume that the length, L , of the pile-up is proportional to the average grain size, d , in a polycrystal, and yielding, flow or fracture occurs at some critical value of stress, σ_c , then the condition can be simply of the form,

$$n(\sigma - \sigma_0) \geq \sigma_c \quad (2.19)$$

where σ is the applied stress, σ_0 is some appropriate friction stress opposing the motion of dislocation in the pile-up along the slip plane, and σ_c is the critical stress necessary to nucleate slip or a crack depending upon whether yielding or cracking occurs in the adjoining grain. Detailed calculations [158] show that,

$$n \propto L^{\frac{1}{2}} \quad (2.20)$$

Eqns. (2.19) and (2.20) combine to give an expression of the form of eqn. (2.18).

(ii) In the work hardening type model [156], the effect of grain size is on the density of dislocations associated with a given amount of plastic strain, the density being greater as the grain size decreases. The higher dislocation density leads to a higher internal stress and thereby to a higher flow stress. The effect of grain size

on the flow stress is therefore an indirect effect through its influence on the density of dislocations. The model in essence, thus emphasizes the increase of internal stress opposing dislocation motion rather than on the stress concentration at the tip of a pile-up at the grain boundary. Here one considers the experimental relation:

$$\sigma_f = \sigma'_0 + \alpha \mu b \sqrt{\rho} \quad (2.21)$$

where σ'_0 and α are constants, μ is the shear modulus and ρ is the dislocation density. Noting that the plastic strain $\bar{\epsilon} = \rho b \bar{x}$, where $\bar{x}$ is the mean free path of the motion of dislocations which, within the limits of the grain boundaries, is taken as proportional to the grain diameter, d ; then with $\rho \propto 1/d$ eqn. (2.21) reduces to the form of eqn. (2.18) in terms of grain size. It should be emphasized however, that σ'_0 (eqn. (2.18)) differs from σ'_0 of eqn. (2.21). Li [159] has proposed an alternative model by which the density of dislocations, ρ , varies as $1/d$, yielding eqn. (2.21) which is based on the generation of dislocations from grain boundary ledges.

(iii) A third way to describe the influence of grain size is by Ashby [133] who showed that a proportionality between the dislocation density and the reciprocal of the grain size follows from a consideration of the density of dislocations required to compensate for the non-uniform deformation which must occur in neighbouring grains during the deformation of a polycrystal as a whole (c.f. fig. 2.3). The model predicts that in addition to the grain size dependence of

the initial yield stress, an increment of flow stress should develop during work hardening which is also proportional to the inverse square root of the grain size. If the work hardening is considered to arise from the increase in internal stress, increasing with increasing strain due to accumulation of dislocations in polycrystals, the total internal stress can be written as [160],

$$\sigma_i(T) = \sigma_{Stat.} + K_y d^{-1/2} + K_\epsilon d^{-1/2} \quad (2.22)$$

where σ_{Stat} is the grain size independent component of the internal stress due to statistically stored dislocation accumulated during plastic flow i.e. it reflects the rate of accumulation of dislocations in a homogeneously deformed single crystal of the same material. The term $K_y d^{-1/2}$ is the grain size dependent internal stress present at the initial yield event. This contribution can only be evaluated by extrapolation to zero plastic strain. The term $K_\epsilon d^{-1/2}$ represents an additional grain size dependent internal stress which increases during plastic deformation. This is considered to be additive to the internal stress due to statistically stored dislocations represented by σ_{Stat} and represents the effect of any additional work hardening imposed by the presence of grain boundaries.

This model differs from the model of Conrad et al. [156] which relate the slip distance to some fraction of the grain diameter in the sense that the boundaries themselves are considered as obstacles which enforce an additional non-homogeneous deformation upon the grains

in order to maintain contiguity. In materials which exhibit planar slip at low temperature (such as brass and zinc) this model explains the experimental result well [160] whereas it fails to describe the grain size effect for other materials in which obstacles to slip are readily created in the grain interior due to easy cross slip and cell formation (such as Cu [161,162]).

2.2.3.2 Correlation with experimental data

The form of equation (2.18) which is applicable to yielding, flow and fracture of a variety of metallic materials is also consistent with the fracture stress data of the majority of brittle polycrystalline ceramics including the rock salt materials [147-150]. Most of the studies concerning the grain size dependence of fracture stress however, have involved explaining the mechanism of fracture. In the discussion of crack nucleation and propagation, a critical (crack) length and a surface energy parameter were always involved in establishing the criteria for fracture. In the dislocation pile-up mechanism, the crack length is taken equal to grain diameter, while the surface energy parameter is approximately the grain boundary or single crystal surface energy. For the crack propagation mechanism, the critical surface energy depends upon the size of the fracture nucleus.

Besides the above aspect of the mechanisms of fracture, for which many excellent discussions are available in the literature, there have not been many attempts to describe the polycrystal

behaviour from other considerations. It has since been shown that in materials like polycrystalline NaCl, LiF and MgO, the brittleness cannot be just attributed to a lack of dislocations in the individual grains or to a failure of these to move and multiply. The critical event that determines the fracture occurrence is the interaction between a grain boundary and the glide bands or between two glide bands that form during the early stages of deformation. Most of the investigators however, have not attempted to explain their observations from yielding criteria. In an attempt to explain the influence of plastic flow on brittle fracture of polycrystalline ceramics, Carlignia [147] has drawn attention to the Hall-Petch behaviour, who plotted published strength data of several authors as a function of $d^{-1/2}$. Amongst the materials of interest here, only the behaviour of polycrystalline MgO was examined. Depending upon the grain size, he found a two-stage relationship, where σ_F vs $d^{-1/2}$ data could be fitted on two straight lines. Data in the finer grain size range obeyed Petch relation, $\sigma_F = \sigma_0 + Kd^{-1/2}$; whereas for the coarser grain sizes ($\geq 150 \mu\text{m}$) the data could be extrapolated to zero at infinite grain size. Fracture behaviour depicted by this latter portion of the curve was attributed to the elastic crack propagation from internal ('pre-existing') cracks or from flaws of the order of grain size in dimension. The other portion of the curve obeying Petch relation at small grain sizes was attributed to some unspecified type of dislocation-initiated yielding process.

In order to understand the Hall-Petch behaviour, Ku and Johnston [124] have provided some interesting results on MgO bicrystals.

It was found that the stress to form a crack at the intersection of a glide band and a grain boundary showed a Hall-Petch type behaviour. The dislocation source was a microhardness indentation placed at a controlled distance, d , from the boundary and the critical orientation with a $\langle 100 \rangle$ direction parallel to loading axis. σ_0 was shown to be the stress for dislocation multiplication rather than the minimum stress to move dislocations, and K (slope of σ_F vs $d^{-1/2}$ plot) gave a measure of the cohesive strength of the boundary. The value of σ_0 (50 MN/m^2) was much less (of the order of 1/4 to 1/5) than the σ_0 values obtained so far [147] from σ_F vs $d^{-1/2}$ plot extrapolation on polycrystalline MgO.

Results on polycrystalline NaCl also indicate similar behaviour. For example, when the data of Stokes and Li [123] on room temperature stress-strain behaviour of polycrystalline NaCl is replotted in terms of (stress) vs (grain size) $^{1/2}$, one finds two interesting features: In the range of grain size above about $100 \mu\text{m}$, it is seen that the yield and fracture stress both show a linear fit according to Hall-Petch relation. Secondly, while the intercept of the yield stress vs $d^{-1/2}$ plot extrapolates somewhat close to single crystal value on the stress axis, the intercept and slope of the fracture stress - $d^{-1/2}$ plot are quite different and larger than for the yield stress. This feature is similar to observations in room temperature experiments with polycrystalline MgO in the present work, even though this material shows only microscopic flow of the order of 10^{-4} plastic strain compared to several percent in NaCl.

Although at present there are not enough data available on the grain size dependence of work hardening behaviour, it should be mentioned that the above observations on NaCl and MgO show important similarity at least qualitatively with the deformation of some metals where either mode of slip or limited multiplicity in slip systems governs the overall polycrystalline plasticity. In the case of metals deforming by planar type of slip, it has been shown previously that the Hall-Petch slope increases with plastic strain [160,163,164], which is similar to the data on NaCl and MgO. Based on the dislocation accumulation model of Ashby [133], the explanation of work hardening behaviour with grain size as suggested by Schankula et al. [160] thus seems reasonable in describing the deformation of polycrystalline rock salt materials. However, in view of the limited data, it is not possible at the present to decide conclusively on the mechanism influencing grain size dependence of flow and fracture of these materials from the viewpoint of other considerations discussed before.

3.0 EXPERIMENTAL TECHNIQUES

3.1 Materials and Specimen Preparations

3.1.1 MgO single crystals

The crystals used in the present investigation were obtained from the Norton Company, Niagara Falls, Ontario, Canada in the form of cleaved (100) slabs of the dimensions $5 \times 1 \times 1 \text{ cm}^3$. They were clear and colorless. The chemical composition as suggested by the manufacturer is listed in Table 3.1.

Compression test specimens were cut from the bulk (100) cleaved crystals of the dimensions $7.00 \times 3.50 \times 3.50 \text{ mm}^3$ using a diamond cut-off saw. Sawing, rather than cleaving was preferred so that the maximum number of specimens could be obtained. After cutting, the specimens were ground flat on metallographic papers using a V-block taking care to make the ends true and parallel and chemically polished in hot ($90^\circ - 100^\circ\text{C}$) orthophosphoric acid (85%) to remove any surface damage due to cutting and grinding.

All of the specimens were given an annealing treatment at 1250°C for 24 hours in air and cooled to room temperature by air-quenching (in 5-6 minutes) to obtain a uniform impurity distribution and also to prevent any impurity precipitation which occurs on slow cooling. Final polishing was done on '600' metallographic papers and then again in acid until the crystal dimensions were 6.50×3.00

x 3.00 mm³. During the entire specimen preparation care was exercised to minimize the mechanical damage during handling, etc.

3.1.2 Polycrystalline MgO

Fully dense, 99.9% pure polycrystalline MgO (trade name: ITRAN 5) was obtained from Eastman Kodak Company, Rochester, New York, U.S.A. in the form of 5.0 x 2.5 x 0.6 cm³ slabs. They were slightly milky in color and in the as-received condition had a very fine grain size of the order of 2-3 μ m. The chemical analysis of this material as supplied by the manufacturer is given in Table 3.2 along with other properties of interest.

The slabs were cut into flat tensile specimens of dimension 5.0 x 0.6 x 0.1 cm, using a precision wafering machine. During the wafering operation, the cutting speed was kept at a minimum to prevent chipping off and/or breaking out of the cut portion from the rest of the material. This also reduced the chances of getting tapered specimens.

After cutting, each specimen was mechanically polished on a series of metallographic papers followed by polishing on cloth-covered laps using a slurry of Al₂O₃ Linde C powder. After several minutes of polishing, the specimen was cleaned and examined microscopically with special note made of the amount and detail of any grain pull-outs. Use of coarser grade metallographic papers were avoided to reduce the depth of damage inflicted by mechanical polishing.

Final polishing was done using $\frac{1}{4}$ μm diamond paste, followed by chemical polishing in hot (80°C - 90°C) orthophosphoric acid.

The specimens were annealed in two different batches. One batch was annealed in a vacuum of 10^{-6} torr at 1800°C while the others were heat-treated in air at 1650°C . In both cases the specimens were cooled slowly in the furnace at a rate of $3\text{-}4^{\circ}\text{C}/\text{min}$ to prevent cracking from thermal shock. Chemical polishing was repeated after the heat treatment. The resulting grain sizes measured by the linear intercept method were up to a maximum of about $120\ \mu\text{m}$ (without using any multiplying factor as suggested by some authors [167] to approximate a 'true' grain size). The thermal treatment and resulting grain sizes are summarized in Table 3.3.

3.2 The Etch-Pit Experiments

Etch pitting was carried out using two different solutions which produce the same results although they etch somewhat differently: (a) a solution consisting of 0.5 molar AlCl_3 in distilled water [168], this etchant gives well-defined square pyramidal pits on (100) surface when used at 55°C , (b) a solution of 50% (by volume) H_2SO_4 in distilled water which gives circular pits at 60°C . Etching with either solution was followed by rinsing first in warm distilled water then in methanol. Though both etchants were capable of distinguishing between 'grown-in' and 'fresh' pits, it was found that the former gave better results in delineating 'grown-in' dislocations. In the case of single

TABLE 3.3 Heat Treatments, Resultant Grain Sizes and Dislocation Density

Heat Treatment	Grain Size, (μm)	Dislocation Pit density/ cm^2	Remarks
(A) (10^{-6} torr vac.) 1800°C/30mts.	5 to 10	N.D.	N.D. - Not de- termined
1 hr.	12 to 18	N.D.	
2 hrs.	27.77	1.42×10^7 +	+ etch pit density in few isolated grains very high, not resolvable un- der optical microscope.
	30.28	4.08×10^6 x	
	28.57	3.2×10^7 +	
	34.72	2.85×10^6	
	37.25	1.4×10^6 +	
(B) (Air an- nealing 1650°C/6 hrs.	23.54	3.36×10^6	x etch pit density in most of the grains very high
	25.0	8.0×10^5	
	26.14	1.05×10^7 x	
	28.41	3.21×10^6	
	28.57	4.08×10^6 x	
	28.69	4.51×10^6 +	
12 hrs.	48.08	5.12×10^5	* very non- uniform etch pit distri- bution
	50.40	5.18×10^5 *	
	51.48	4.2×10^5	
	52.34	3.9×10^5	
	55.54	2.1×10^5 *	
14 hrs.	60.12	1.3×10^5	
	62.42	2.1×10^4	
	64.32	3.2×10^5 *	
16 hrs.	74.07	5.0×10^5	
	75.0	4.8×10^4	
	84.2	7.0×10^4	
	85.0	1.3×10^5 *	
20 hrs.	92.15	2.3×10^4	
	105.26	2.08×10^5 *	
	108.62	6.4×10^4	
	115.74	7.2×10^4	
	120.5	8.51×10^4	

crystals it could be shown by matching the etch pits on two opposite cleavage faces, that the pits actually correspond to dislocation emergence points. In the case of MgO etch pits have a 1:1 correspondence with dislocations was shown by Stablein [169] by simultaneous observation of etch pits and dislocations using transmission electron microscopy. It is believed that in the range of dislocation density involved in these experiments, a one-for-one correspondence was present.

The as-annealed dislocation density in single crystals was about $3 \times 10^5/\text{cm}^2$ from etch pit counts. In polycrystalline specimens, the initial dislocation density was found to be dependent on the grain size of the annealed specimens. Dislocation pit density on about 20 to 30 grains were measured on each specimen. These measurements are included in Table 3.3. In order to study the slip initiation and propagation, the load-unload-etch technique, in which a polished specimen is stressed to a pre-determined level, unloaded and etched again, was employed. Due to faster reaction along grain boundaries in polycrystalline MgO, etchant (b) was found to give better results than the etchant (a) while etching time was also shorter compared to single crystals.

3.3 Mechanical Testing

3.3.1 Compression testing of MgO single crystals

Compression testing was carried out using a special self-

aligning jig, made of stainless steel, which was mounted on a floor model Instron (fig. 3.1). When this jig was pulled in tension, a compressive stress was applied to the specimen in the centre of the jig. A $\frac{1}{2}$ " stainless hemisphere was positioned over a minor depression mark on the lower platen onto which the specimen rested during the deformation. This was introduced to take care of eccentricity in loading even if the two ends of the polished specimens were not perfectly flat. Very thin teflon sheets or molybdenum foils (at higher temperatures) were used as a lubricant between the specimen ends and compression platens.

For testings at low temperatures, suitable baths (e.g. at 77°K , liquid nitrogen bath; at 208°K , dry ice and acetone mixture bath and at 473°K , silicon oil bath) were used, whereas for tests above 473°K , the jig and specimen assembly was enclosed with a split-type furnace equipped with automatic temperature controller having a temperature control of $\pm 1-2^{\circ}\text{C}$. Temperatures were measured using Pt - Pt/10%Rh thermocouples placed next to the specimen. A time period of at least 30 minutes was allowed to ensure that the grip assembly reached a steady state temperature before running the tests.

The basic strain rate used was $1.3 \times 10^{-5} \text{sec}^{-1}$ and, to study the effect of strain rate, changes to $1.3 \times 10^{-4} \text{sec}^{-1}$ were made. For the stress relaxation experiments, the motion of the Instron cross head was stopped at the desired strain level and the decrease in load was recorded on chart paper running at a known speed.



FIGURE 3.1: Compression testing jig.

3.3.2 Tensile testing of polycrystalline MgO

Tensile testing of polycrystalline specimens was carried out using a special tensometer designed to facilitate the uniaxial and friction-free motion of the crosshead during loading. Considering the brittle behaviour of polycrystalline MgO, the requirements to be met in the construction of a tensile testing facility were:

- (a) to have minimal mechanical vibration during tests, (b) the ability to apply and measure the tensile load with a minimum complexity, (c) to avoid mechanical contacts with the specimen, and (d) to devise a method of gripping that would not itself introduce any stresses to the specimen ends and at the same time permit uniaxial loading.

The above problems were solved after encountering considerable difficulty and the tensile testing facility which was finally developed is shown in fig. 3.2. Construction was all of stainless steel including even the pins and screws. It was assured that none of the parts yield before approximately twice the fracture load of the specimens. Since one of the objectives of the present work on polycrystalline MgO was to study the behaviour of residual lattice strains, the tensometer was designed so as to fit onto the specimen holder stage of a Phillips x-ray diffraction machine. The basic design however, was such that it could also be mounted on the Instron machine without any major alterations for dynamic recording of the stress-strain curve.

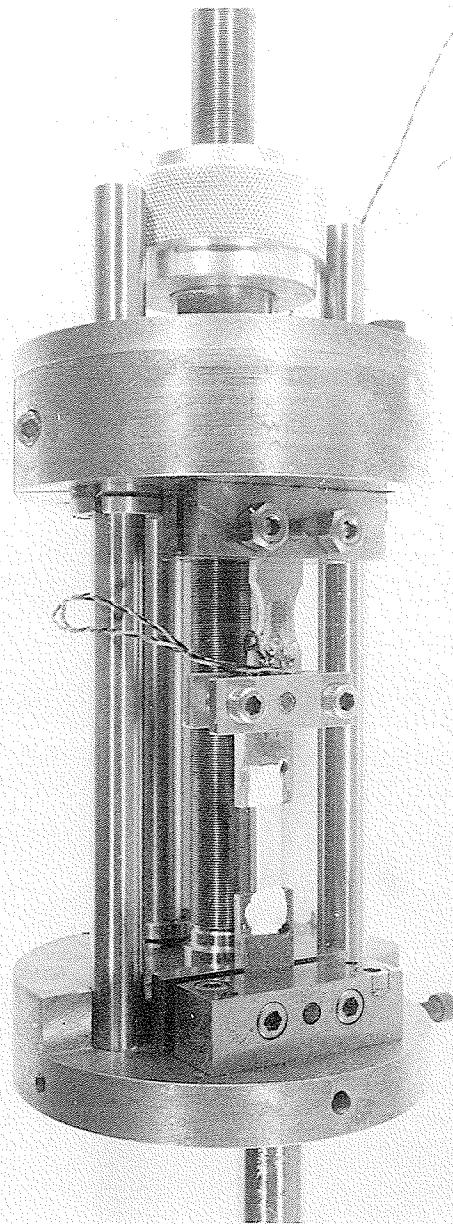
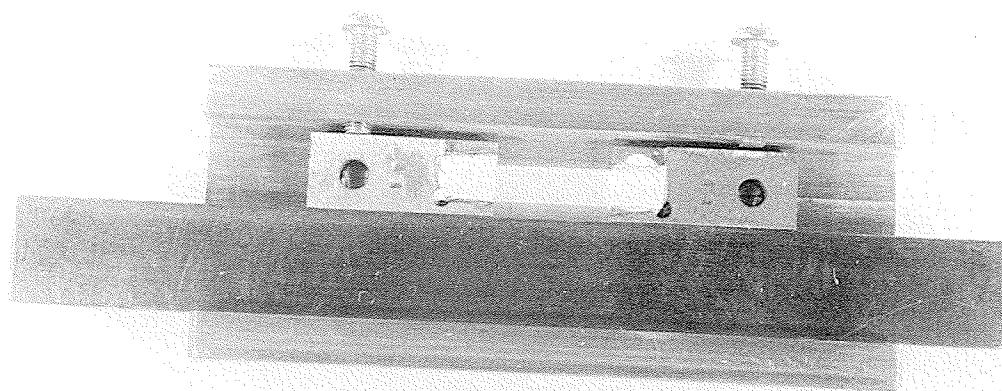


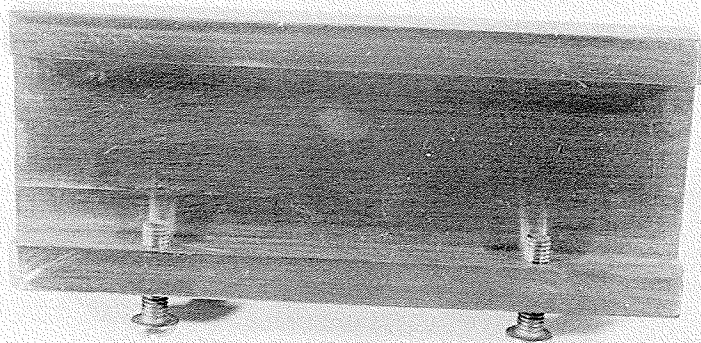
FIGURE 3.2: Tensile testing jig used in the present investigation. Specimen cemented on grip-ends coupled in line with load cell is shown. Stress is applied by screwing the knob at the top which is fastened with the movable upper cross head.

The load on the specimen was measured by an internally fixed and calibrated stainless steel load cell. The calibration of the load cell was done by applying a known load on an Instron machine and measuring the strain with the help of an external strain indicator capable of giving a sensitivity of $\pm 1 \times 10^{-6}$. A calibration curve was thus plotted after repeating the loading and unloading of the load cell (specimen) several times to ensure the reproducibility and linearity up to the working stress range. This calibration curve was then used to determine the applied load to the specimen at any value of strain, since the load cell was directly attached to the specimen grip-ends. The strain in the specimen was measured independently through separate strain gages.

The tension specimens were cemented onto the grooved pieces shown in fig. 3.3(a). Special care was necessary in setting the specimen over the grip-ends so that the specimen was cemented on the centre line. To help facilitate parallellism between the grips as well as to keep the specimen aligned during the cementing operations, a parallel-bar type alignment jig was made. This is shown in fig. 3.3(b). Sauereisen' cement was used to hold the specimen in place. Care was exercised in applying the cement so that it did not contaminate the gage length portion of the specimen. After the cement was dried (which took about 10 to 12 hrs. at room temperature), the specimen was transferred to the tensometer.



a



b

FIGURE 3.3: Device used for aligning the specimen during cementing operation onto the grip ends.

4.0 EXPERIMENTAL RESULTS

4.1 Compressive Deformation of MgO Single Crystals

4.1.1 General deformation characteristics

The general stress-strain behaviour of the [100] crystals obtained in compression are shown in fig. 4.1 for the six temperatures of 77° , 208° , 293° , 473° , 573° and 673° K. Although some variation was found in the yield stress due to surface effects from specimen to specimen at one temperature, the general shape of the curves remained the same. No yield points were observed in any of the specimens within the above temperature limits. Since all tests were confined to $\langle 100 \rangle$ loading axis, the shear stresses and shear strains were calculated for the active $\{110\} \langle 110 \rangle$ primary slip systems. Between three and four samples were deformed under a given set of conditions.

4.1.2 Temperature dependence of CRSS

Figure 4.2 gives the temperature dependence of the critical resolved shear stress on $\{110\} \langle 110 \rangle$ slip systems. In general, the CRSS increases sharply with decreasing temperature in a manner commonly observed in b.c.c. metallic systems. The values of σ_i (athermal component of flow stress) and T_0 (the critical reference

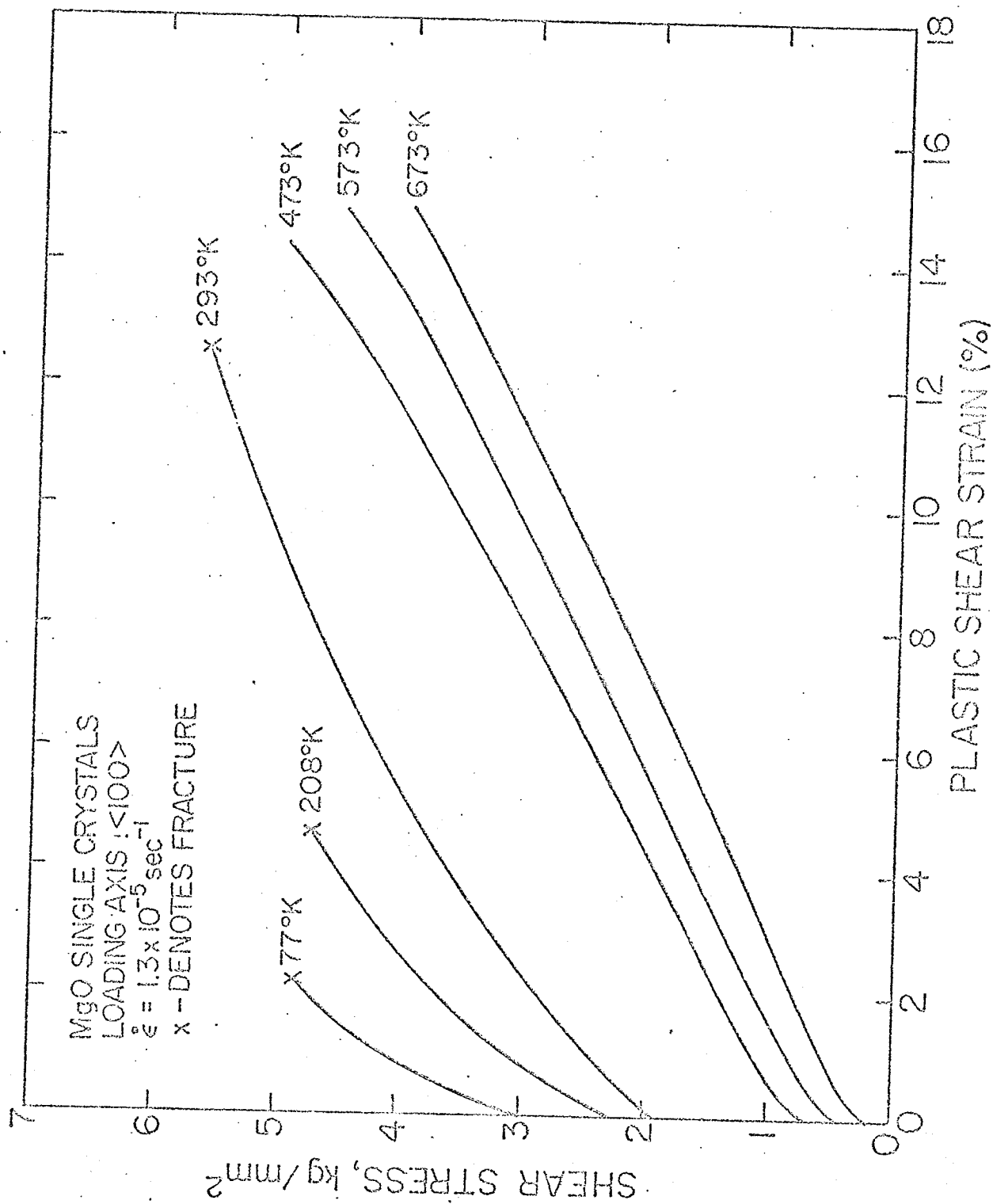


FIGURE 4.1: Shear stress-shear strain curves for MgO single crystals.

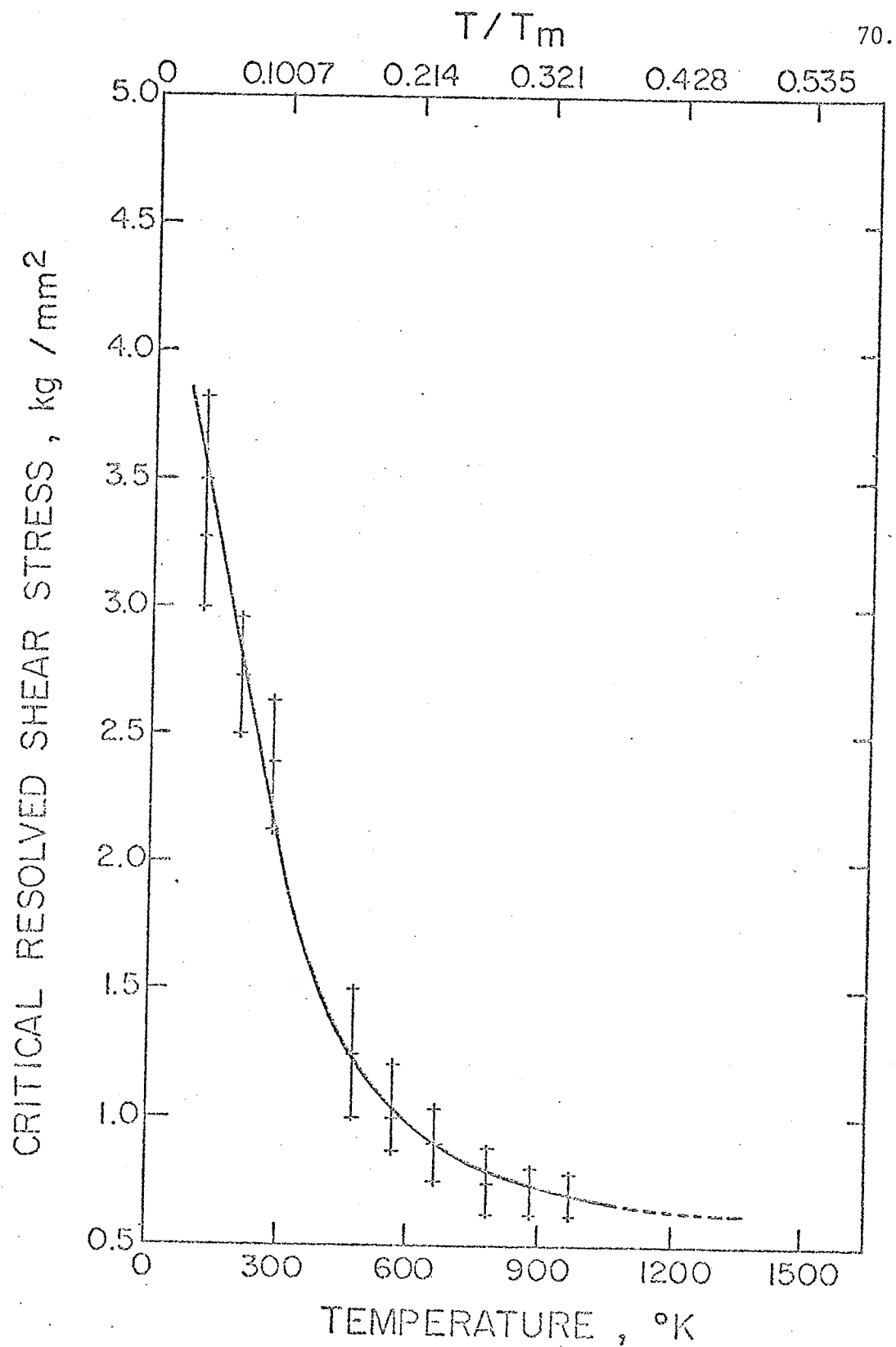


FIGURE 4.2: Temperature dependence of the CRSS for MgO crystals.

temperature where the thermal contribution to flow stress is vanishingly small) deduced from this plot are 0.65 kg/mm^2 and $\sim 1400^\circ\text{K}$ respectively. The temperature variation of shear modulus $[(C_{11}-C_{12})/2]$ is plotted in fig. 4.3.

4.1.3 The strain rate sensitivity of flow stress at various temperatures

Strain rate change experiments were performed by changing the strain rate upwards by a factor of 10 from the base strain rate of $1.3 \times 10^{-5} \text{ sec}^{-1}$ over a range of temperature from 77°K - 673°K . The change in stress, $\Delta\sigma$, due to change in strain rate is plotted in fig. 4.4 against true plastic strain for various temperatures. The values of $\Delta\sigma$ are plotted against temperature in fig. 4.5.

Since the stress relaxation technique is also capable of yielding necessary informations for evaluating various thermal activation parameters, this technique was also employed in conjunction with the strain rate change method. Following the strain rate changes from $\dot{\epsilon}_1$ (base) to $\dot{\epsilon}_2$ and back to $\dot{\epsilon}_1$, loading was stopped and stress relaxation curves recorded for about 5 to 6 minutes. The loading was continued either immediately after relaxation or after complete unloading to check work hardening and/or strain ageing effects, and this sequence was repeated for various increasing amounts of plastic strains. Within the experimental errors in measurements and reproducibility limits of $\sim 10\%$ from specimen to specimen, it was found that $\Delta\sigma$ remained practically constant, independent of strain over the strain

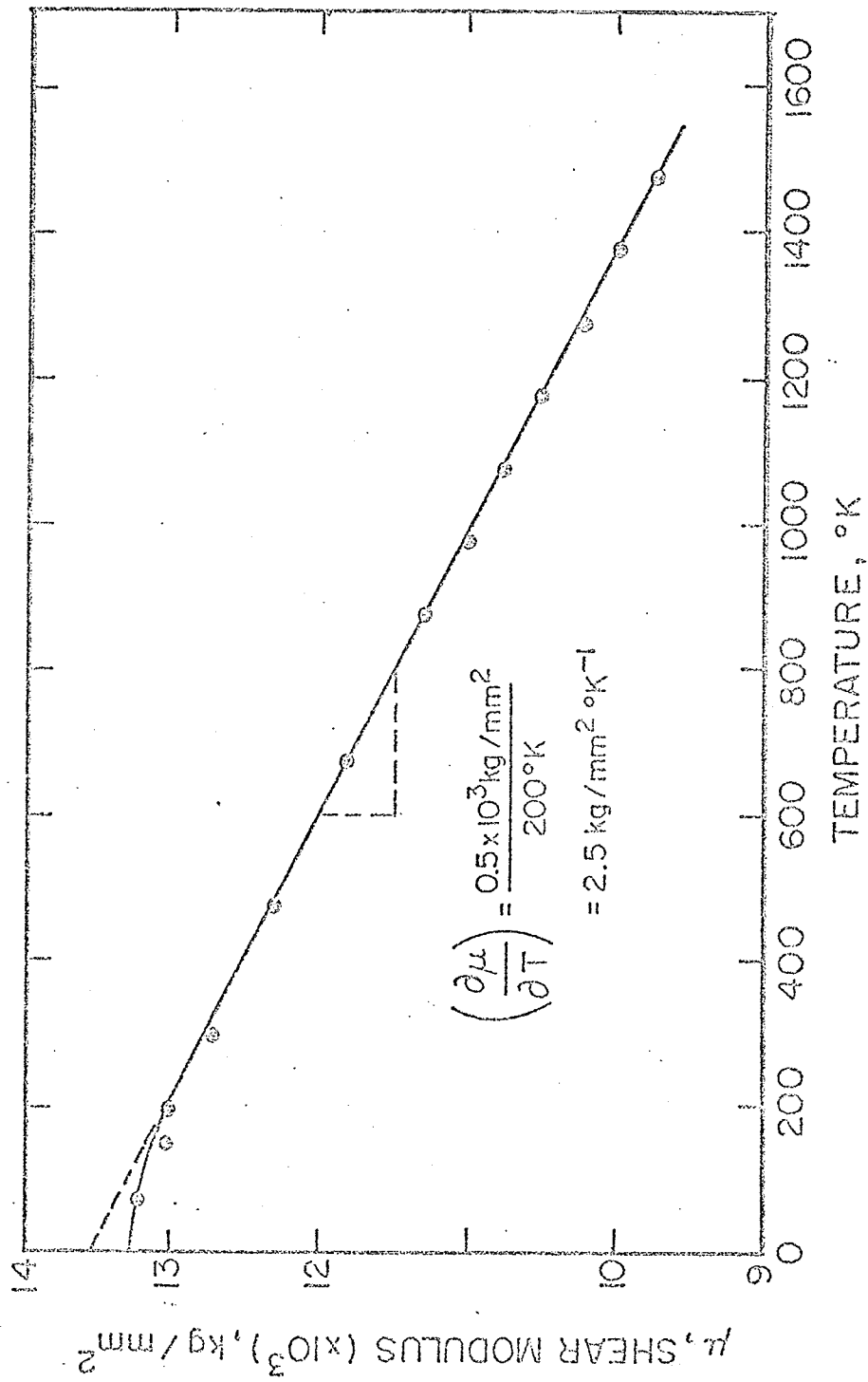


FIGURE 4.3: Temperature dependence of the shear modulus for MgO (from ref. [64]).

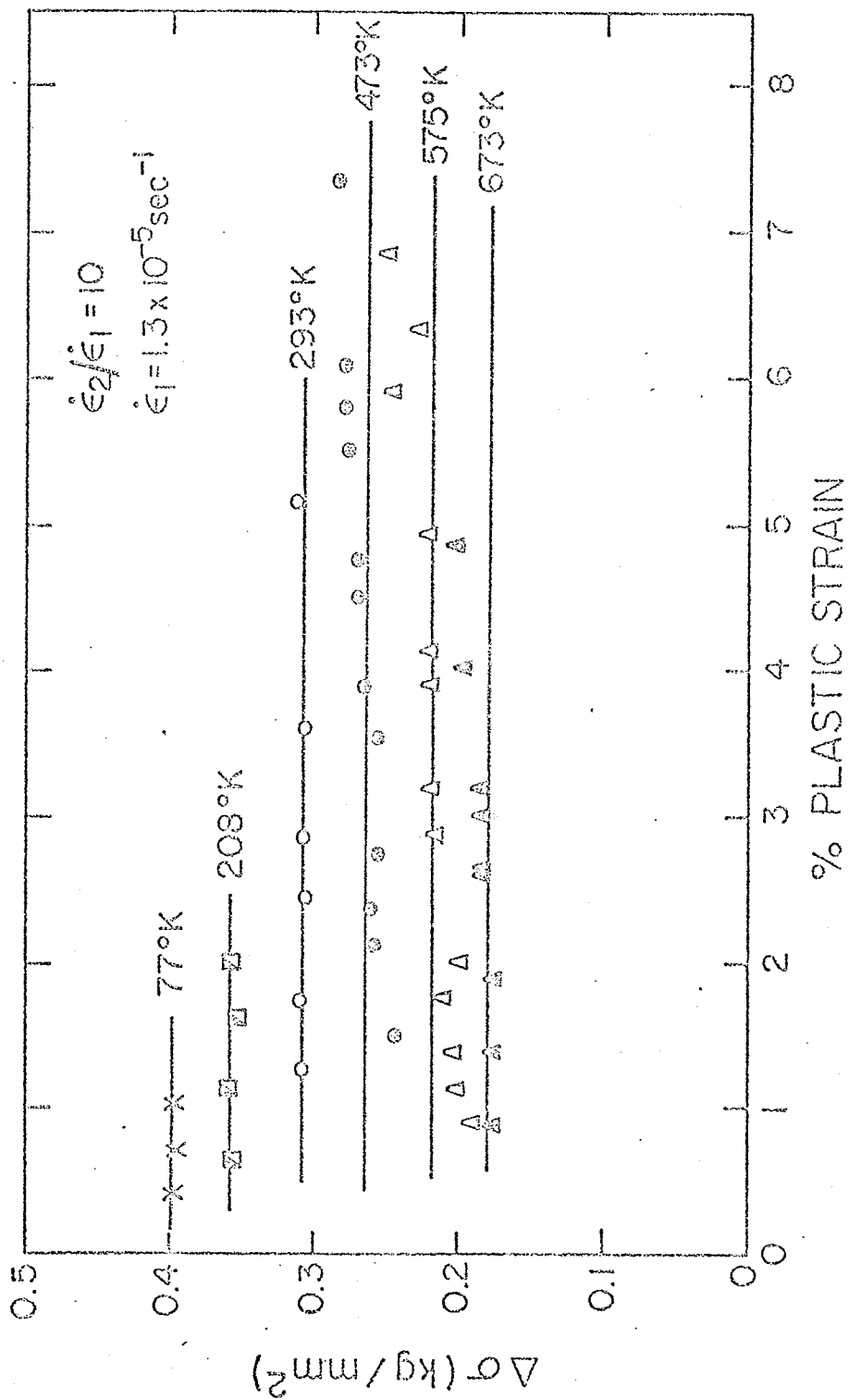


FIGURE 4.4: Change in stress due to change in strain rate as a function of plastic strain for different temperatures.

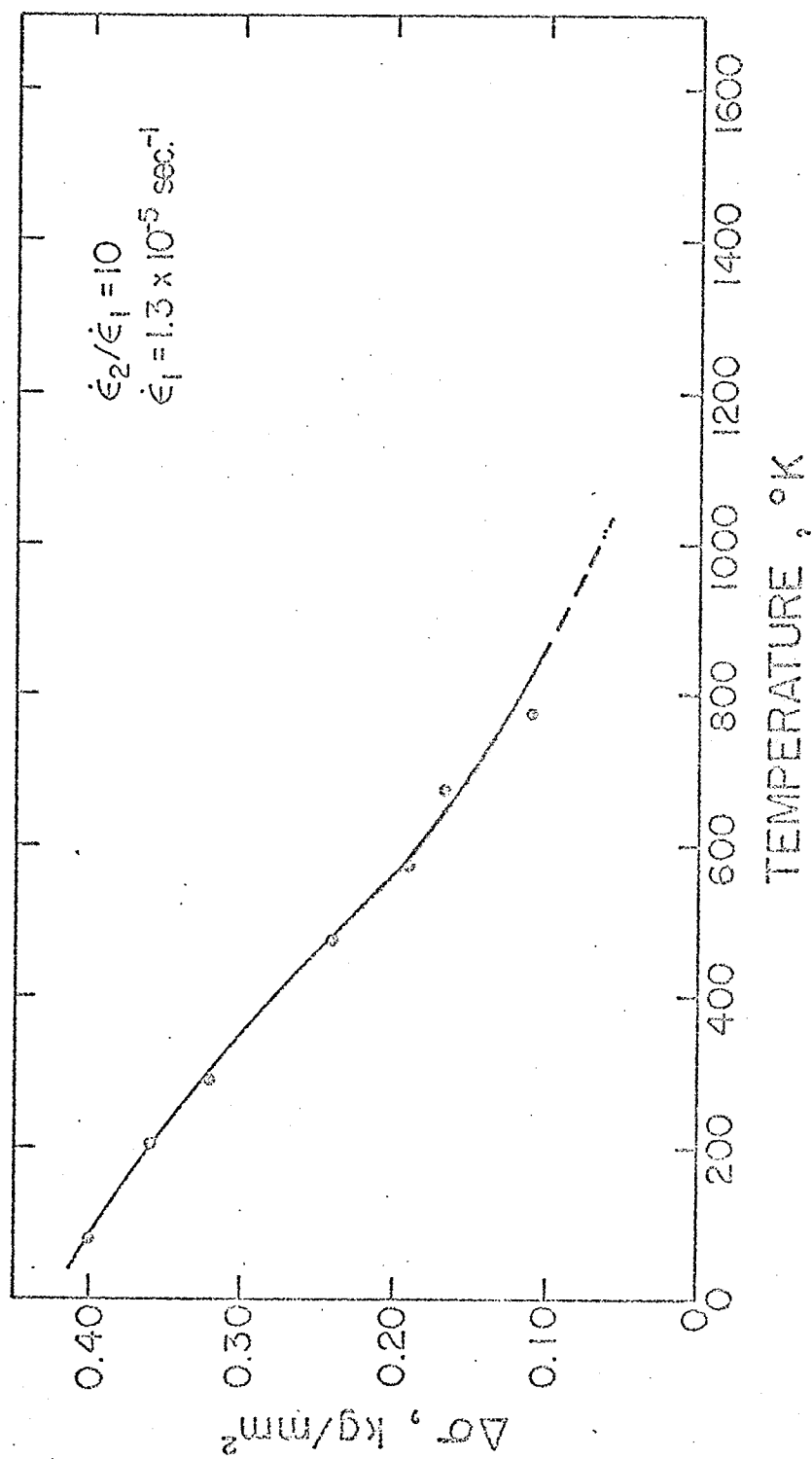


FIGURE 4.5: Change in stress due to change in strain rate as a function of temperature considered at an equivalent plastic strain of 1.0%.

range investigated.

4.1.4 Evaluation of the dislocation velocity - effective stress exponent, m^*

4.1.4.1 Stress relaxation technique.

The stress relaxation technique of analyzing deformation kinetics in crystalline solids has been extensively used in recent years for many metallic [49] and ionic [65] materials. The theoretical background for determining the dislocation velocity - effective stress exponent, m^* , from this technique and its comparison with other techniques has been discussed previously by many workers. In particular, Li [49] and Gupta and Li [66] have applied this technique to NaCl and LiF crystals. Typical stress relaxation curves obtained on MgO crystals in the present work are shown in fig. 4.6.

The dislocation velocity - effective stress exponent, m^* , from this method is calculated from the slope of the linear portion of a log - log plot of the negative of stress-rate ($-\partial \sigma / \partial t$) vs. time (t), via the relation:

$$m^* = (\text{slope}/\text{slope}+1) \quad (4.1)$$

In fig. 4.7 the logarithm of the stress rate is plotted against the logarithm of time. In order to include all the experimental data

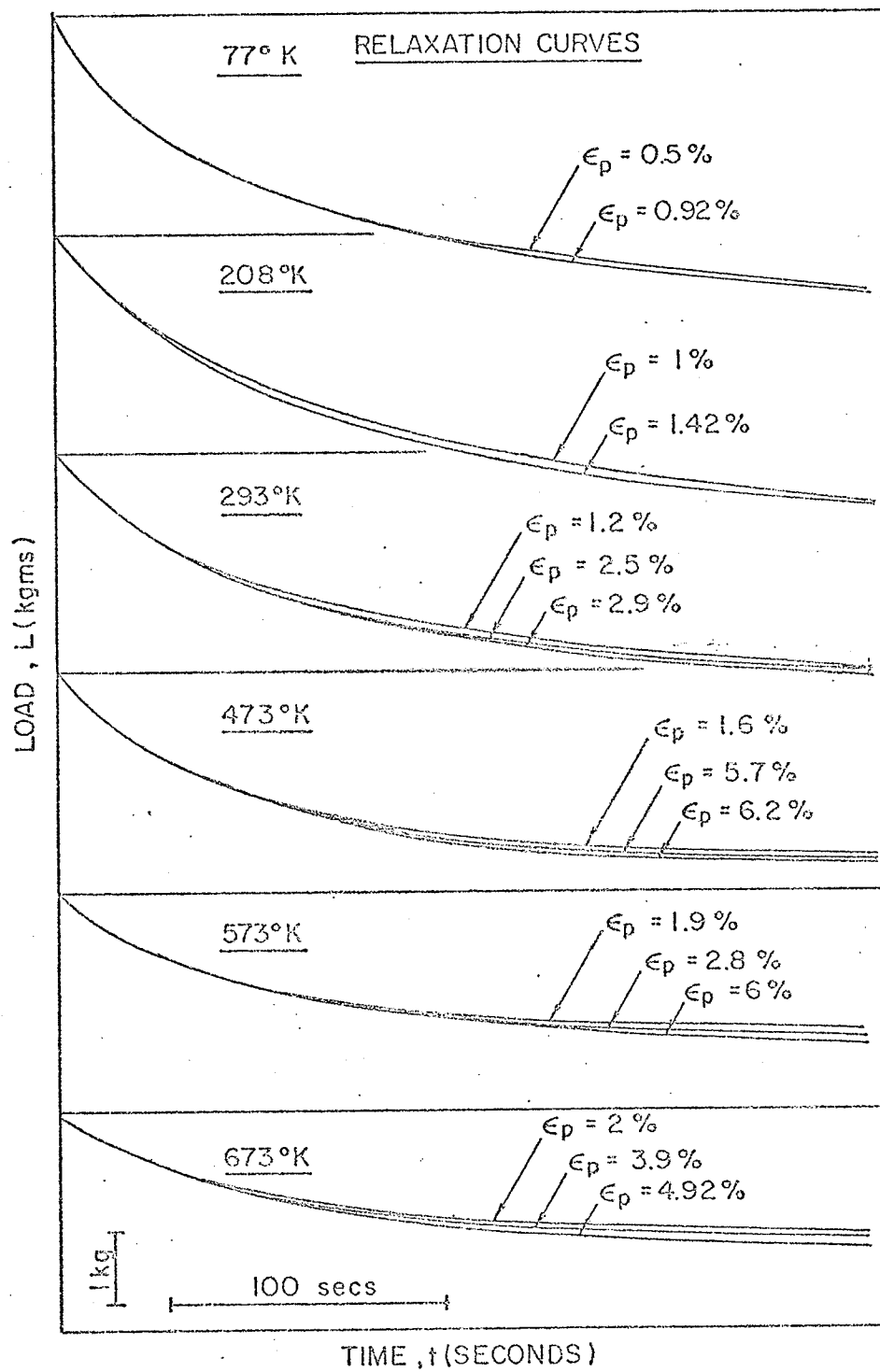


FIGURE 4.6: Stress relaxation curves at different temperatures for various plastic strains.

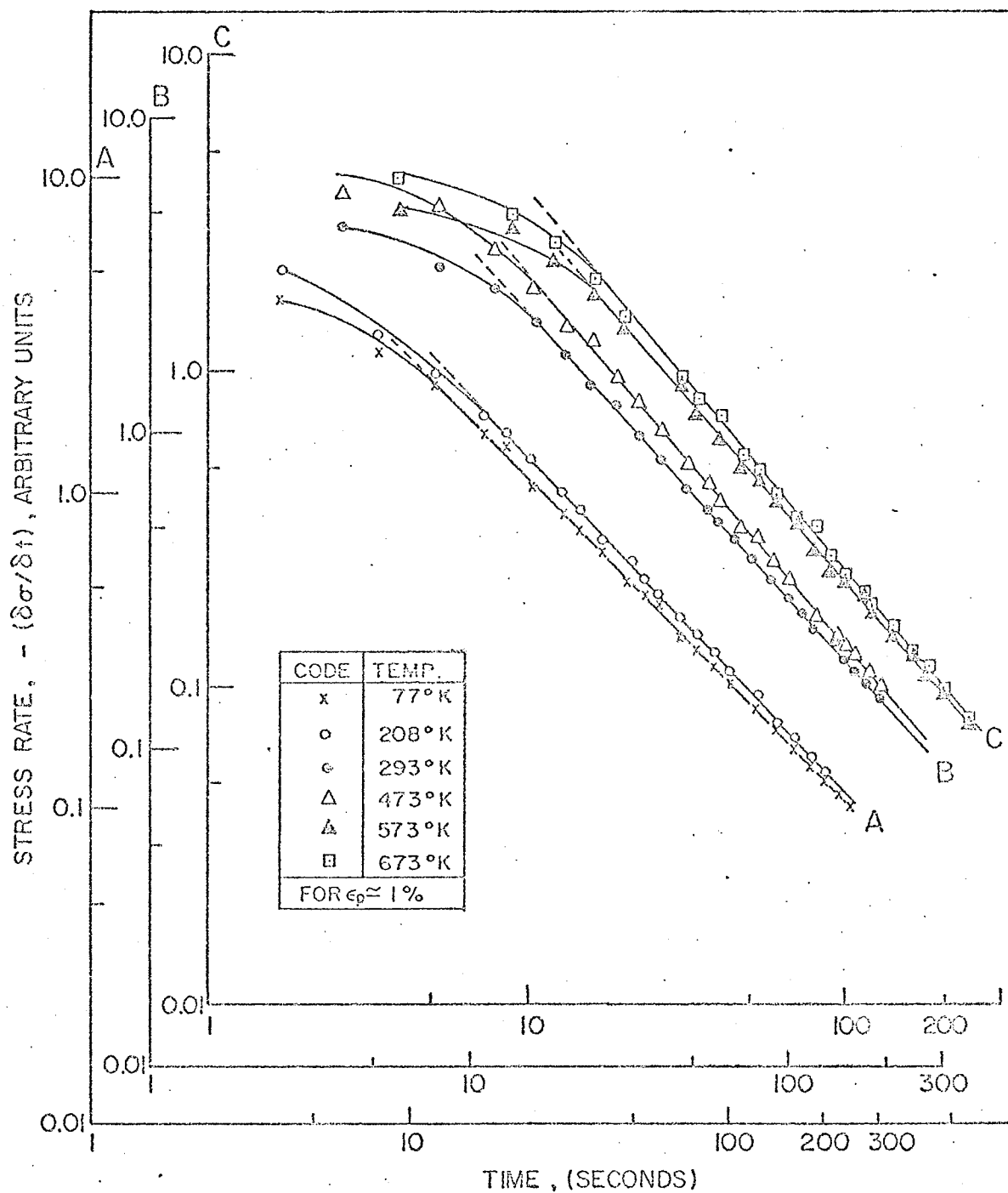


FIGURE 4.7: Log - log plots of the stress rate vs. relaxation time for different temperatures.

obtained at different temperatures and for $\epsilon_p \sim 1\%$ of plastic strain, the co-ordinates are suitably shifted. It is seen from this plot that a linear relationship holds at long times to yield a limiting slope according to eqn. (4.1). Furthermore, the experimental data showed approximately the same slope at all plastic strains greater than $\sim 1.5\%$, and in all cases the absolute value of the slope of the linear portion is larger than unity to yield positive m^* .

In the case of experiments done above room temperature, the fluctuations in temperatures of the bath or furnace were the major sources of troubles which affected the profile (curvature) of the stress relaxation curves. Secondly, as can be seen from the plots in fig. 4.7, a slight variation in slope measurements gives a large error in the results on the absolute magnitude of m^* . This can be specially so for the materials whose m^* values are large, since the slope in a log - log plot of the stress rate ($-\partial\sigma/\partial t$) versus time (t) becomes too small to evaluate m^* accurately. The measurements done in the present work, therefore, were repeated on several samples to check the reproducibility of the stress relaxation curves. In addition, the magnitudes of m^* were also determined by other techniques as a check on the applicability of various techniques as well as for the reliability in the magnitudes of m^* .

Using the stress relaxation curves of fig. 4.6, the athermal component of flow stress, σ_i , at any plastic strain was determined by using the relation [66]:

$$\left(\frac{\sigma_1 - \sigma_i}{\sigma_2 - \sigma_i}\right) = \left(\frac{t_2 + a}{t_1 + a}\right)^{1/m^*-1} \quad (4.2)$$

where σ_1 and σ_2 are the flow stresses after times t_1 and t_2 on a stress relaxation curve and 'a' is the deviation in linearity in the log - log plots of fig. 4.7. Assuming linear additivity of the thermal and athermal components of the flow stress, the thermal or effective stress component, σ^* , was obtained by subtracting the value of the athermal stress from the flow stress. Figure 4.8 summarizes the results of the variation of flow stress and its components against plastic strain at different temperatures. It is seen that, except in the early stages of deformation at 473°K and above, σ^* remained constant with strain while the internal stress increased in the same manner as the applied stress. The temperature dependence of effective stress is shown in fig. 4.9 the effective stress increasing with decreasing temperature.

4.1.4.2 Extrapolation and other techniques

Using the method suggested by Johnston and Stein [165], the values of m^* were also evaluated from the data of strain rate cycling test.

Since by definition:

$$m = \left(-\frac{\partial \ln \dot{\epsilon}_p}{\partial \ln \sigma}\right) \quad (4.3)$$

m^* can be obtained by extrapolating m (m and m^* are different in the

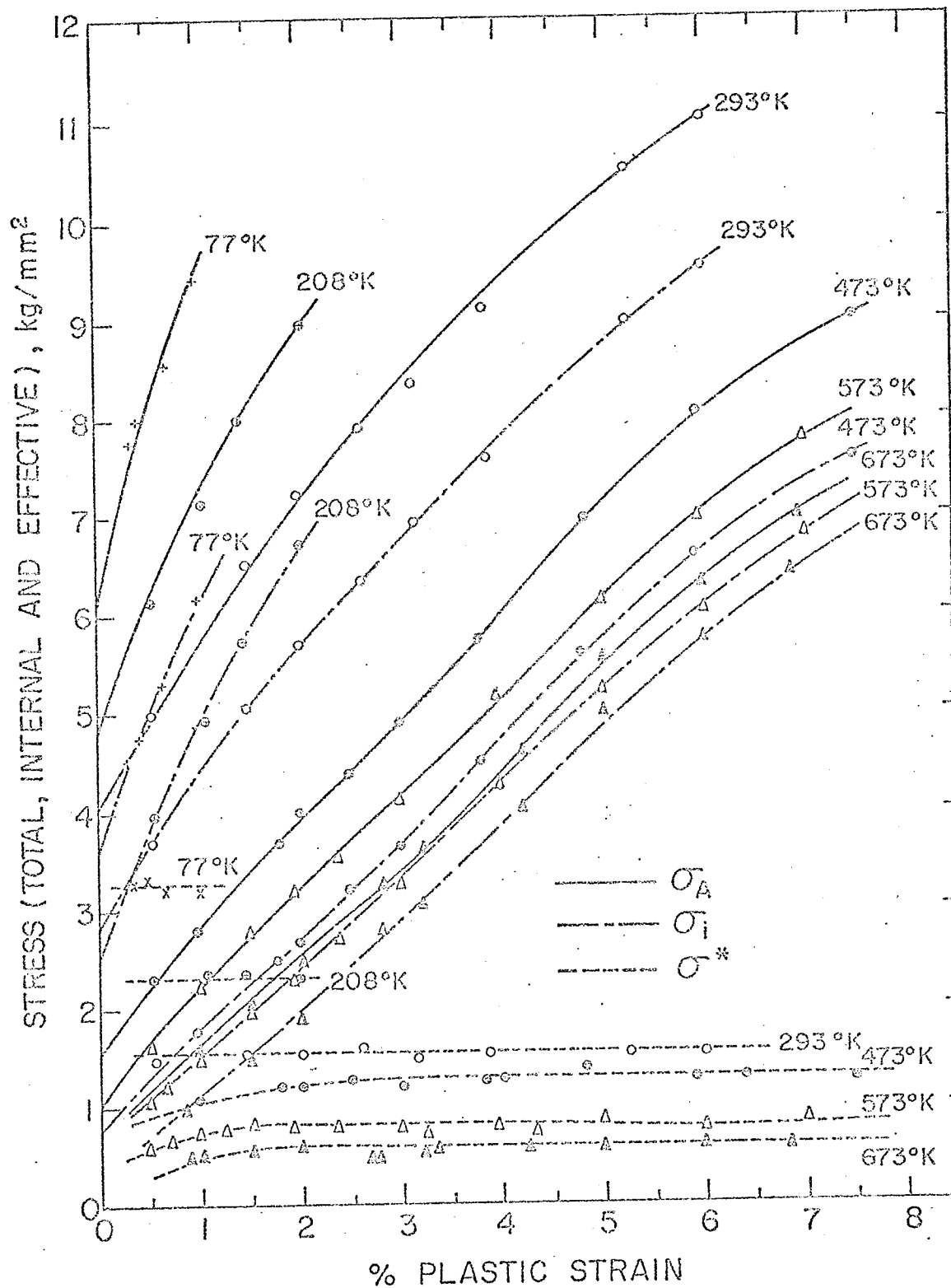


FIGURE 4.8: The dependence of applied stress (σ_A), internal stress (σ_i) and effective stress (σ^*) on plastic strain.

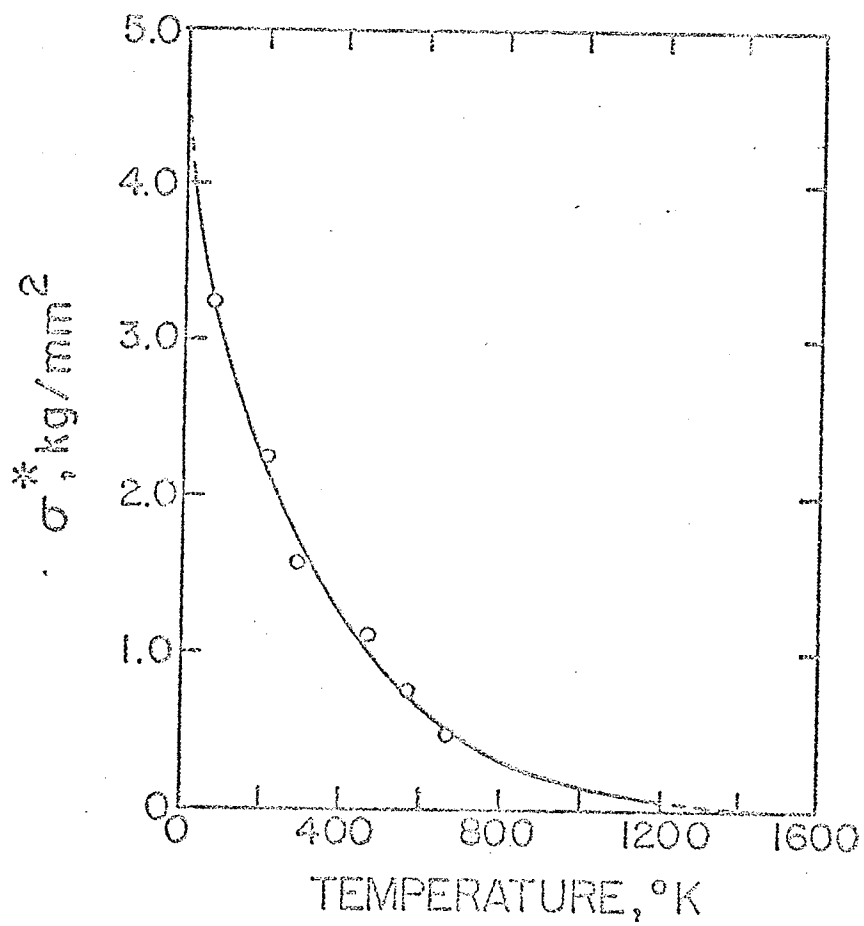


FIGURE 4.9: The variation of the effective stress (σ^*) with temperature.

sense that m represents the value of m^* in the work hardened state [49,61,166]) to zero plastic strain where $\sigma_i = 0$. From which it follows that:

$$m^* = \left(\frac{\partial \ln \bar{v}}{\partial \ln \sigma^*} \right) \equiv \left(\frac{\partial \ln \dot{\epsilon}_p}{\partial \ln \sigma} \right)_{\epsilon \rightarrow 0} \quad (4.4a)$$

and then the relationship between m and m^* becomes

$$m = \left(\frac{\partial \ln \dot{\epsilon}_p}{\partial \ln \sigma} \right) = \left(\frac{\partial \ln \bar{v}}{\partial \ln \sigma^*} \right) \sigma = \left(\frac{\sigma}{\sigma^*} \right) m^* \quad (4.4b)$$

The values of m obtained by using eqn. (4.4) are plotted in fig. 4.10 against plastic strain and show the values of m^* corresponding to extrapolation at $\epsilon_p = 0$ for various temperatures. The behaviour of m with plastic strain bears a resemblance to that in the stress-strain curve (fig. 4.8). In order to reduce the arbitrary extrapolations which is unavoidable in plots such as those of fig. 4.10, an alternative procedure was followed by taking advantage of the parabolic nature of curves between 77°K to 293°K. Accordingly, a plot of m against square root of plastic strain, $\epsilon_p^{1/2}$, gave a linear relationship in the temperature range of 77° - 293°K as shown in fig. 4.11.

A further alternative way of obtaining m^* is by using the strain rate sensitivity of flow stress which is measured by strain rate cycling tests. Noting that m^* is defined from eqn. (4.4a) to be

$$m^* = \left(\frac{\partial \ln \bar{v}}{\partial \ln \sigma^*} \right)$$

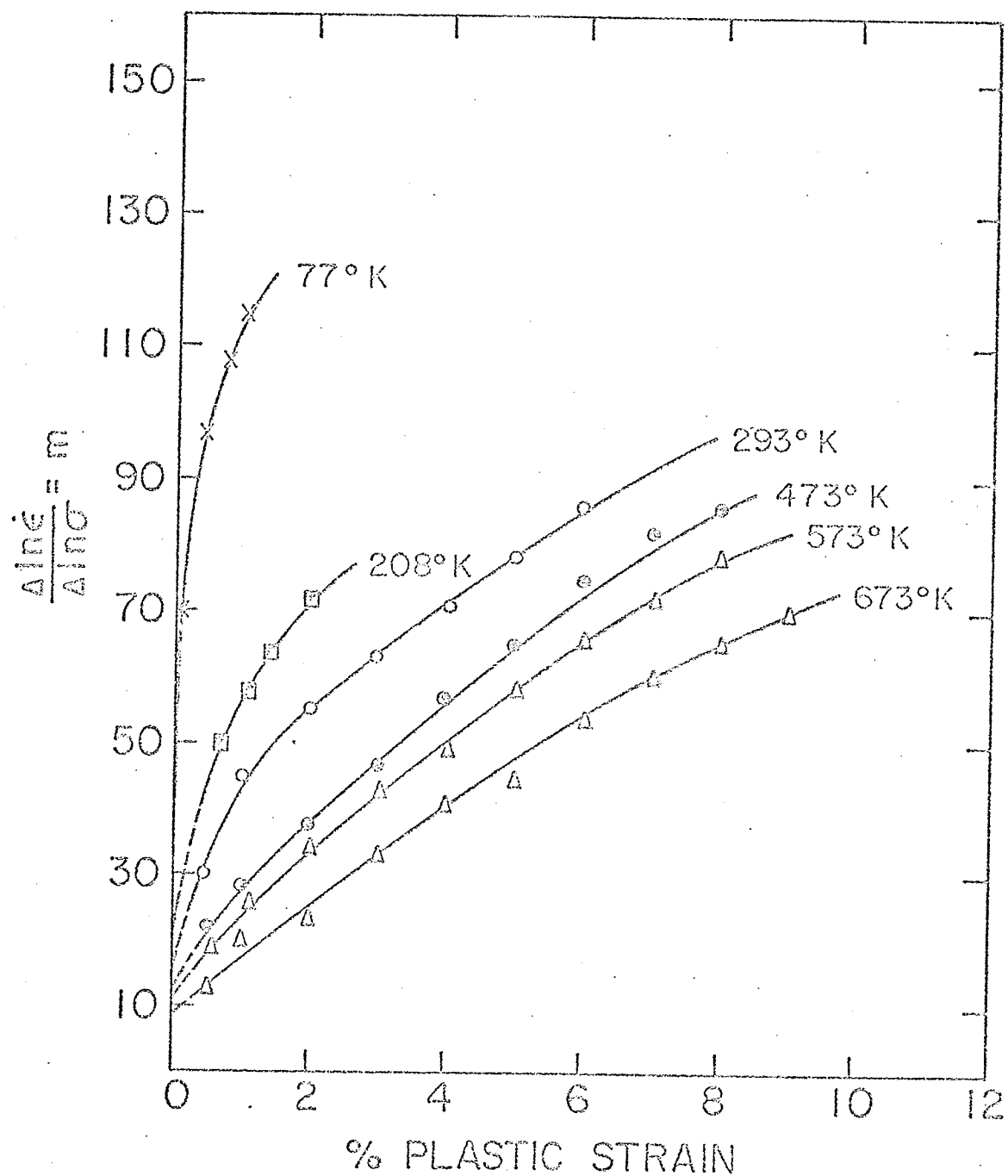


FIGURE 4.10: The variation of the dislocation velocity-stress exponent, m , as a function of plastic strain.

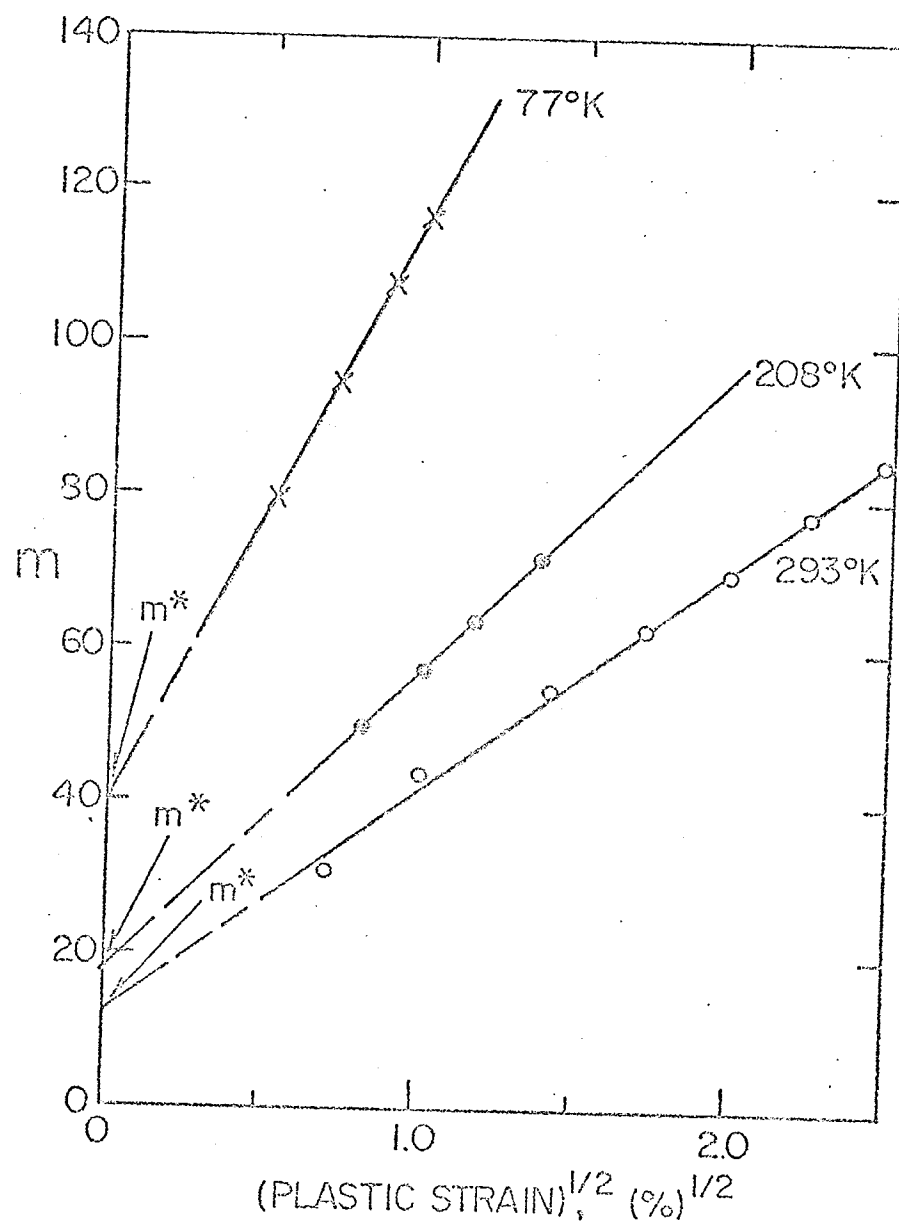


FIGURE 4.11: $(\text{Strain})^{1/2}$ dependence of m for 77°K, 208°K and 293°K.

we find,

$$m^* = \left(\frac{\partial \ln \dot{\epsilon}_p}{\partial \ln \sigma^*} \right) = \left(\frac{\partial \ln \dot{\epsilon}_p}{\partial \sigma} \right) \sigma^* \equiv \frac{V^* \sigma^*}{kT} \quad (4.5)$$

where V^* is the activation volume for yielding, defined as

$$V^* = kT \left(\frac{\partial \ln \dot{\epsilon}_p}{\partial \ln \sigma^*} \right)_{T,P} \quad (4.6)$$

Therefore, m^* can be deduced from strain rate cycling test by calculating the activation volume, V^* , using eqn. (4.6). In fig. 4.12, the values of m^* obtained by Gupta - Li technique of stress relaxation and those obtained via eqn. (4.5) are compared and plotted against plastic strain. Beyond 673°K, where dynamic strain ageing was observed m^* values were determined by a log - log plot of the strain rate vs. stress at the proportionality limit (fig. 4.13) which effectively gives σ^* . Summarized in Table 4.1(a) are the results on m^* obtained by various techniques in the present investigation. Values from the literature are also shown for comparison in Table 4.1(b).

The m^* values of the present work are plotted against temperature in fig. 4.14 and show a sharp increase with decreasing temperature.

4.1.5 The Activation Volume

Values of the activation volume, V^* , derived by using

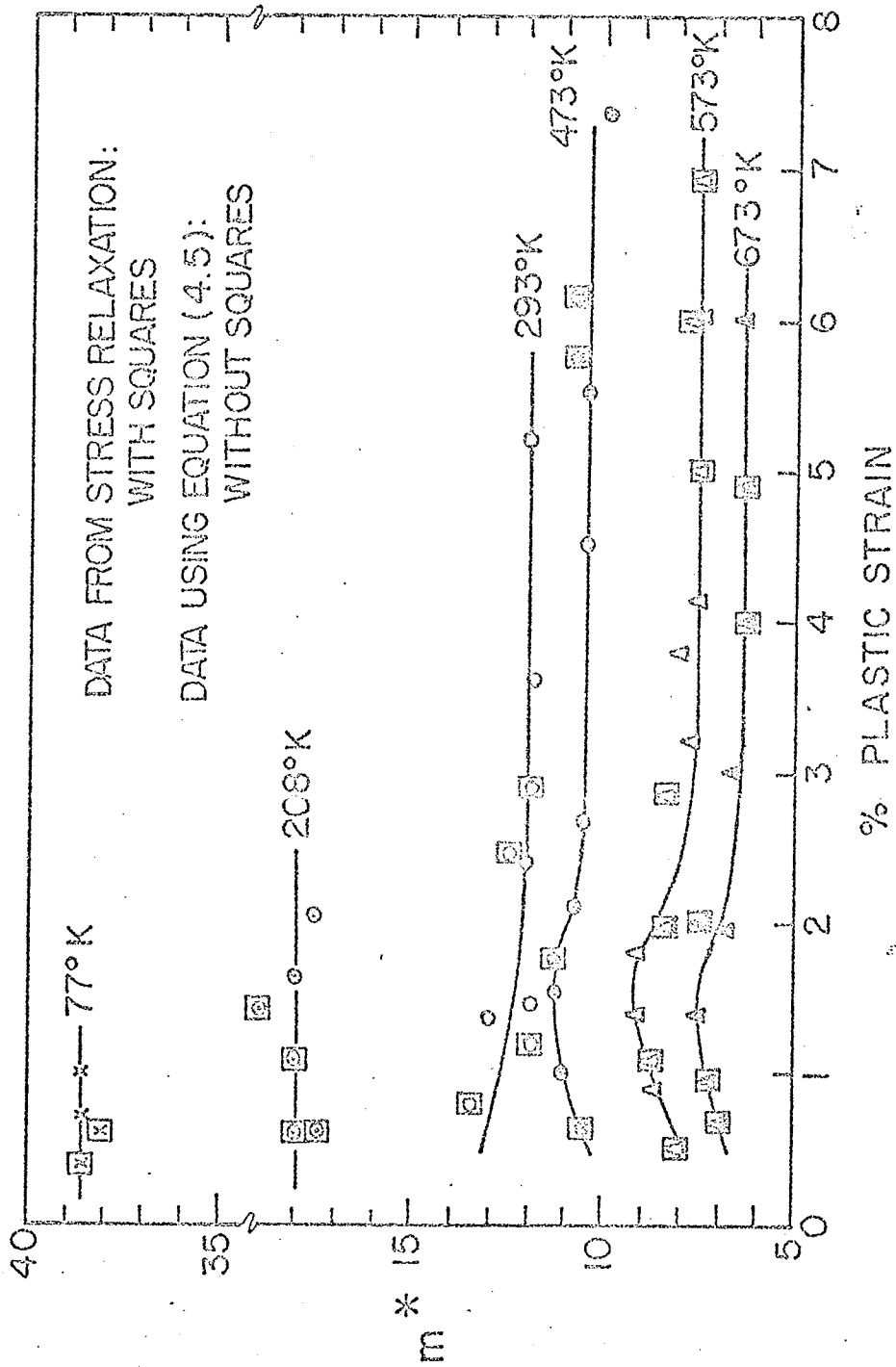


FIGURE 4.12: Velocity-effective stress exponent, m^* , as a function of plastic strain.

TABLE 4.1(a): Comparison of results for dislocation velocity - effective stress exponent, m^* , from different studies.

Reference	Major Impurity (in p.p.m.)	Evaluation Technique	m^* T($^{\circ}$ K)	Remarks
[46]	?	Stress pulse etch pit	22 R.T.	applied stress, σ , was used in stead of effective stress, σ^* .
[183]	Fe ⁺³ $\approx$ 80	Strain rate sensitivity of proportionality limit	30 77 $^{\circ}$ 17 200 $^{\circ}$ 12 300 $^{\circ}$ 8.5 473 $^{\circ}$ 7.0 673 $^{\circ}$ 6.3 873 $^{\circ}$	m^* values are taken from author's curve of ($\frac{\partial \ln \dot{\epsilon}}{\partial \ln \sigma}$) vs. temperature (see also Ref. [49]).
[15]	Fe ⁺³ $\approx$ 100	constant stress rate tests	33 R.T. 2 1573 $^{\circ}$	applied stress σ , was used in stead of eff- ective stress, σ^* .
[47]	Fe ⁺³ $\approx$ 150	Stress pulse-etch pit	11.45 (edge) R.T. 11.06 (screw)	
[64]	Fe ⁺² = 50	Extra- polation method Stress- relaxation Double strain- rate change	70 77 $^{\circ}$ 52 195 $^{\circ}$ 55 295 $^{\circ}$ 46 473 $^{\circ}$ 32 673 $^{\circ}$ 39 295 $^{\circ}$ 4.5 295 $^{\circ}$	

TABLE 4.1(b): m^* values of the present investigation obtained by different methods.

Evaluation techniques and m^* values				
stress relaxation	Extrapolation techniques	Using eqn. $m^* = V^* \sigma^* / kT$	Strain rate sensitivity of proportionality limit	$T(^{\circ}K)$
38.5	40.0	39.0	-	77 ^o
18.0	18.0	20.0	-	208 ^o
12.5	12.0	12.0	-	293 ^o
10.0	11.2	10.5	-	473 ^o
8.5	10.5	8.0	-	573 ^o
6.5	8.5	6.0	-	673 ^o
-	-	-	5.0	773 ^o
-	-	-	6.2	873 ^o
-	-	-	3.9	973 ^o

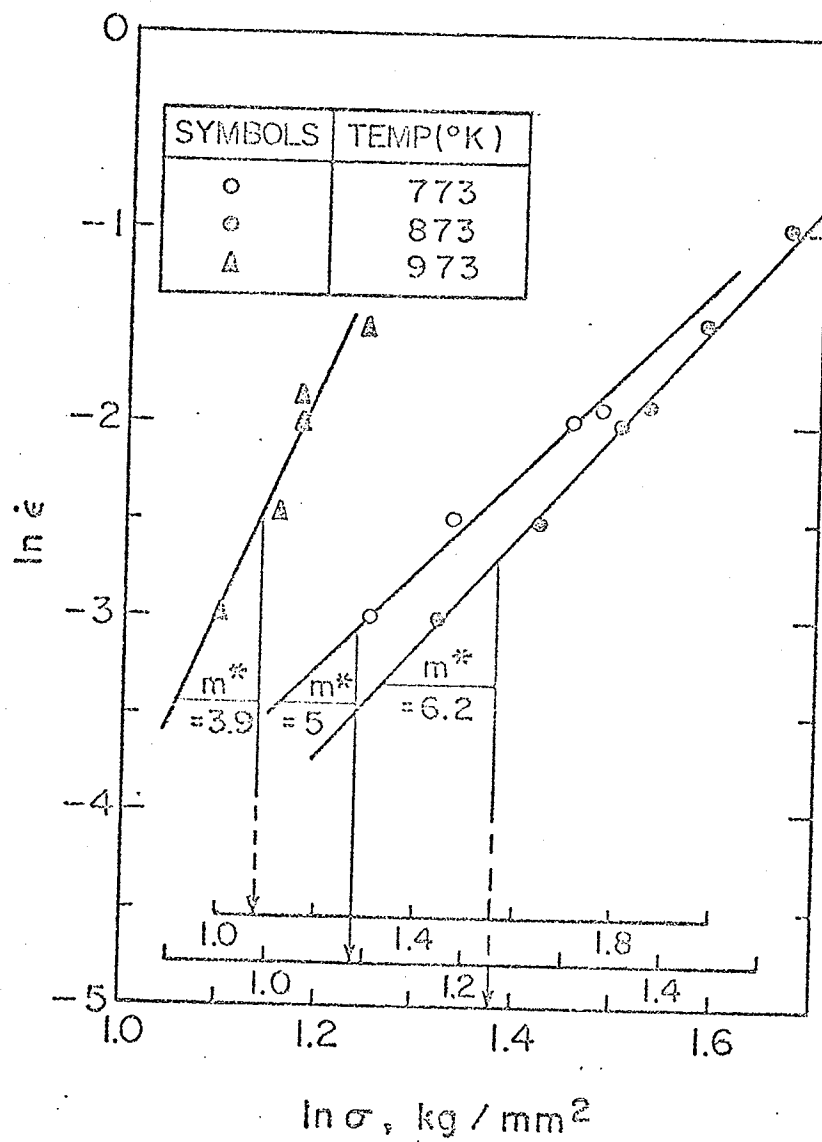


FIGURE 4.13: $\ln \epsilon$ vs. $\ln \sigma$ plots for 773°, 873° and 973°K.

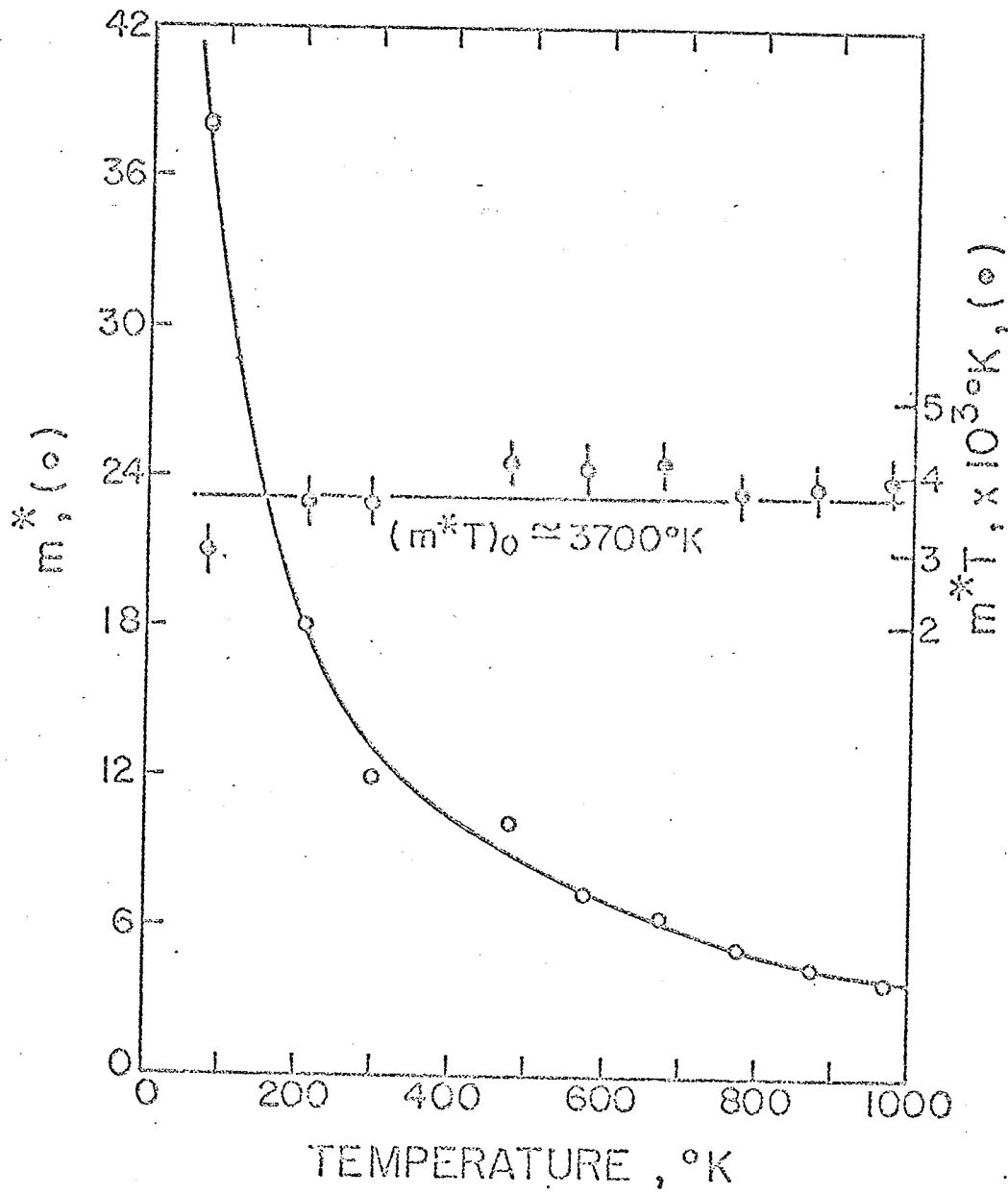


FIGURE 4.14: The temperature dependence of m^* and m^*T .

eqn. (4.6) are plotted as a function of effective stress, σ^* , in fig. 4.15, where V^* values (in units of b^3) have been considered at a plastic strain of 2% for temperatures 473°K and above, since fig. 4.16 shows constant V^* only beyond about 2% strain in this range of temperature. The temperature variation of V^* is shown in fig. 4.17.

4.1.6 The Activation energy

The activation energy for yielding was calculated from the relationship:

$$\Delta H = -kT^2 \left(\frac{\partial \ln \dot{\epsilon}}{\partial \sigma^*} \right)_T \left(\frac{\partial \sigma^*}{\partial T} \right)_\epsilon \quad (4.7)$$

where the variables in eqn. (4.7) are the same as those defined previously.

Assuming that the motion of dislocations is controlled by a single thermally-activated mechanism, the stress-dependent enthalpy (ΔH) of the above equation is related to the total enthalpy (H_0) of the obstacles by:

$$H_0 = \Delta H + \int_0^{\sigma^*} V^* d\sigma^* \quad (4.8)$$

Using eqn. (4.8), the values of H_0 were calculated, in which the integral term was evaluated by graphical integration of the area under the curve of V^* against σ^* in fig. 4.15. Alternatively, H_0 can also

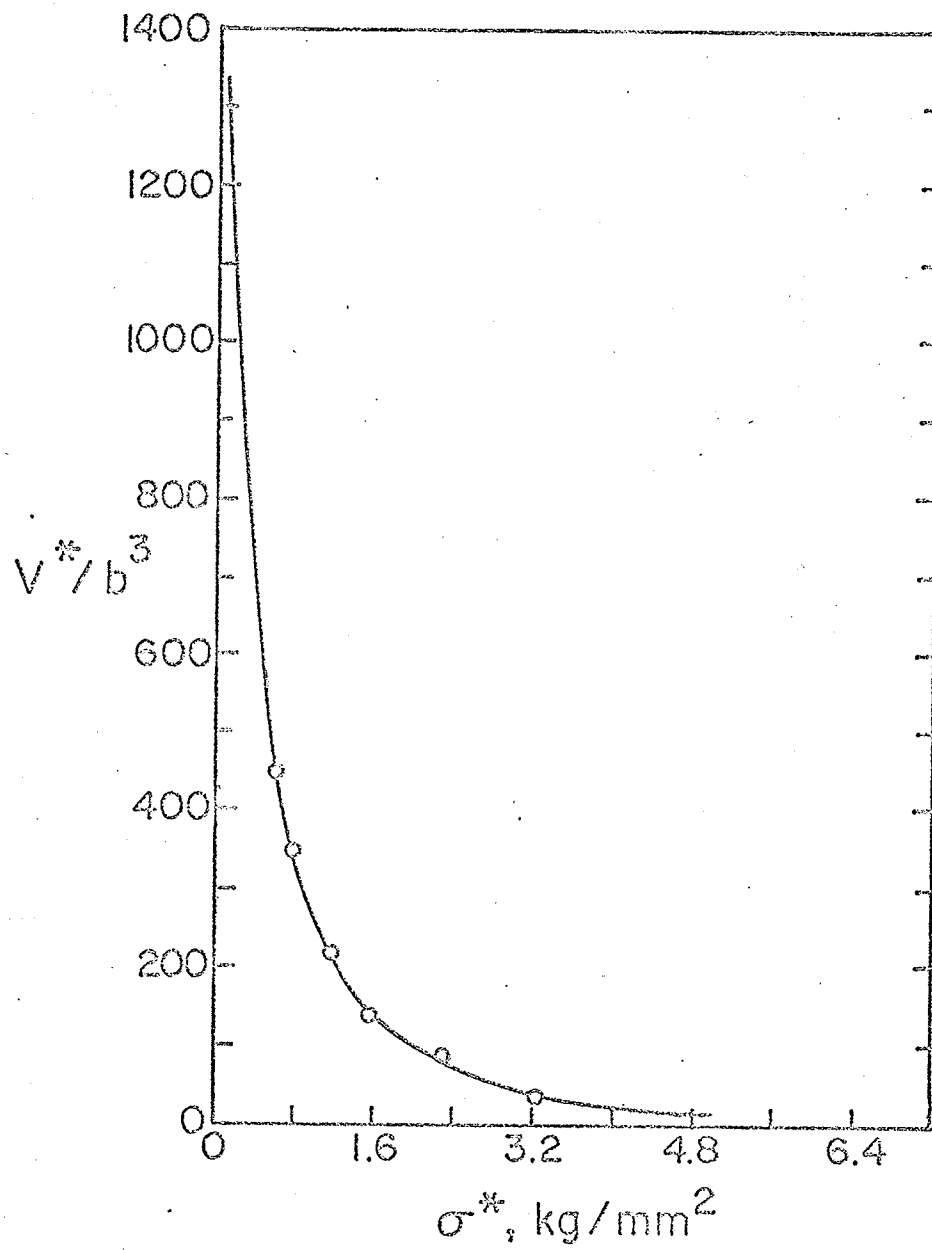


FIGURE 4.15: Plot of activation volume against effective stress.

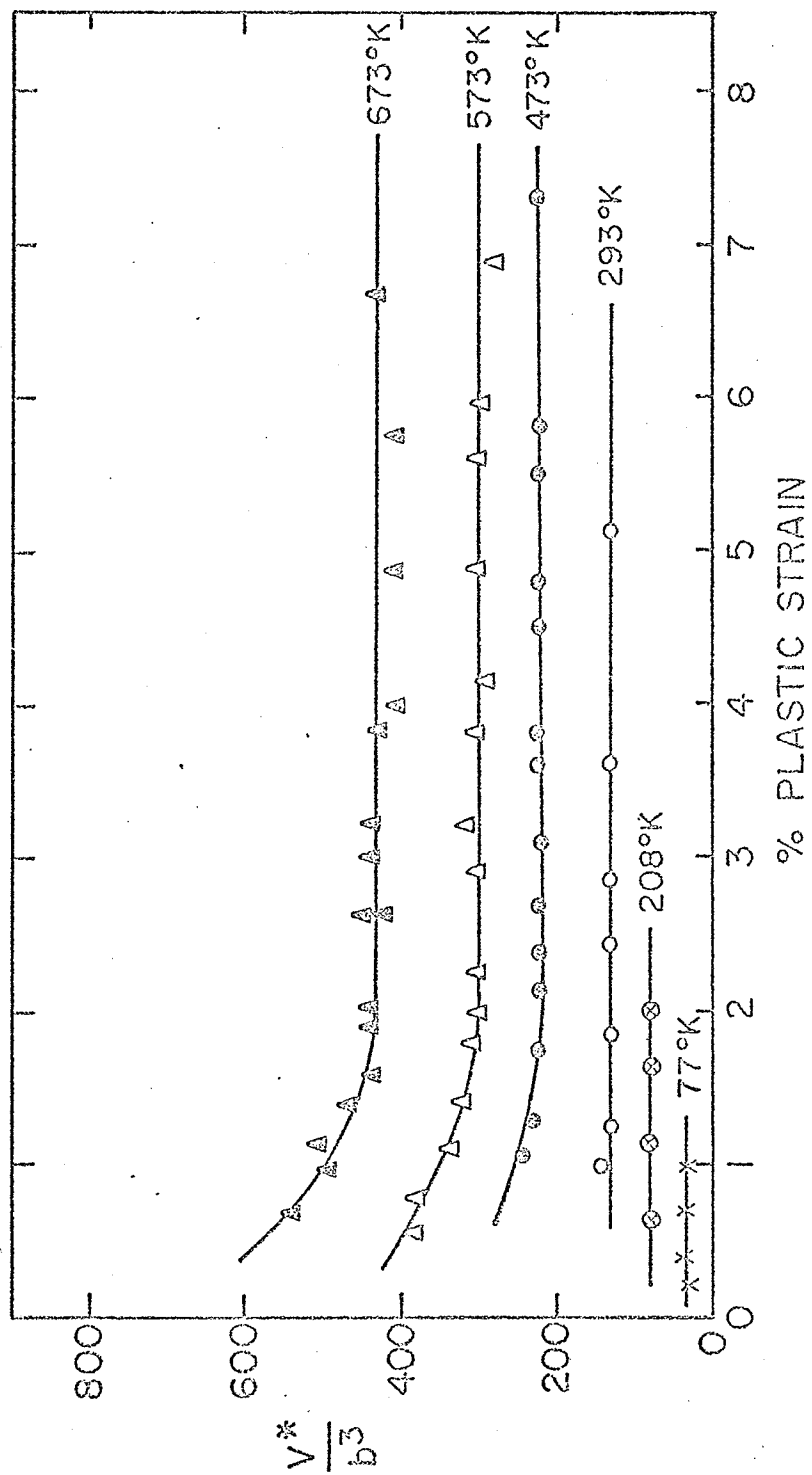


FIGURE 4.16: Activation volume as a function of plastic strain for different temperatures.

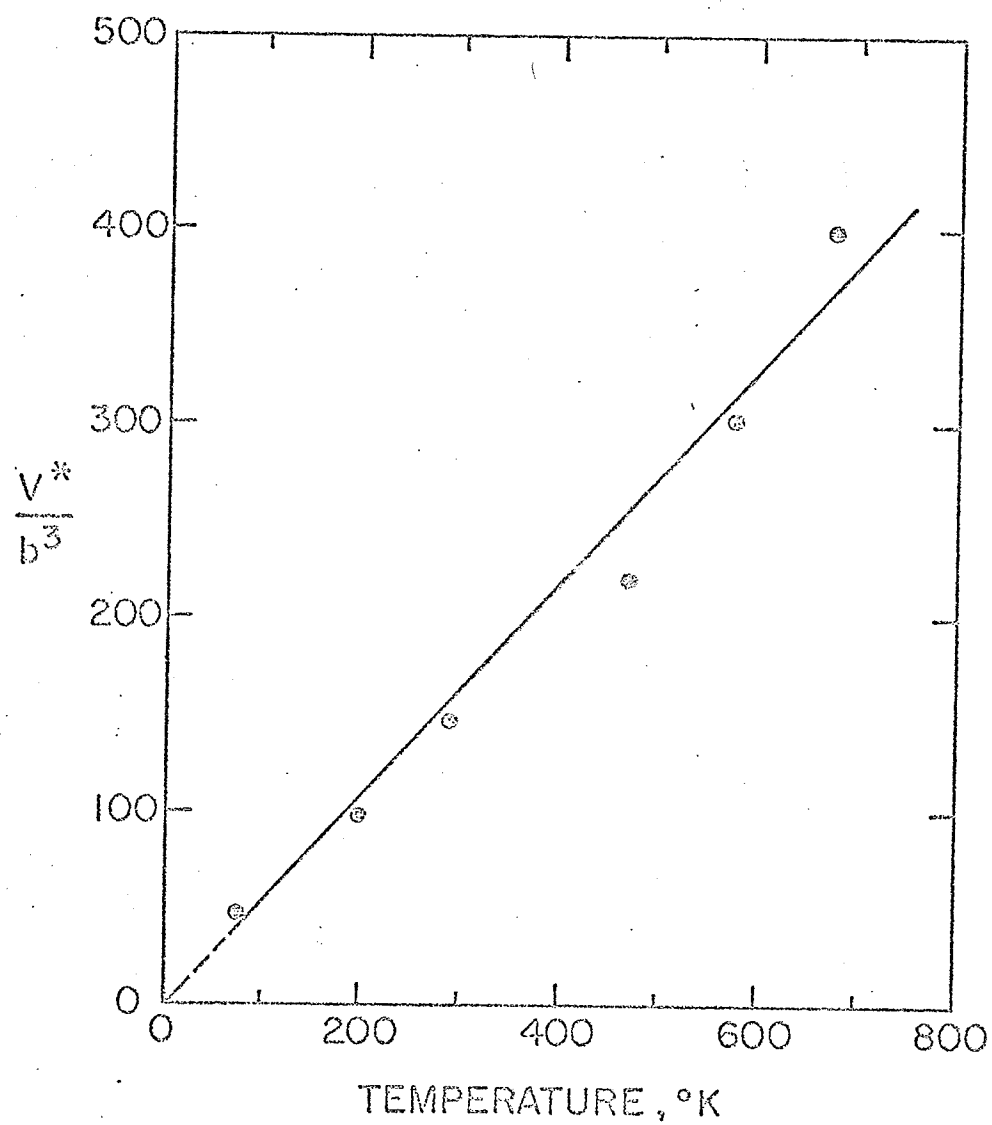


FIGURE 4.17: The variation of activation volume as a function of temperature.

be estimated from a plot of ΔH against σ^* , because ΔH equals H_0 at $\sigma^* = 0$. But this latter method relies greatly on the value of ΔH at low effective stresses which can be more prone to errors due firstly to the general experimental difficulty in obtaining accurate measurements of the small magnitudes of the strain rate sensitivity and temperature dependence of the effective stress from which ΔH in eqn. (4.7) is calculated and secondly because it depends on the manner of extrapolations used. In contrast, although the calculation of H_0 from equation (4.8) also requires an extrapolation of V^* versus σ^* plot to $\sigma^* = 0$ [c.f. fig. (4.15)], the contribution to the total area from the unreliable low effective stress region of the plot is relatively small. The temperature dependence of ΔH and H_0 are shown in fig. 4.18. It is seen that H_0 is temperature independent except for temperatures above 500°K , where there is a general difficulty in obtaining accurate effective stress data and the integration of the $V^* - \sigma^*$ plot becomes increasingly uncertain. Figure 4.18 also shows that the activation enthalpy varies linearly with temperature.

4.1.7 Work hardening in MgO single crystals

The work hardening curves (i.e. resolved shear stress versus resolved shear strain curves) in compression are shown in fig. 4.1. At lower temperatures, below 473°K , the flow stress increases rapidly in a parabolic manner on account of high work hardening. Above this temperature, two-stage hardening begins to appear. The changes in

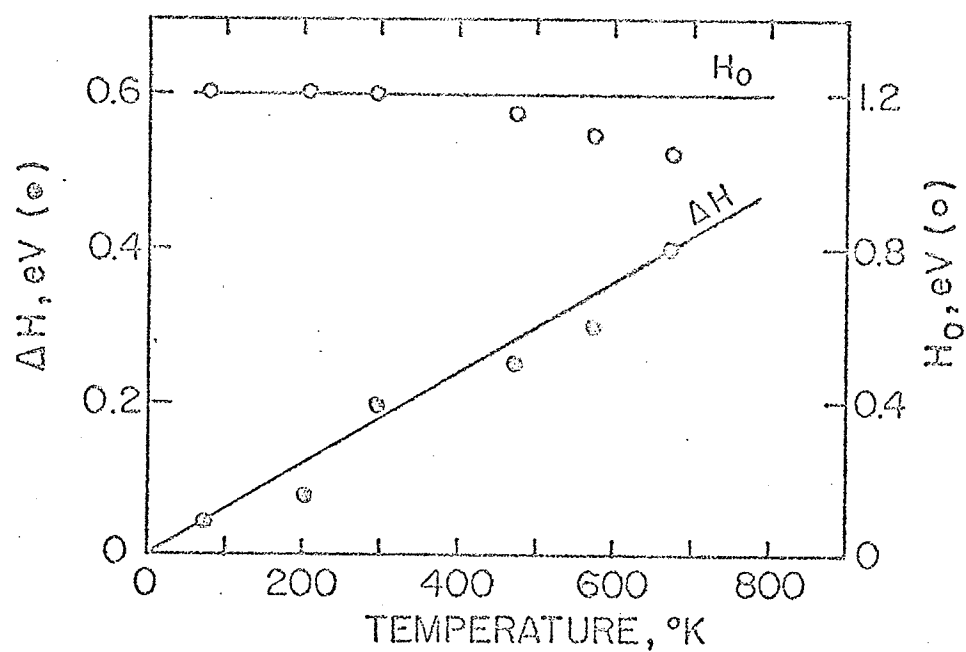


FIGURE 4.18: ΔH and H_0 against testing temperature. The values of H_0 are calculated from eqn. (4.7) and graphical integration of the experimental $V^* - \sigma^*$ curve of fig. 4.15.

the rates of hardening are summarized in fig. 4.19. In this figure, the work hardening rates, θ (slope of shear stress/shear strain curves), normalized with respect to the shear modulus, are plotted for the plastic shear strains of 1%, 2% and 6%.

4.1.8 Etch-pit studies on the dislocation structures of MgO crystals

4.1.8.1 As-annealed structures

A typical 'as-annealed' dislocation structure observed by etch pitting is shown in fig. 4.20. The photograph was taken at low magnification such that a whole face of the specimen could be examined. The dislocation structures of the as-received material and subsequent to the annealing treatment were essentially similar. However, in the case of annealed material a tendency of agglomeration of dislocations were observed in the form of many low dislocation density sub-boundaries. Counting of the etch pits within such sub-boundaries gave a dislocation density on the average of 10^5 to $10^6/\text{cm}^2$. It was ensured by repeated polishing in orthophosphoric acid and etching that there were no substantial change in dislocation density, only the pits became larger and larger.

4.1.8.2 Distribution of slip in deformed specimens

Micro-observations of dislocation bands were made by etch

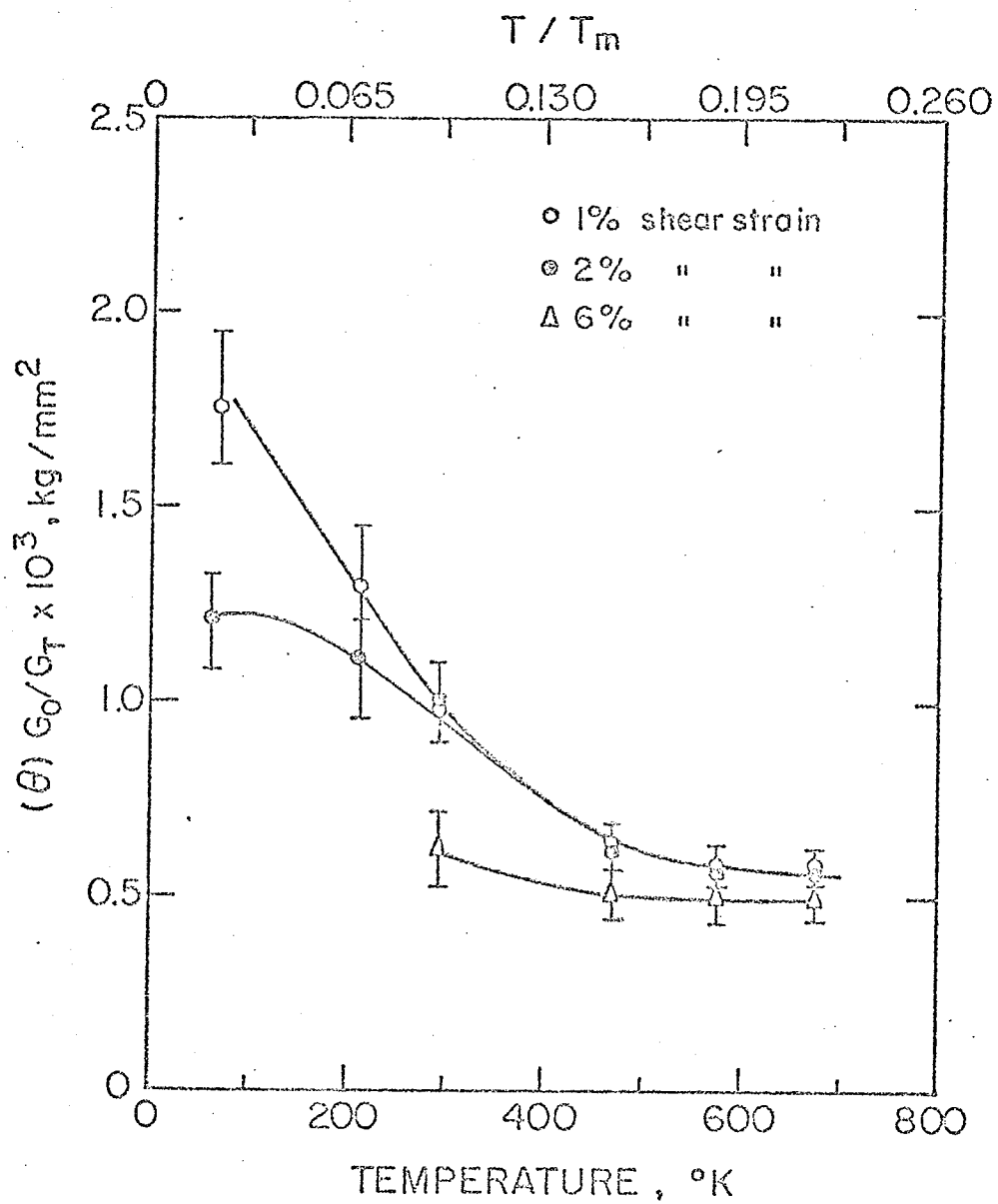


FIGURE 4.19: Work hardening rates ($\partial \sigma / \partial \epsilon$) as a function of temperature plotted for the three plastic strains of 1%, 2% and 6%.

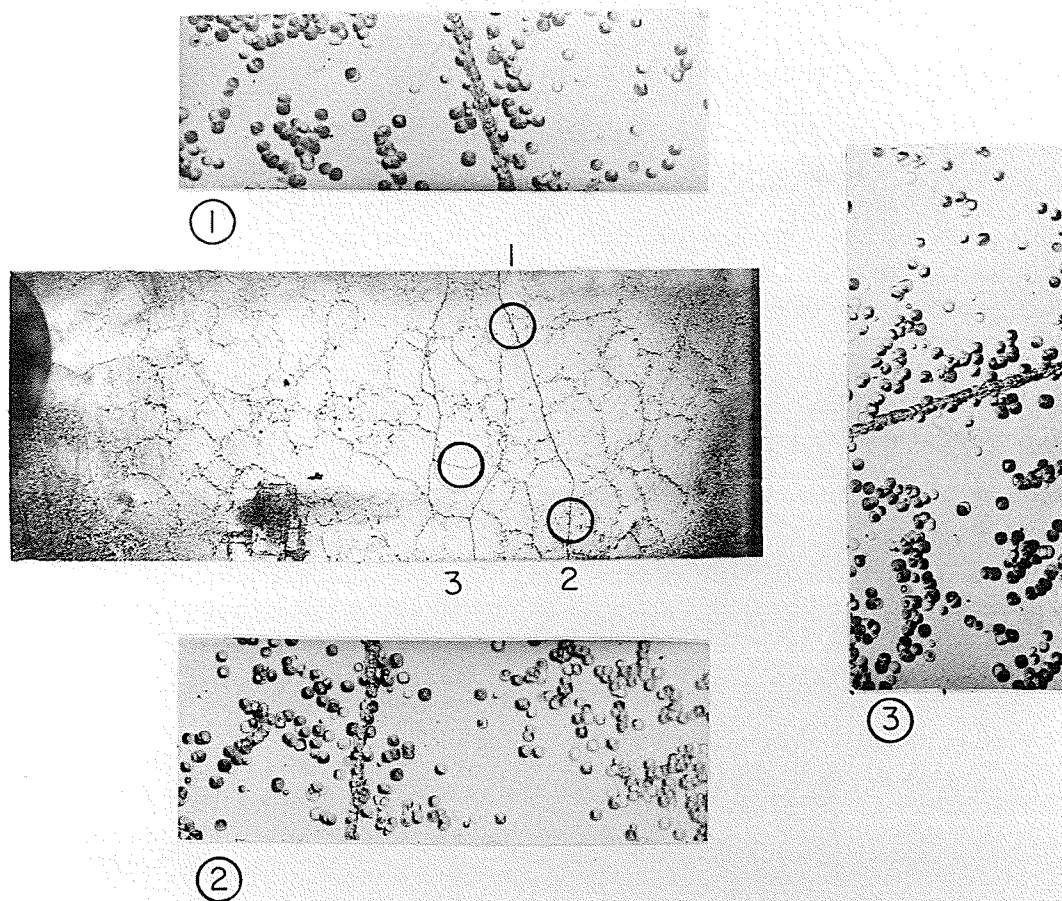


FIGURE 4.20: As-annealed dislocation sub-structure in MgO single crystals.

pitting on polished faces of a number of crystals deformed at various temperatures to increasing amounts of plastic strains. The main observations revealed by these experiments are:

(i) Upto the temperature investigated (i.e. up to 673°K), dislocation source initiation were always found to be from mechanical contacts of samples with the testing platens. When the specimen ends were flat and parallel, edge dislocation bands either on one or two of the $\{110\}$ sets of planes (intersecting orthogonally) which are equally stressed, could be seen operating diagonally to the faces of the crystal; thus confirming the earlier observations that edge dislocations move faster than the screw dislocations in MgO similar to NaCl and LiF. Typical examples are shown in fig. 4.21. In general the first slip bands at and below room temperature appeared at about $\frac{1}{4}$ th of the critical resolved shear stress required to produce macroscopic yielding at these temperatures. The stress values are: 0.80 kg/mm^2 (for one specimen only), 0.60 to 0.74 kg/mm^2 (for two specimens) and 0.25 to 0.35 kg/mm^2 (for two specimens) for the three temperatures of 77° , 208° and 293°K respectively.

(ii) Observations after deformation to the stress levels corresponding to the CRSS between 77° to 473°K revealed that although there was considerable activity of slip on all four equally-stressed $\{110\} \langle 110 \rangle$ slip systems in this temperature range, deformation at 77° and 208°K was mainly accompanied by obliquely-intersecting slip bands. At room temperature, there were almost about equal numbers of

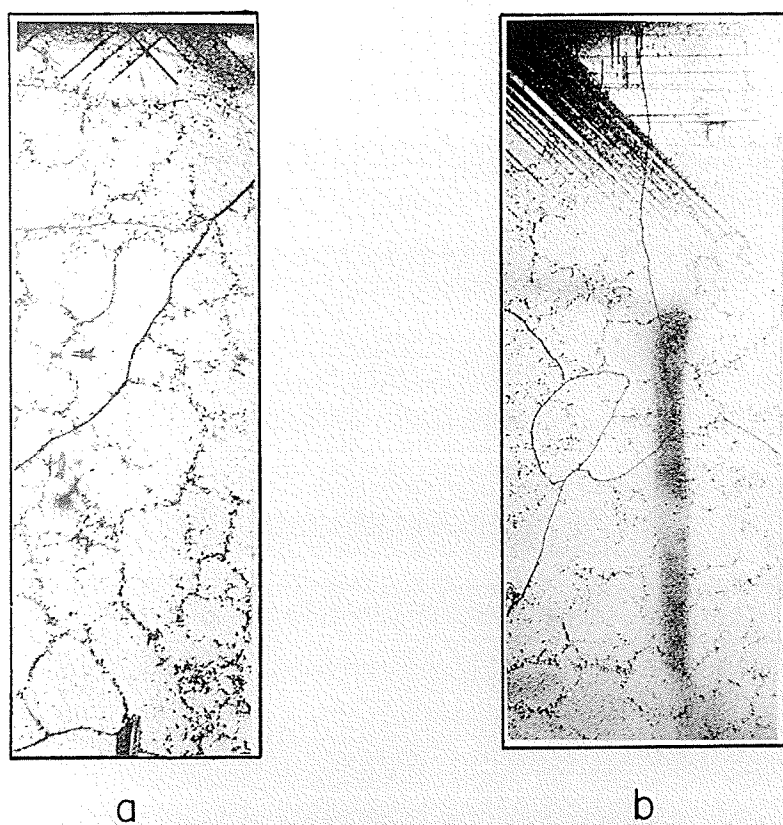


FIGURE 4.21: Examples of slip initiation in MgO single crystals.

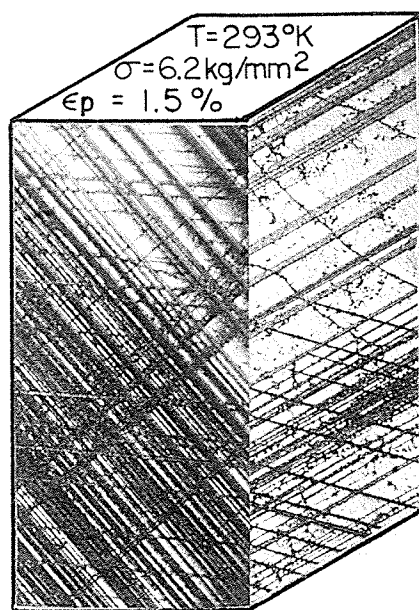
orthogonal and oblique bands. At higher temperatures, plastic deformation was accompanied mainly by the widening of one of the band out of an orthogonal pair.

(iii) The distribution of slip bands below plastic strain of about 1% was extremely inhomogeneous. But as the deformation increased, further propagation and widening of the existing bands took place such that a one-to-one correspondent of the glide bands occurred between the adjoining side faces of the crystal. Figure 4.22 gives some of the typical examples in the form of isometric view of part of the crystal showing the intersecting bands matched from the two adjacent faces as expected from the slip geometry of rock salt structure.

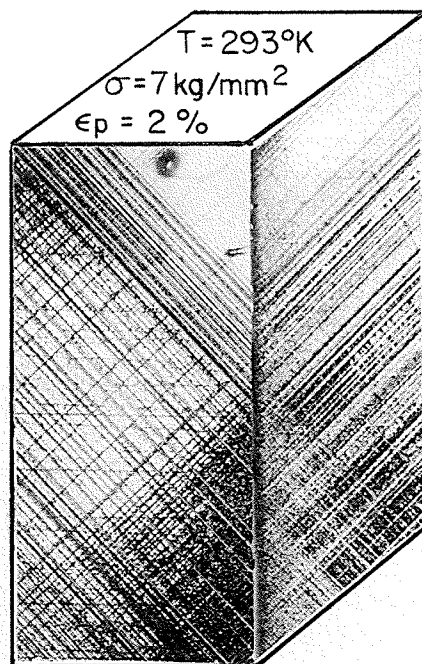
4.2 Tensile Deformation of Polycrystalline MgO

4.2.1 Stress-strain results

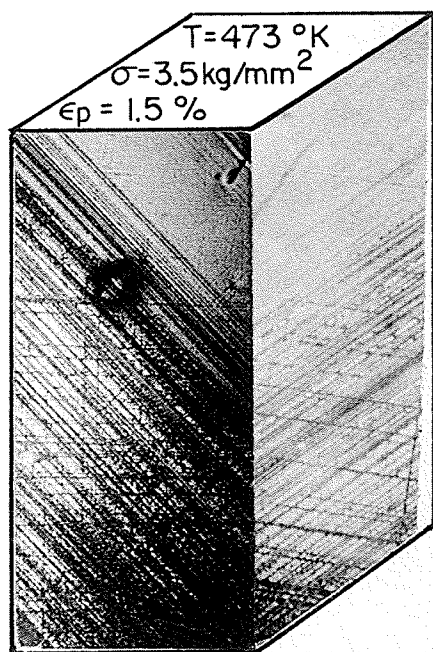
Figure 4.23 is a typical plot of total strain and lattice strain (for (420) reflecting planes) against stress for two grain sizes. Up to a certain value of applied stress the lattice strain is proportional to the applied strain and this is the elastic region of the curve. Beyond this region of proportionality the lattice strain deviates from the total strain and on unloading there is a residual lattice strain (this can be seen by drawing a line parallel to the elastic line from the lattice strain curve to the strain axis). The



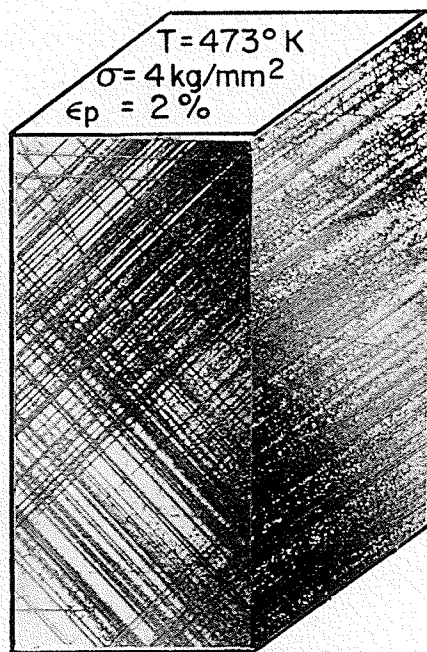
a



b



c



d

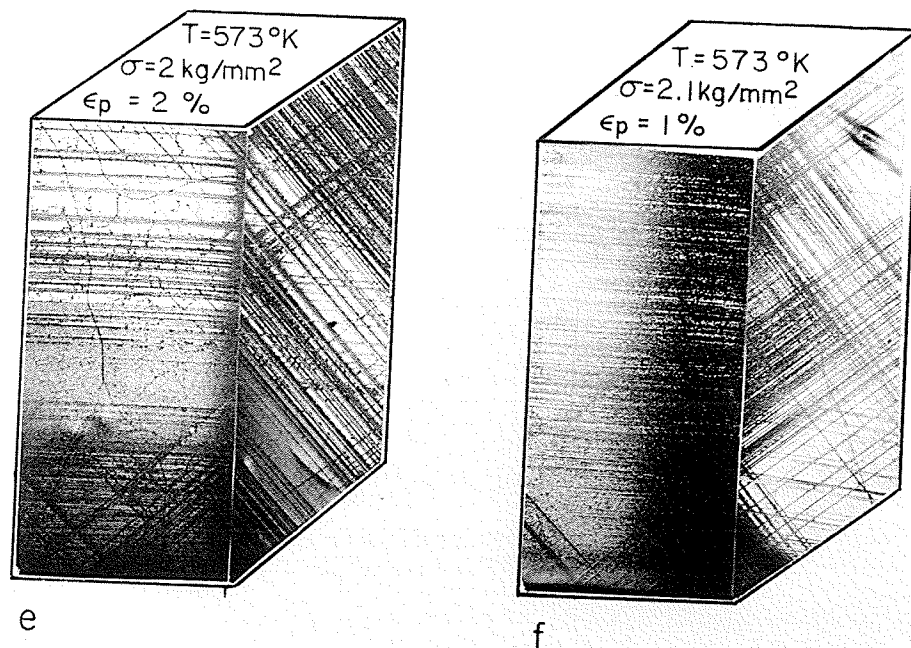


FIGURE 4.22: Reconstructed views of MgO crystals as observed by etch pitting after deforming at different temperatures in low strain regimes, showing sub-boundaries, grown-in dislocation structures and glide bands. Diagonal lines on a $\{100\}$ surface consist of edge dislocations; horizontal $\langle 100 \rangle$ lines consist of screws.

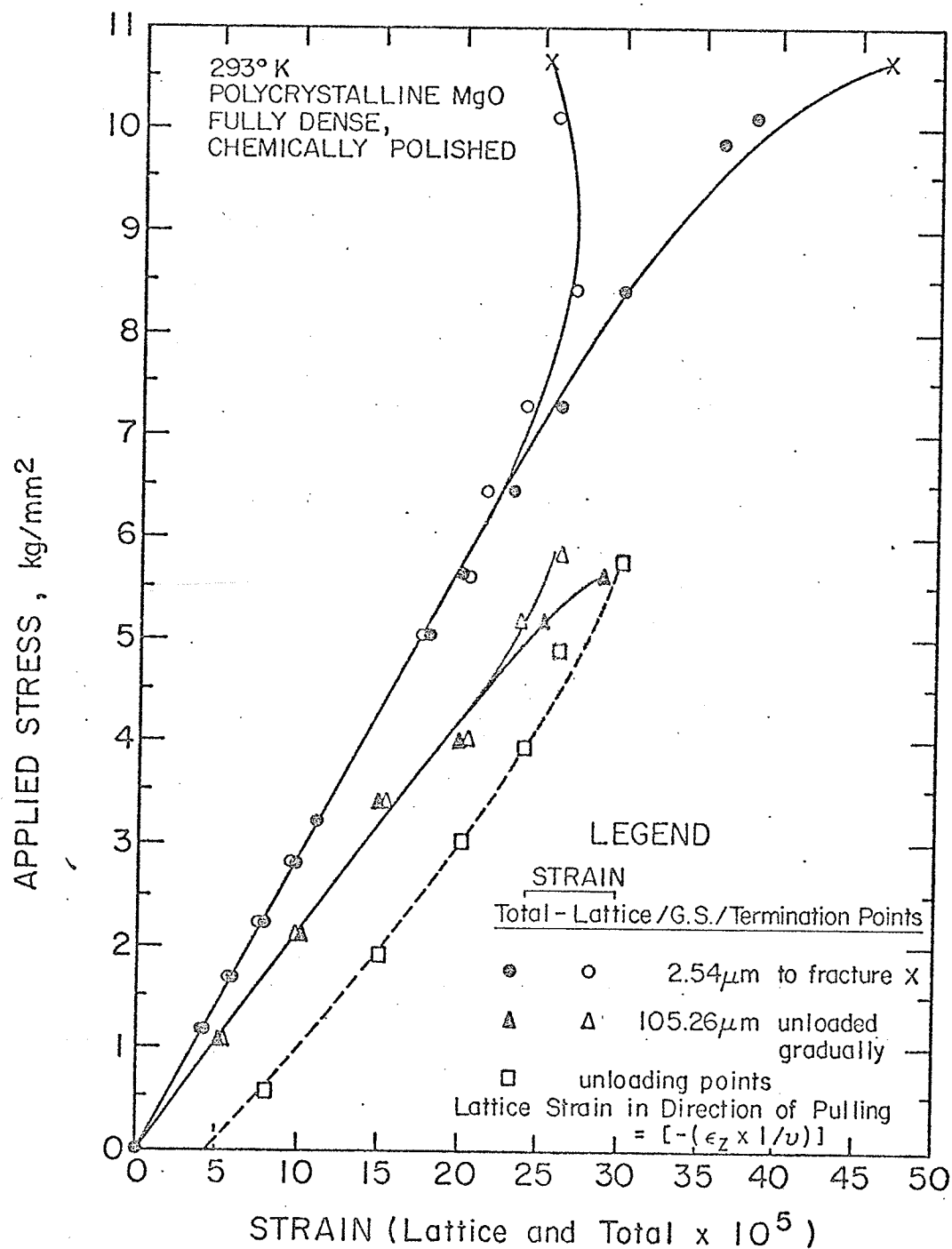


FIGURE 4.23: Applied stress against lattice and total strain.

observance of residual lattice strain is therefore clearly indicative of plastic flow [170,171] in the present experiments. In view of the limits of accuracy with which strain measurements were made, the microyield stress represents the flow stress for about 5×10^{-6} strain. In Table 4.2, the results of microyield stress for different grain sizes are compared with the stress at which lattice and total strain deviate. The curves showing the microplastic behaviour are drawn in a more familiar form in fig. 4.24 where stress is plotted against plastic strain for three grain sizes.

4.2.2 Grain size effect

Figure 4.25 is a plot of the grain size dependence of the stress at which slip activity was first detected by etch pitting, of the microyield stress, of the flow stress at 3×10^{-5} (plastic) strain and of the tensile fracture stress. It is apparent that the microyield, flow and fracture stresses obey a Hall-Petch relationship within the experimental error. However, the intercepts and gradients of the curve differ. The stress at which slip was first detected by etch pitting is relatively independent of grain size over the range of grain sizes where reasonably reproducibility could be obtained. The magnitudes of maximum plastic strain achieved up to the fracture for different grain sizes is shown in fig. 4.26. It should be noted however, that the plastic strain values in fig. 4.26 and in fig. 4.24 include any strain resulting from crack formation

TABLE 4.2: Results of microyield stress measurements on Polycrystalline MgO at room temperature

Grain Size, (μm)	σ_m (mechanical)*, kg/mm^2	σ_m (x-ray)**, kg/mm^2	Definition
2.5	6.5	6.6	* taken at a plastic strain of 5×10^{-6} . ** taken at the point where the (total) stress-strain curves deviate from the lattice strain (c.f. fig. 4.23).
4	6.25	6.32	
10	5.8	5.94	
25	5.55	5.62	
40	5.15	5.26	
43	4.97	5.00	
45	4.80	4.85	
48	4.74	4.79	
62	4.62	4.67	
68	4.55	4.60	
75	4.57	4.66	
90	4.60	4.65	
97	4.65	4.75	
100	4.68	4.75	

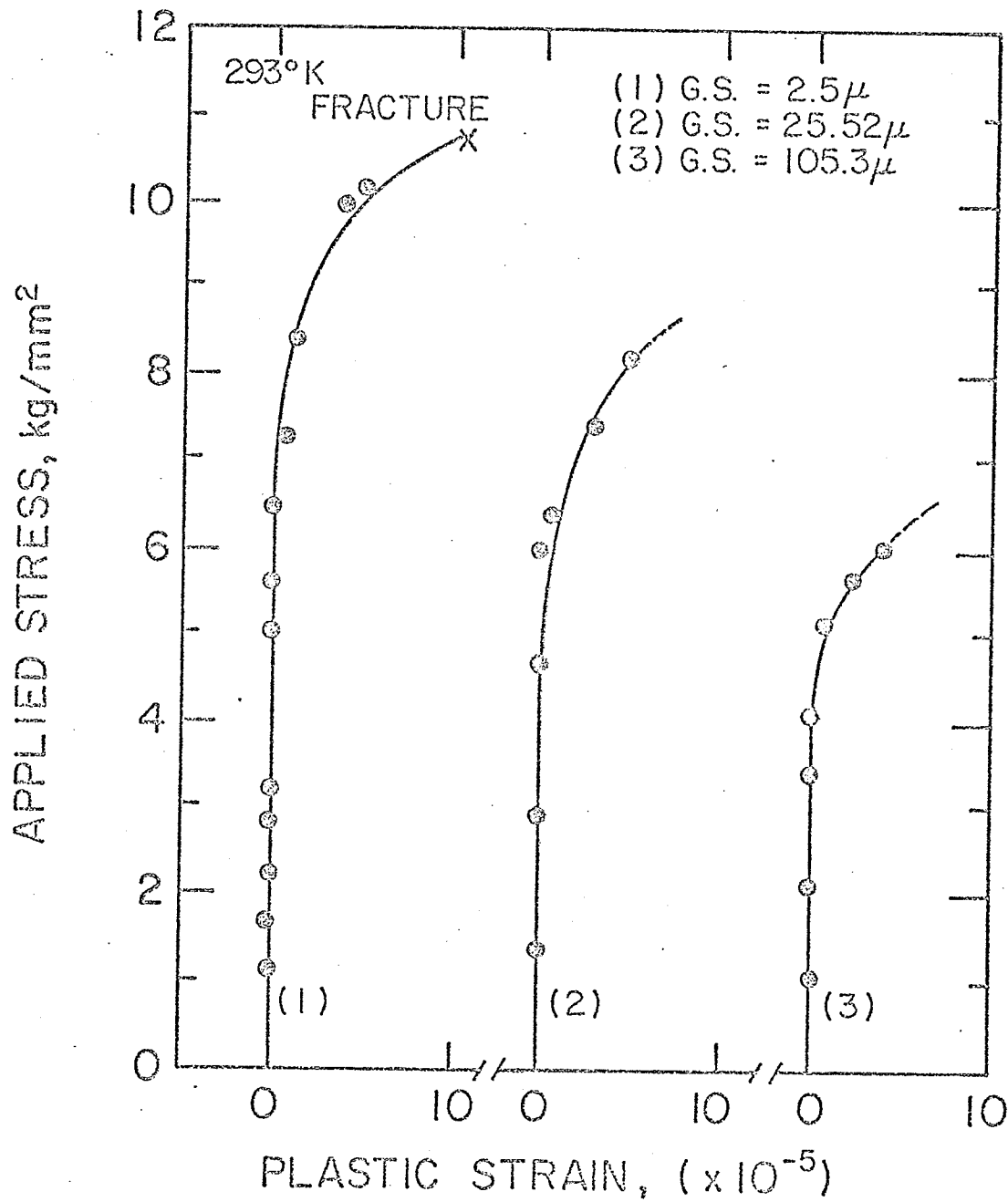


FIGURE 4.24: Stress vs. micro-plastic strain curves for different grain sizes.

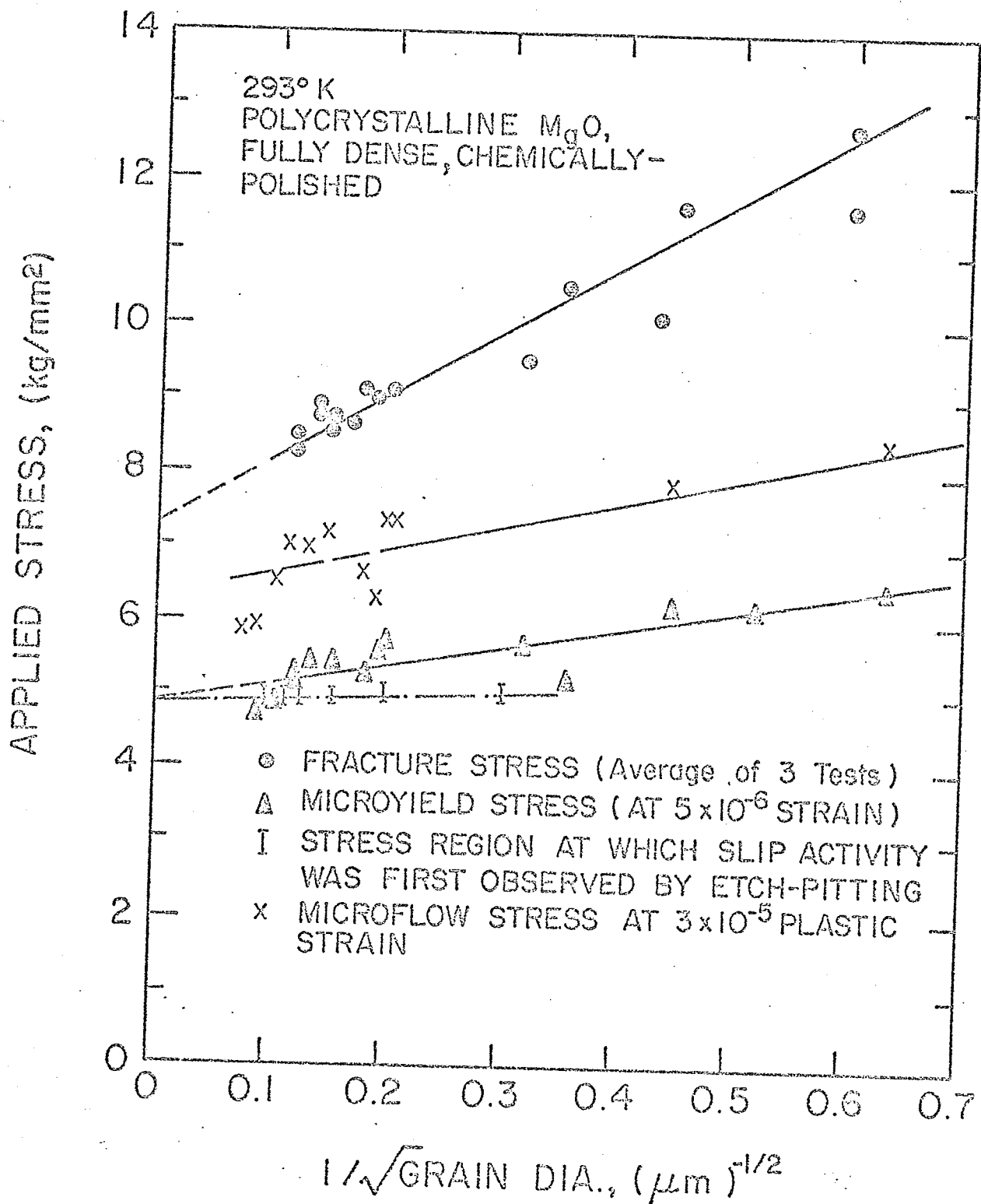


FIGURE 4.25: Stress-grain size plots for the slip initiation stress, σ_d , microyield stress, σ_m , microflow stress at 3×10^{-5} plastic strain and fracture stress, σ_F .

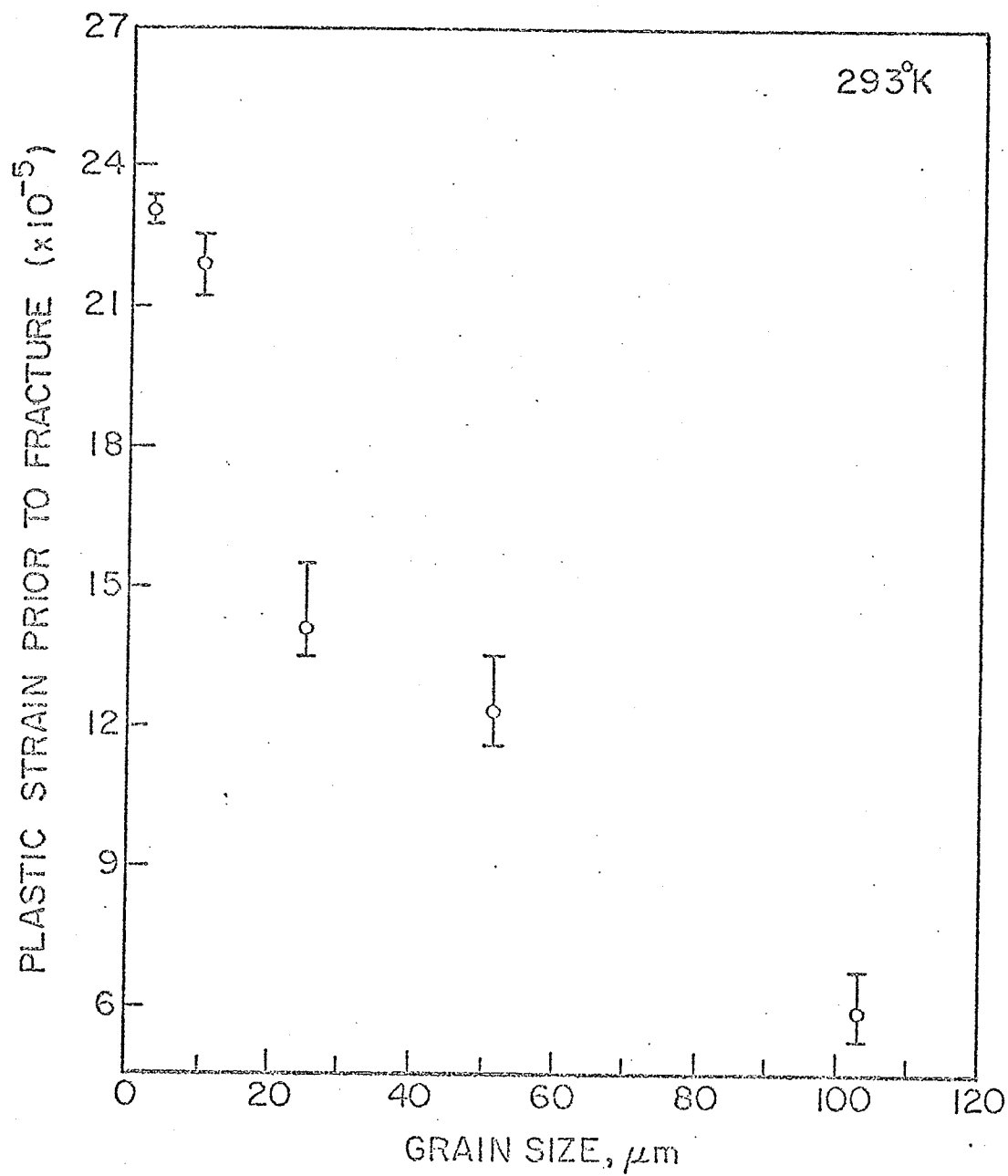


FIGURE 4.26: Maximum plastic strain achieved before fracture for different grain sizes.

as well.

4.2.3 Etch pit studies on polycrystalline MgO

The initial dislocation density (ρ_0) of polycrystalline MgO specimens after heat treating was obtained by etch pit measurements using the formula $\rho = M^2 \times N/A$ where, ρ = pit density (etch pits/cm²) and N = number of pits observed in area A on a photomicrograph taken at magnification M . $AlCl_3$ solution was used as an etchant which produced well-defined square and flat-bottomed pits marking the positions of 'grown-in' dislocations. Examples are shown in the photomicrographs of fig. 4.27. About 20 to 30 grains were measured on each specimen. Figure 4.28 shows that the initial dislocation density is grain size dependent, increasing with decreasing grain size. The results of these measurements are summarized in Table 3.3. It should be noted however, that dislocation etch pitting on MgO is to some extent, orientation dependent. Thus the absolute values of the dislocation densities in fig. 4.28 are likely to be low, while the profile of the curve is not expected to be greatly in error.

Figure 4.29 shows a typical example of the first evidence of slip activity, and it can be seen that this initial slip is closely associated with the grain boundaries, often occurring in regions of stress concentrations such as triple points. Figure 4.30 illustrates another typical situation where slip bands are seen coming out from both grain boundaries across a grain, but there is no matching between

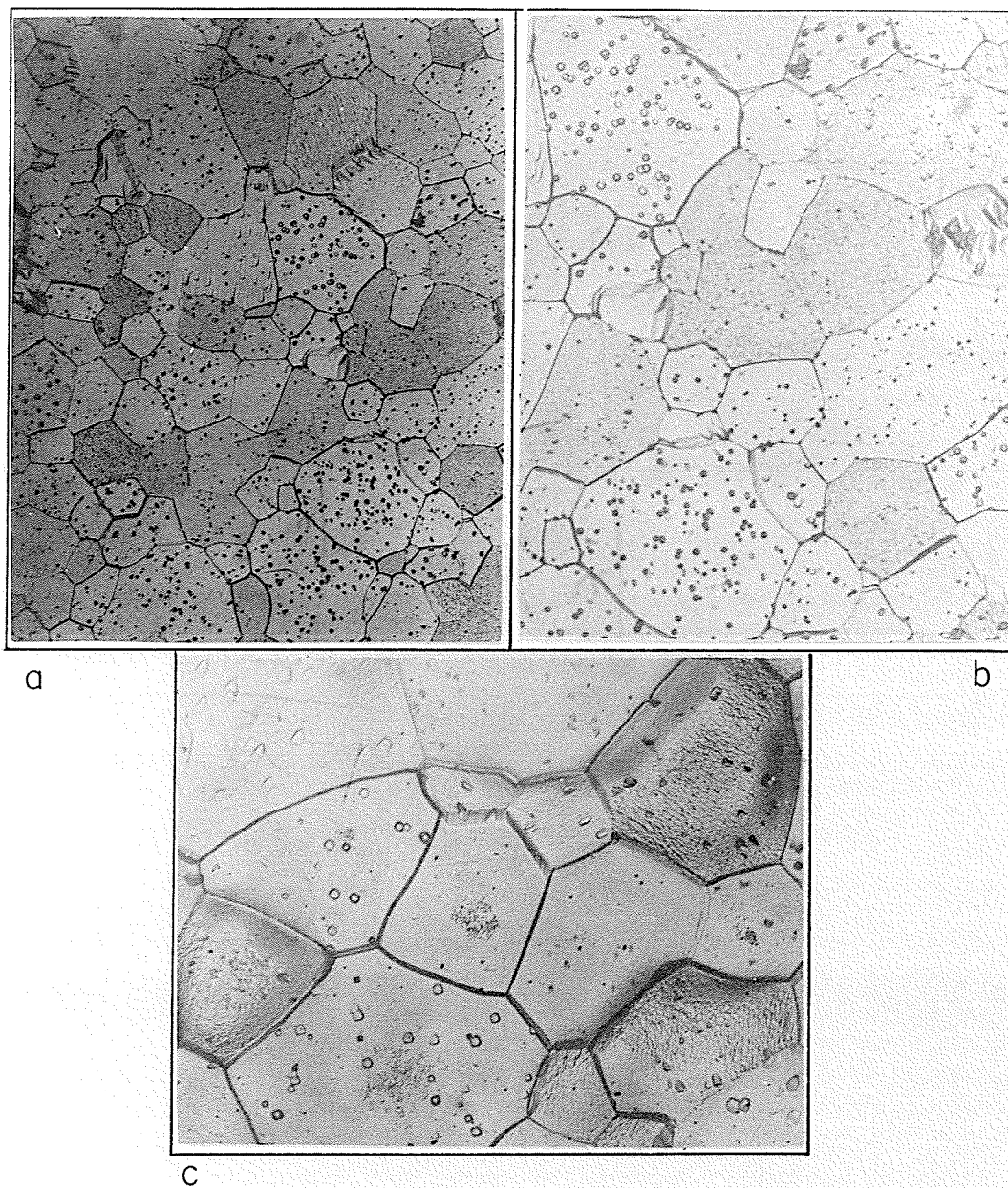


FIGURE 4.27: Typical 'grown-in' dislocation pits in polycrystalline MgO revealed by etching in AlCl₃ solution.

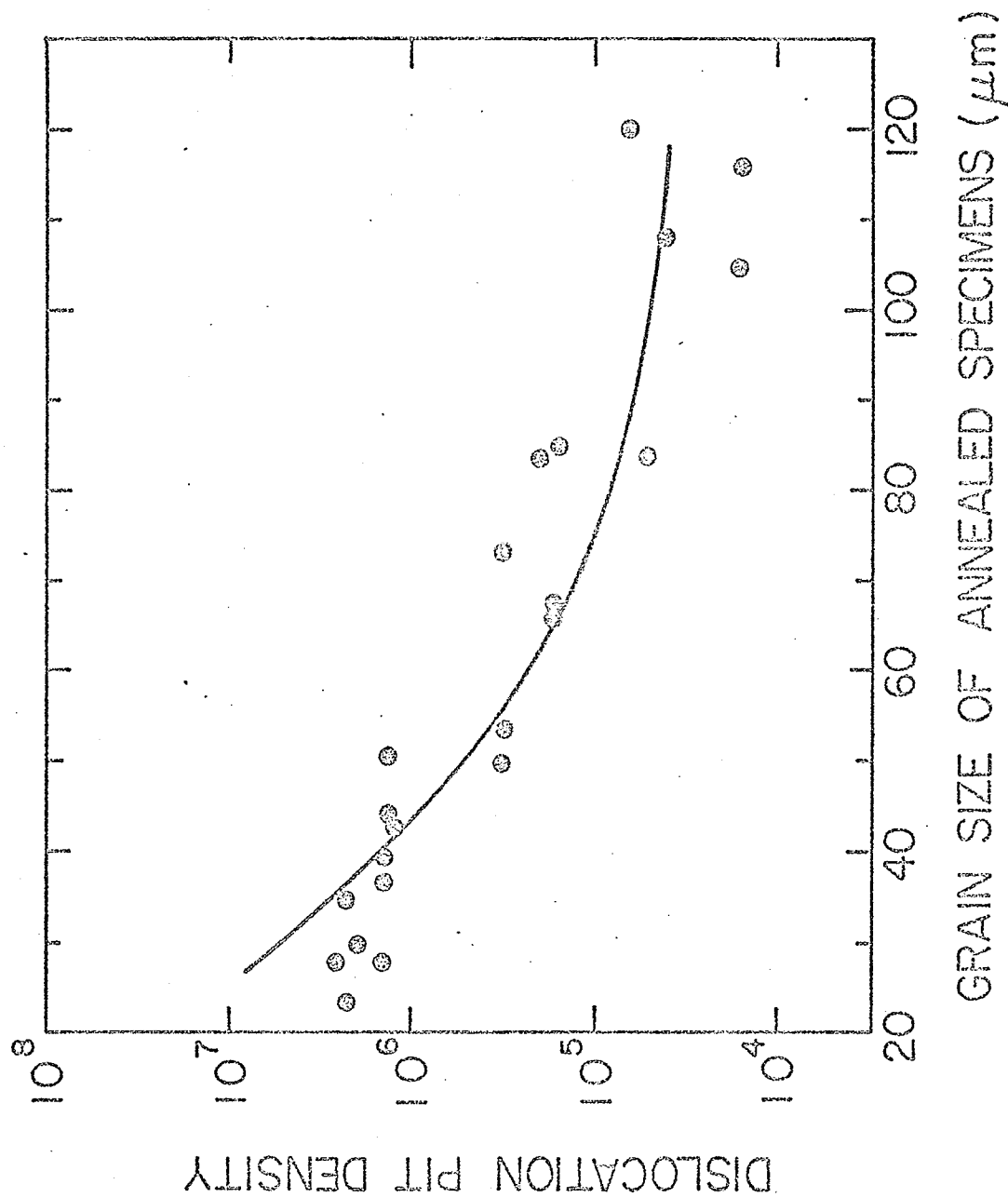


FIGURE 4.28: Graph showing the variation of initial dislocation density with grain size.

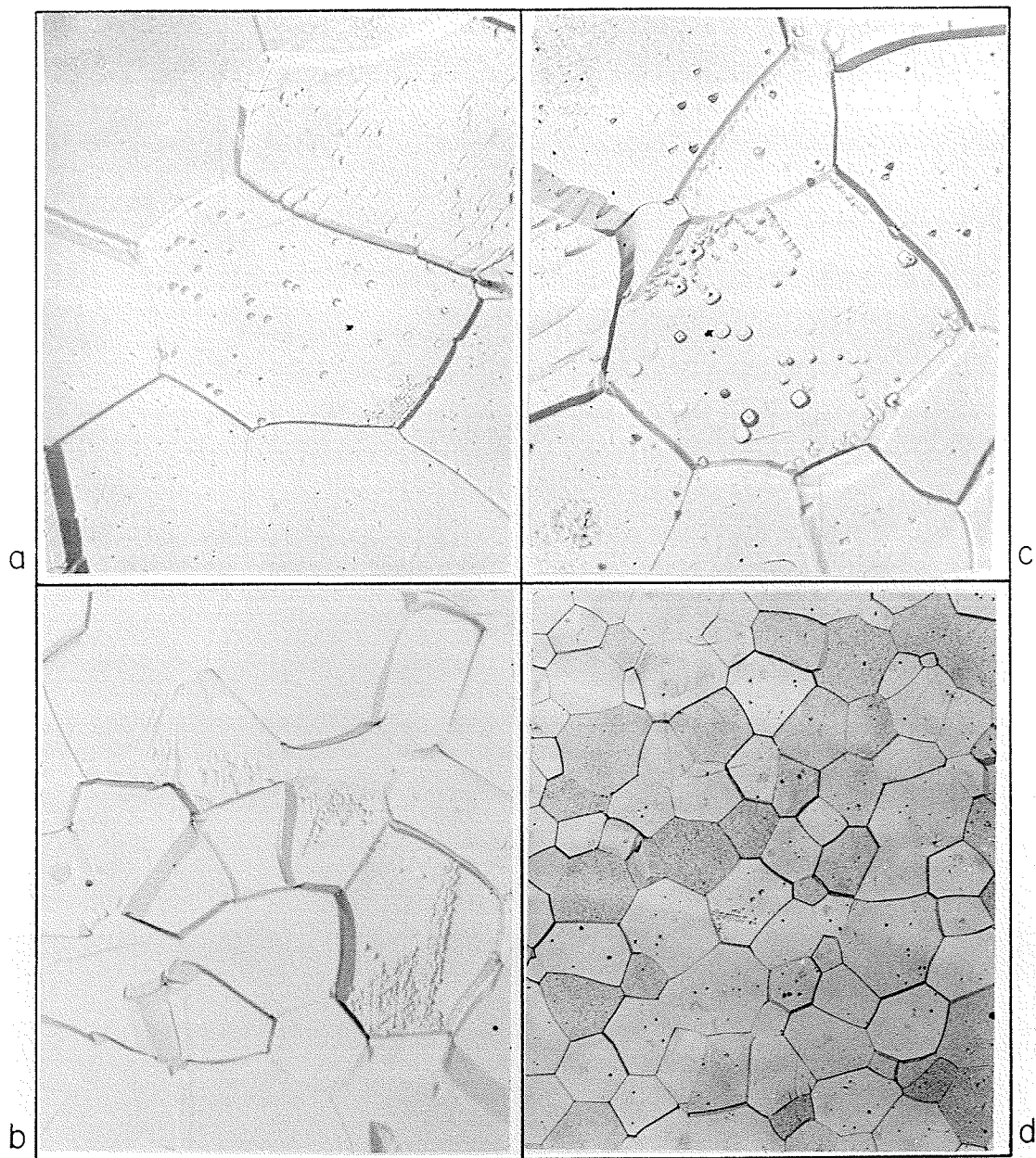


FIGURE 4.29: Examples of first slip initiation from grain boundaries. Note the dislocation activity at grain corners and triple points in (a), (b) and (c).

the bands from the opposite sides. This observation is consistent with the assumption that slip bands are in fact nucleated at the grain boundaries; otherwise, the slip band would have to be matched by slip bands in the grain on the other side of the grain boundary. Besides the grain interfaces, occasionally slip bands were nucleated at inclusions as shown in fig. 4.31.

As the stress is increased the extent of slip activity also increases until at the microyield stress slip has spread across the major portion of the grain diameter (fig. 4.32). With further increase in stress the slip bands broaden and gradually fill the grain interior (fig. 4.33). In specimens deformed to stress levels of ~ 70 to 80% of the fracture stress, localized plastic flow by spawning of secondary dislocation bands from the primary bands were also observed. This spawning phenomena is believed to be due to an increase in localized stress concentrations. Figure 4.34 illustrates some of the typical examples of this. In cases where glide bands of different width intersected each other, kinking of the weaker bands were seen similar to the previous observations on MgO single crystals by Argon and Orowan [19,20]. It may also be mentioned that the grown-in dislocation substructure did not obstruct the growth of glide bands at any stress level. Though grain boundaries were observed to be the main barriers to slip propagation, the incidence of slip breakthrough into neighbouring grains was uncommon.

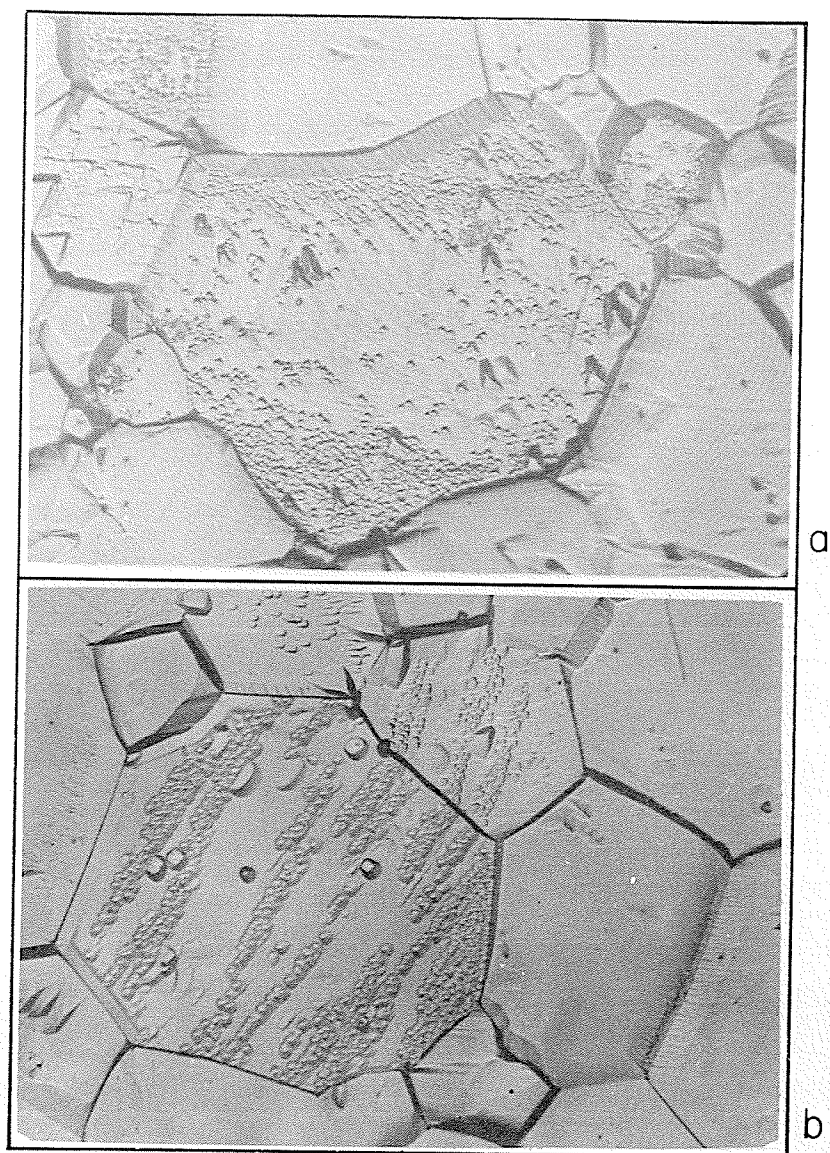


FIGURE 4.30: Slip bands coming out from both grain boundaries across a grain, but there is no matching between the bands from opposite sides.

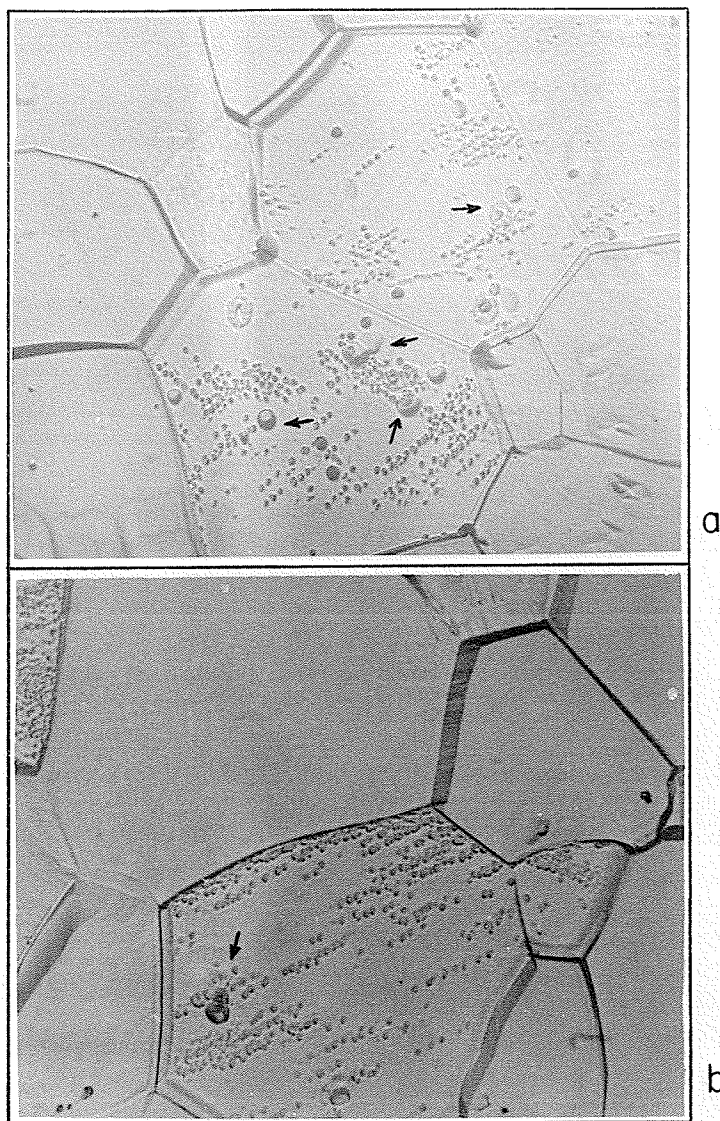


FIGURE 4.31: Slip bands activity about inclusions (indicated by arrows).



FIGURE 4.32: Representative micrographs showing the slip bands traversing the entire grain diameter corresponding to microyield stress levels.

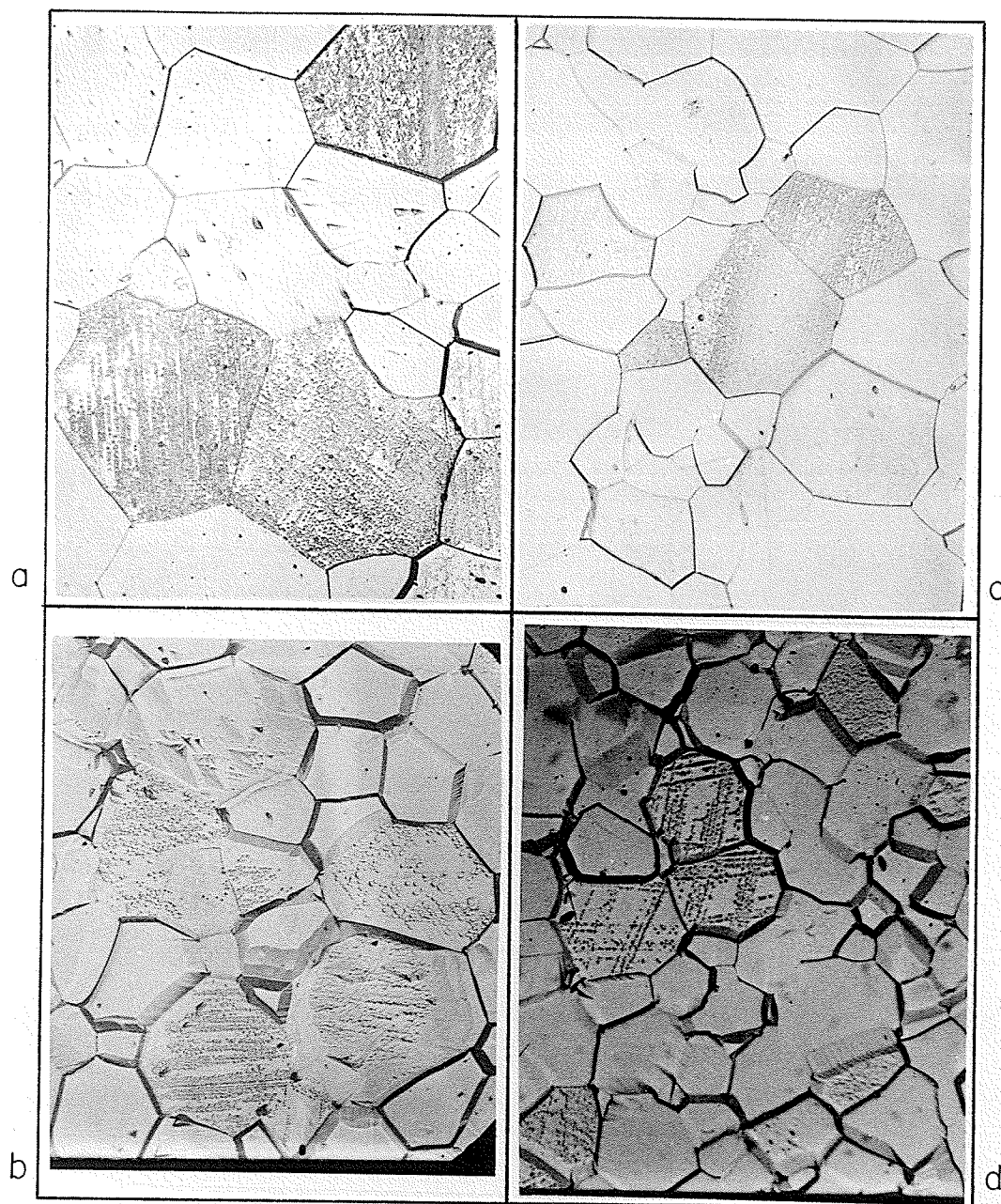


FIGURE 4.33: Micrographs showing slip activity and the widening of bands at stresses approximately 80% of fracture stress.

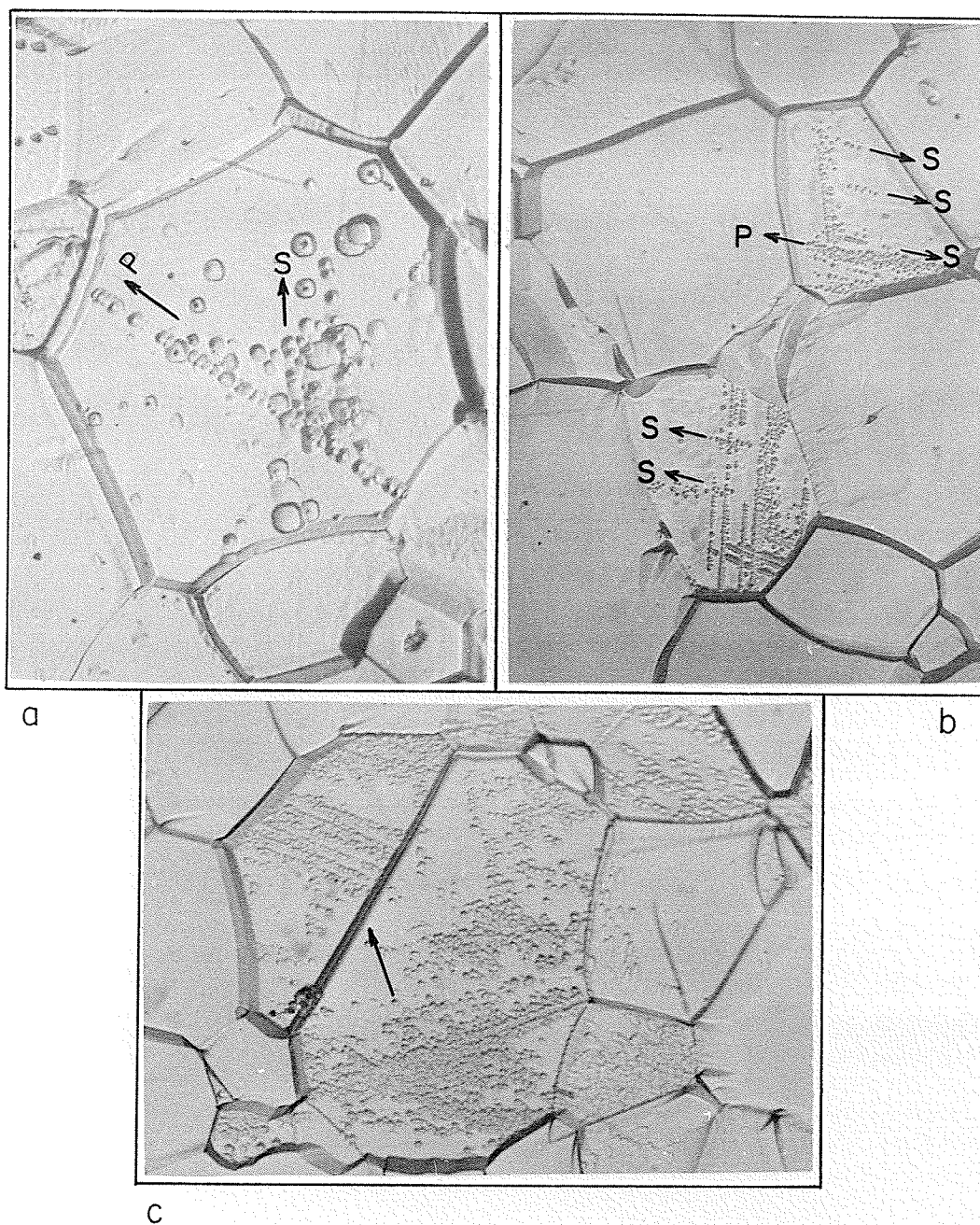


FIGURE 4.34: Spawning of secondary bands (marked s) from the main primary bands (P).

5.0 DISCUSSION

5.1 Dislocation Dynamics and Thermally-activated Deformation of MgO Single Crystals

5.1.1 Considerations of a singly-activated mechanism

Before considering the experimental results on the rate-controlling mechanisms of MgO single crystals, it is important first of all to establish that below a certain limiting critical temperature a single thermally-activated mechanism is operating and that within the framework of its analysis the experimental results satisfy all the criteria under which predictions of a theory of rate-controlling mechanism of plastic deformation are based. With the help of the formalism of the reaction rate theory however, specially with respect to its predictions for stress dependencies on activation enthalpy, it is well known that if a singly-activated mechanism is rate-controlling, the total activation enthalpy, H_0 , should remain constant and independent of effective stress, σ_0^* , or temperature. Figure 4.18 indicates this to be the case for the present work over the temperature range 77° to 673°K . It is seen that H_0 is temperature independent except for temperatures above $\sim 500^\circ\text{K}$, where there is a general difficulty in obtaining accurate effective stress data as pointed out earlier (section 4.1.6). In addition, the value of ΔH given by eqn. (4.7) is strictly valid only when σ^* is large because thermally-activated

motion of dislocations in a direction opposed to the local stress is neglected [79,172]. In view of these, it can be said that the relatively small differences in calculated H_0 values at small σ^* as compared to the data at large σ^* are within the range of experimental error in the temperature range between 500° to 673°K .

Some other observations which seem to further support the operation of a single rate-controlling mechanism is worth mentioning. For instance, if the deformation processes are considered as strain rate and temperature controlled, there is a strict variation of the activation volume and activation energy with temperature to be obeyed. That is, if there is only one deformation mechanism rate-controlling, then the activation energy, ΔH , should be a linear function of temperature and likewise no break or discontinuities should be observed in the activation volume and effective stress plot. Furthermore, the slip band configuration should not change much with temperature within the temperature limits considered.

Thus if the present data is considered, it is seen from plots such as those in figs. 4.15 (V^*/b^3 vs. σ^*) and 4.18 (ΔH vs. T) that a unique relationship exist between the various activation parameters: no discontinuities are observed in the $V^* - \sigma^*$ plot and ΔH varies linearly with temperature. Previous experimental evidence based on etch pit [173] and electron transmission microscopy [27] of deformed MgO single crystals shows that the structure of slip bands does not change significantly upto about 700°K and in a way lend support to the present findings since if the nature of

slip bands were not the same at all temperatures, a temperature sensitivity would be reflected in the above parameters. This then further supports our conclusion that a singly-activated mechanism controls the deformation over the whole range of temperature considered in the present experiments.

The experimental results of fig. 4.8 show that from above 473°K, the effective stress, σ^* , is slightly strain-dependent in the early stages of deformation unlike the observations at larger strains. Similar behaviour has been observed by Gupta and Li [66] in the case of NaCl crystals and it was concluded that a pre-macroyield region exists where a slight structural instability causes the effective stress to be strain-dependent. It is tentatively proposed that the strain dependence of σ^* upto about 1.5% of plastic strain in the present experiments is also because of the inhomogeneous nature of plastic flow in this temperature and strain regime.

5.1.2 Evaluation of the rate-controlling deformation mechanism

The rate-controlling mechanisms can be considered as either structure-sensitive or structure-insensitive. Amongst the structure-sensitive mechanisms most of the phenomena which are believed to influence the structure during the deformation of rock salt type crystals are: (i) cross-slip, (ii) jog-dragging and (iii) forest intersection. The experimental results described indicate that up to 673°K all the activation parameters such as V^* , σ^* and H_0 are

independent of strain. Thus the rate-controlling mechanism is structure-independent, which rules out the above mechanisms. Room temperature work on single crystals of MgO containing 75 p.p.m. of Fe^{+3} by Kumar [114] is also similar to the present results where no change in activation volume was observed with strain up to 6 percent strain.

Sodium chloride and silver chloride have the rock salt structure as does magnesium oxide. In the case of sodium chloride, Haasen and Hesse [174] and Appel and Messerschmidt [175] found that the thermal component increased with strain and suggested that jog-dragging may be rate-controlling, while in the case of pure sodium chloride crystals (containing total impurity content of less than 1 p.p.m.) recent work of Argon and Padawer [40] suggests a forest intersection mechanism similar to that in f.c.c. metals. Evans and Pratt [39] results on NaCl crystals and Lloyd and Tangri's [104] work on polycrystalline AgCl show that the thermal component is constant with strain and that the increase in work hardening is associated with increasing internal stress, which is comparable to the present data on MgO.

The most probable structure-insensitive mechanisms are the Peierls-Nabarro lattice resistance mechanism and the dislocation-impurity atom interactions. In the classical Peierls model, in which the nucleation of double kinks in a sinusoidal potential is considered to be rate-controlling, it has been shown by Dorn and Rajnak [100] that the ratio $U_n/2U_k$ ($\approx T/T_0$) is a unique function of σ^*/σ_0^* , where U_n = activation energy required to nucleate a pair of

kinks which is a function of σ^* , and U_k = energy of a kink. In this analysis, at T_0 , $\sigma^* = 0$ and the energy is $2U_k$, and at absolute zero, where $U_n = 0$, $\sigma^* = \sigma_0^*$. Assuming $U_n/2U_k \sim T/T_0$, its functional dependence on σ^*/σ_0^* is shown by the normalized curve in fig. 5.1 along with the experimental data, taking $\sigma_0^* = 4.5 \text{ kg/mm}^2$ and $T_0 = 1350^\circ\text{K}$ from fig. 4.9. As can be noted from fig. 5.1, to move the experimental curve onto the theoretical curve of Dorn-Rajnak requires that either σ_0^* or T_0 be considerably reduced. The former argues against a high Peierls stress and the latter argues against the Peierls-Nabarro mechanism. It is thus seen that the deformation data does not agree with the predictions of a Peierls mechanism based on the double kink theory.

An important feature of the Peierls mechanism is its small activation volume. It usually ranges from about 10 to $20 b^3$. In contrast the activation volume for solute atom-dislocation intersection might fall in the same range for one concentration of impurities, the Peierls mechanism predicts that the activation volume is independent of the amount and state of dispersion of impurity. In the present experiments it is found that the activation volume is in the range of 45 to $450 b^3$, which is much larger than the $10 - 20 b^3$ expected on the basis of Dorn and Rajnak [100] model. Furthermore, if comparison is made for crystals containing different amounts of impurities, it is seen that the magnitudes of activation volume range from ~ 50 to $10^3 b^3$ [47].

Another important feature of the Peierls mechanism concerns its physical origin based on the nucleation of a pair of kinks. The

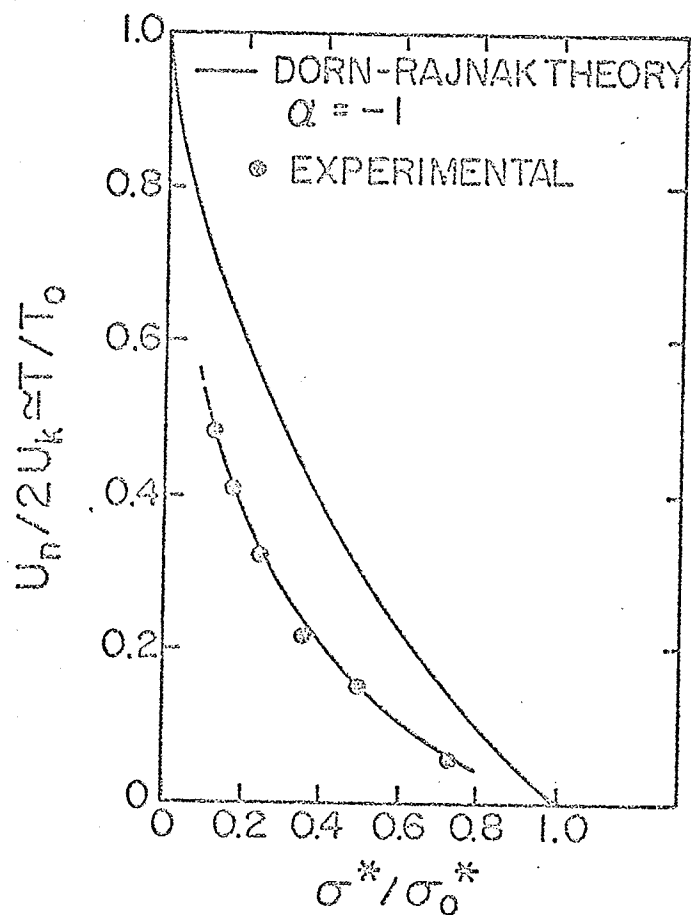


FIGURE 5.1: Thermally-activated components of the flow stress against activation energy in dimensionless units. $H_0 \approx 2U_K$ = activation enthalpy at $\sigma^* = 0$ and σ_0^* = effective stress at 0°K . Experimental plot is the data taken from fig. 4.9.

value of σ^* at 0°K which is expected to represent the Peierls stress should be independent of the impurity content for a Peierls mechanism. However, collected data on MgO crystals from different sources (fig. 5.2) indicate that σ_0^* is proportional to $\sqrt{C}$ (C = concentration of Fe impurity), thus suggesting an impurity mechanism. In addition, if calculations are made for σ_0^* , H_0 or T_0 following the suggestions by Guyot and Dorn [68], it is found that the calculated values do not agree with the actual experimental values. All these results are therefore in disagreement with the double kink theory based on the Peierls mechanism.

Based on the idea of dislocation-solute interactions, several theories have been proposed to explain the yielding and flow behaviour of ionic solids. Eshelby et al. [176] suggested that since the dislocations in ionic solids are charged and surrounded by a vacancy atmosphere of predominantly opposite charge to maintain charge neutrality; the stress required to overcome the electrostatic attraction (i.e. to break away from the charged cloud) may determine the yield stress. While this effect may be rate-controlling in the beginning of yielding it is unlikely to operate at larger strains at low temperatures since it involves segregation of impurities and vacancies around the dislocation. Since there is no observed yield point in the present experiments and σ^* is constant and independent of strain, the above mechanism is not thought to be rate-controlling in the present case.

An alternative approach is that the hardening results from interaction of the dislocations with non-symmetrical distortions.

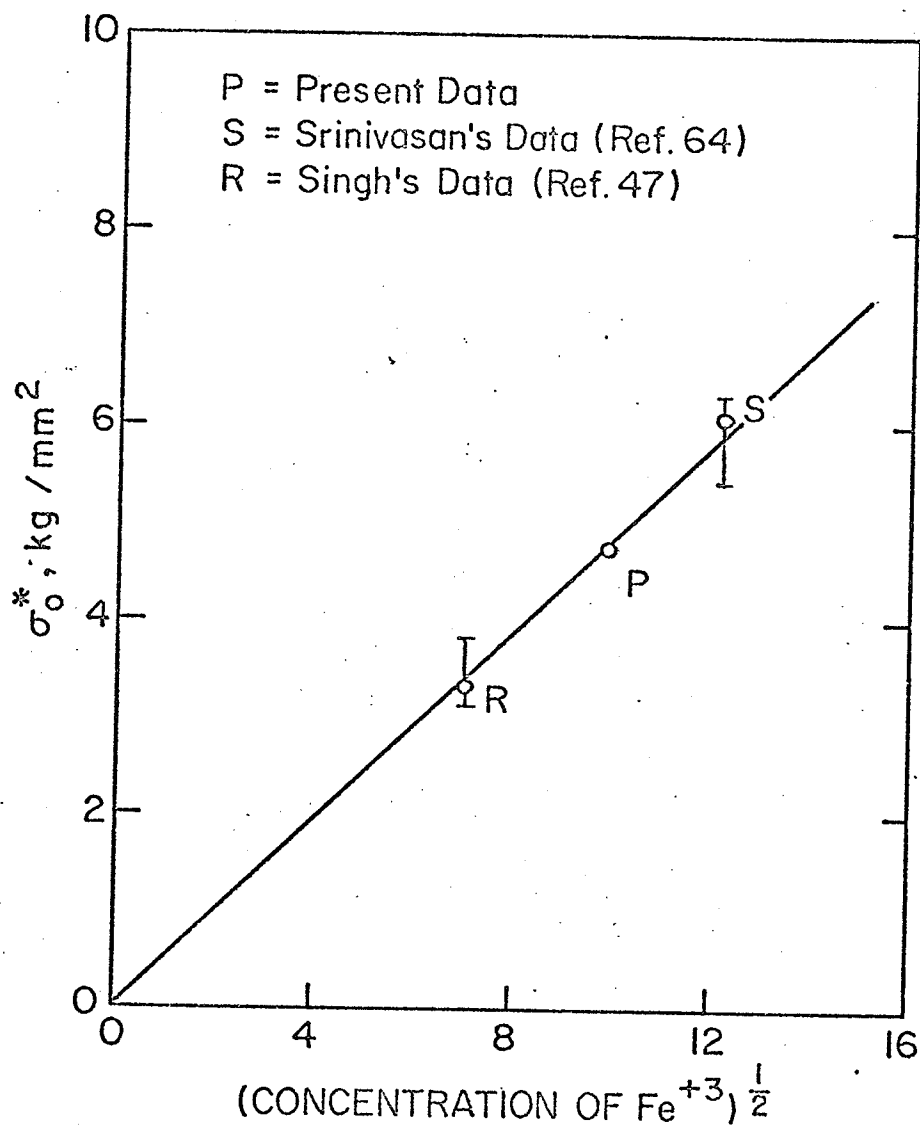


FIGURE 5.2: Plot of σ_0^* against (concentration of Fe^{+3}) $^{1/2}$. Data collected from different sources fit the relation suggested in the Fleischer's model. Error bars represent the author's uncertainty in reading others graphs.

Fleischer [87,95], Pratt et al. [105] and Chang and Graham [106] have all considered the interactions between a dislocation and the impurity-vacancy dipole which occur naturally in impure NaCl type structure. Fleischer's model assumes that a dislocation moving on a slip plane interacts strongly only with defects lying within one atom spacing of the glide plane. The flow stress at absolute zero is then found by maximizing the rate of change of interaction energy with respect to the distance along the slip plane. On the basis of this theory, the following relation was derived for the flow stress in a NaCl type structure hardened by $\langle 110 \rangle$ tetragonal distortion, given in a general form by:

$$\tau_0 = \frac{\mu_0 \sqrt{C}}{A_0} \quad (5.1)$$

where,

τ_0 = flow stress at 0°K ,

μ_0 = shear modulus in $\langle 110 \rangle$ direction at 0°K ,

A_0 = a constant, which can have different values for different materials; calculated to be $= 3.3/\Delta\epsilon$ for LiF [87], in which $\Delta\epsilon$ = difference between longitudinal and transverse strain of the tetragonal distortion, and

C = concentration of tetragonal defects

The relationship between σ^* , V^* and ΔH is given by:

$$(\sigma^*/\sigma_0^*) = [1 - (T/T_0)^{1/2}]^2 \quad (5.2)$$

$$(\Delta H/H_0) = [1 - (\sigma^*/\sigma_0^*)^{1/2}]^2 \quad (5.3)$$

$$\text{and} \quad V^* = H_0/\sigma_0^*[(\sigma^*/\sigma_0^*)^{1/2} - 1] \quad (5.4)$$

where σ^* and σ_0^* are the thermal components of flow stress at temperature T and at 0°K respectively and T_0 is the temperature above which the flow stress becomes athermal. From eqns. (5.2) and (5.3) plots of $(\sigma^*)^{1/2}$ against $(T)^{1/2}$ and $(\sigma^*)^{1/2}$ against $(\Delta H)^{1/2}$ should be linear. Figure 5.3 shows this to be the case for the present results for MgO containing 100 p.p.m. of iron. The intercepts of fig. 5.3 based on the functional relationships of eqns. (5.2) and (5.3) give $\sigma_0^* = 4.84 \text{ kg/mm}^2$, $T_0 = 1370^\circ\text{K}$ and $H_0 = 0.85 \text{ eV}$. Alternatively values of $\sigma_0^* = 4.5 \text{ kg/mm}^2$ and $T_0 = 1350^\circ\text{K}$ are obtained from fig. 4.9 and a value of $H_0 = 1.2 \text{ eV}$ is derived from fig. 4.18. It is seen that the two sets of values (c.f. fig. 5.5) of σ_0^* and T_0 are in good agreement, whereas the agreement between H_0 values is rather poor. This is not unexpected considering the extensive extrapolations involved in deriving H_0 values.

The theoretical slope of the $(\sigma^*)^{1/2}$ versus $(T)^{1/2}$ plot is given by the expression [87]:

$$[\partial (\sigma^*)^{1/2} / \partial (T)^{1/2}] = \frac{\alpha k}{\text{lb}^2} \quad (5.5)$$

where,

$$\alpha = \log[\text{fb}/\sqrt{V}(4C/3)^{1/2}]$$

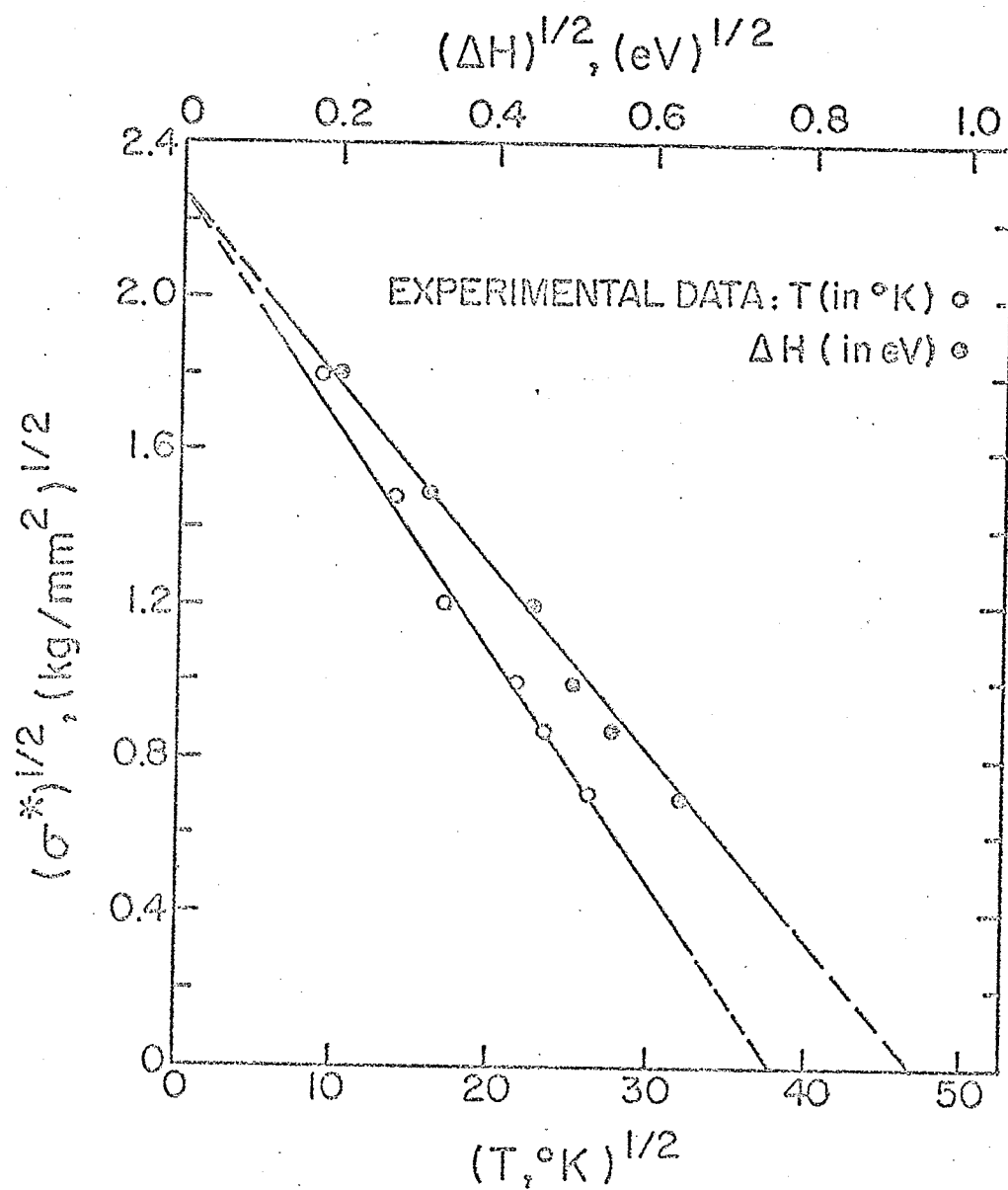


FIGURE 5.3: The relationships between $(\sigma^*)^{1/2}$ versus $(T)^{1/2}$ and $(\sigma^*)^{1/2}$ versus $(\Delta H)^{1/2}$.

with f = vibrational frequency of a dislocation = $v_D \cdot b / \lambda$, v_D = Debye frequency,

$\bar{v}$ = average velocity of dislocations at the yield stress,

C = atomic concentration of defects

b = Burgers vector (= 2.96×10^{-8} cm for MgO),

k = Boltzmann's constant, and

$L = b / (4C/3)^{1/2}$ for $\langle 110 \rangle$ tetragonal defects

Provided that neither μ , C or $\Delta\epsilon$ varies with temperature, the experimental slope of $(\sigma^*)^{1/2}$ versus $(T)^{1/2}$ in fig. 5.3 for 100 p.p.m. of Fe in MgO is calculated to be $0.25 \text{ [kg/mm}^2 \text{ degree]}^{1/2}$ in contrast to $0.17 \text{ [kg/mm}^2 \text{ degree]}^{1/2}$ found from eqn. (5.5) by choosing a value of $f = 10^{10}/\text{sec}$, $\alpha = 14$ and $\bar{v} = 3 \times 10^{-2} \text{ cm/sec}$. These values compare not too unfavourably considering the fact that f and $\bar{v}$ have not been measured directly in the present material and also since the final concentration of iron is assumed to be the same as the initial amount prior to heat treatment.

Fleischer's analysis also makes a quantitative prediction of the value for the atomic defect concentration, C , which is related to σ_0^* by the equation [87]:

$$\sigma_0^* = \frac{\mu \Delta\epsilon (C)^{1/2}}{3.3} \quad (5.6)$$

Although an exact value for the tetragonal strain associated with the

defect pairs in MgO is not available, a value of ~ 0.44 similar to that for LiF (containing divalent Mg^{+2} as the main impurity [87]) will not be in great error. Taking $\mu_0 = 13.25 \times 10^3 \text{ kg/mm}^2$ (fig. 4.3), σ_0^* (experimental) = 4.5 kg/mm^2 , the calculated defect concentration from eqn. (5.6) is only 8 p.p.m. which is far less than the actual amount of impurity present in the material. The theory thus gives an inconsistent result for the defect concentration. As pointed out by others, [110,177,178] Fleischer's calculation [179] indicates that the parameter A_0 in eqn. (5.1) will vary from about 100 for divancancies or substitutional impurities to 3 to 10 or more for defects producing large assymetrical strain such as impurity-vacancy dipole or interstitials. With Fe-doped (150 p.p.m.) MgO, Davidge's [110] result show $A_0 \approx 35$ which is close to a value of 29 for the present work on MgO having about 100 p.p.m. of Fe as the main impurity.

Another important correlation that further help eliminate the Peierls mechanism should be briefly mentioned at this stage. Curves for relationships, namely V^*/b^3 versus $[(\sigma^*/\sigma_0^*)^{1/2} - 1]$ and ΔH versus $[1 - (\sigma^*/\sigma_0^*)^{1/2}]^2$ which allow [179] differentiation between a lattice hardening and the impurity mechanism are included in figs. 5.4 and 5.6. A linear relationship found can be taken as further proof for the applicability of impurity mechanism as suggested by Fleischer [179]. In a recent work on MgO crystals containing 75 p.p.m. of Fe^{+3} as the main impurity, Kumar [114] has similarly concluded that the rate-controlling mechanism is in agreement with Fleischer's model, where for another instance, it was shown that the magnitude of activation volume

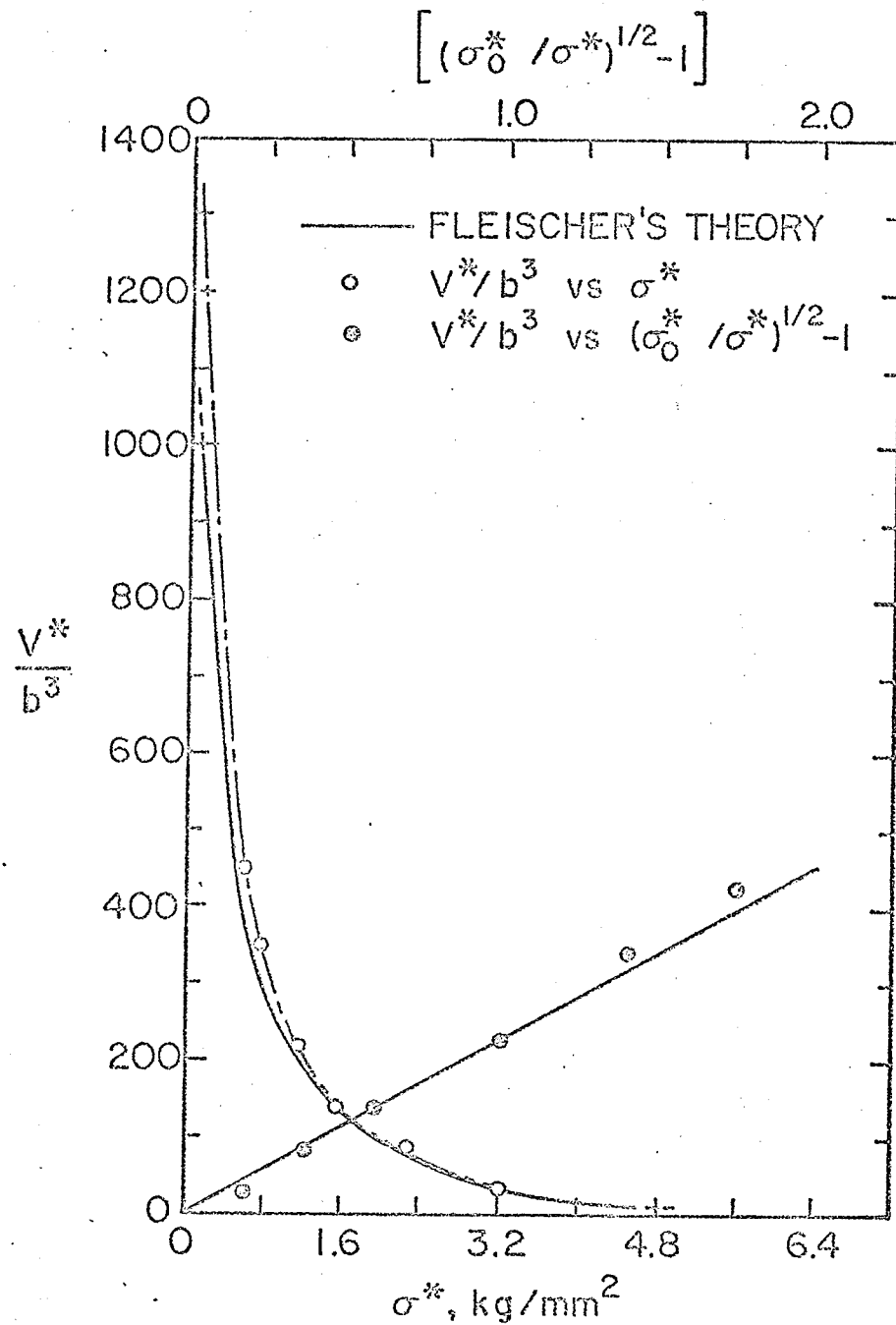


FIGURE 5.4: The stress (effective) dependence of the activation volume for slip in MgO crystals. The solid curves represent eqn. (5.4). The straight line plot is shown as a test of the impurity hardening mechanism according to Fleischer [179].

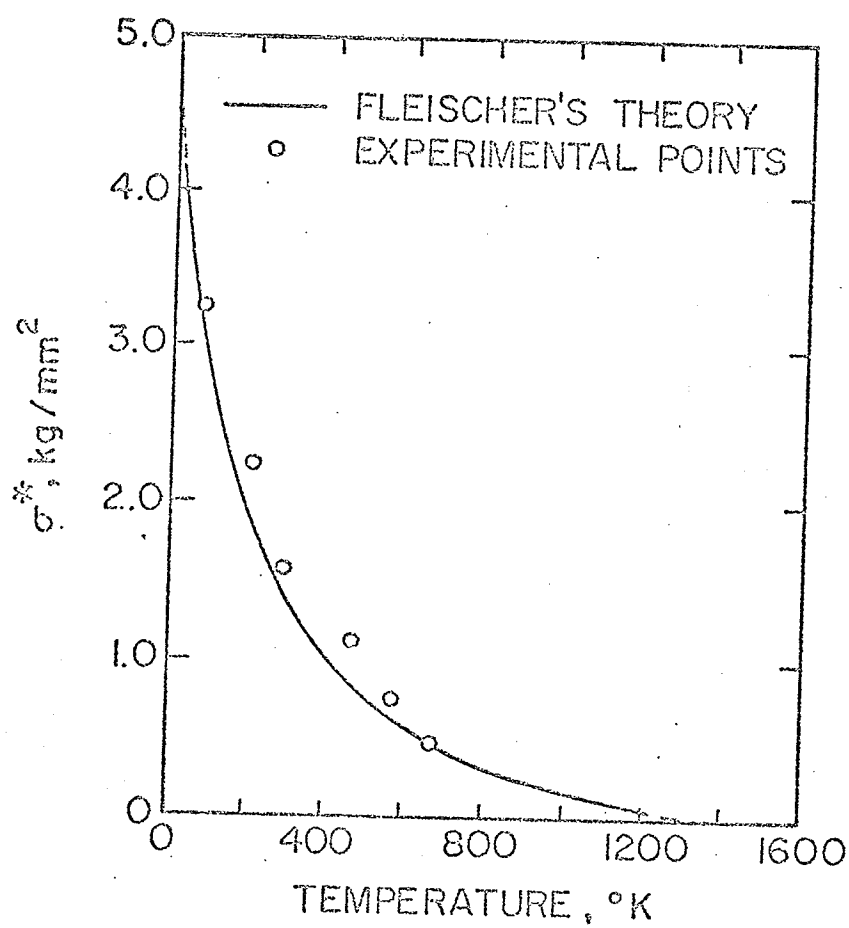


FIGURE 5.5: The experimental σ^* values plotted against temperature and compared with Fleischer's theoretical curve (solid curve) representing eqn. (5.2).

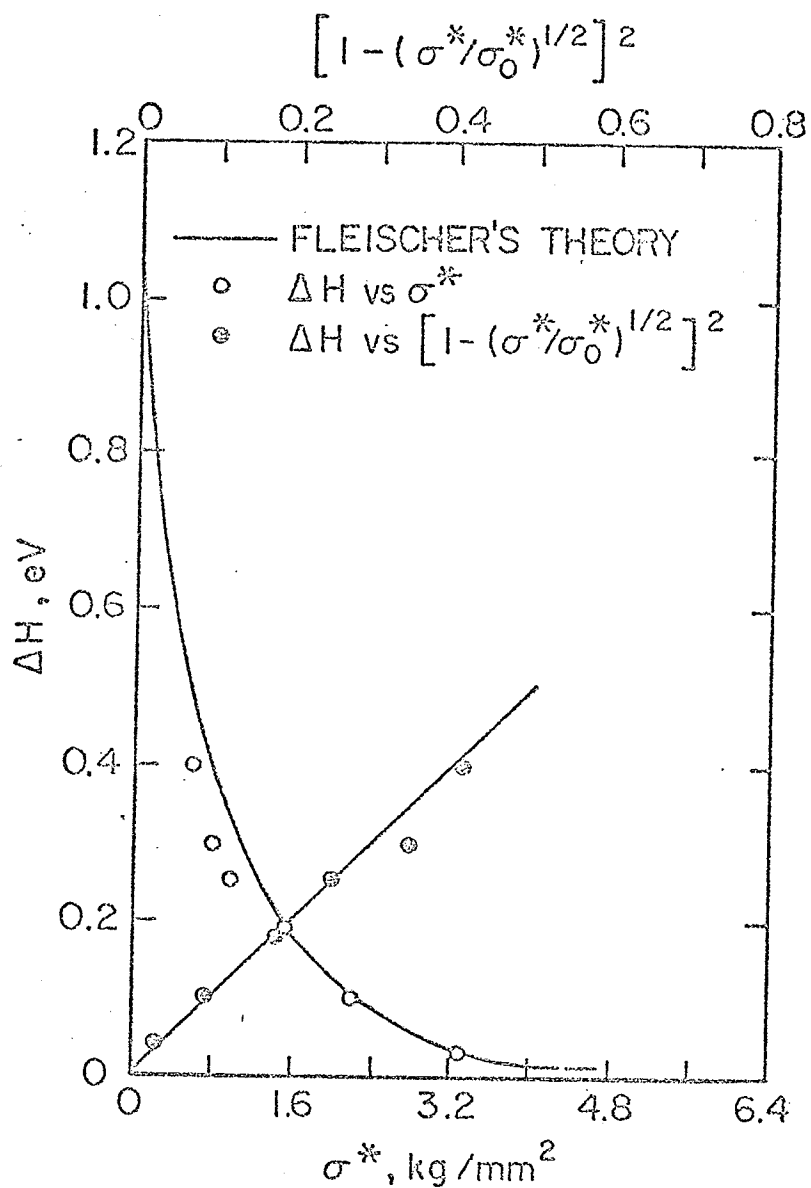


FIGURE 5.6: The stress (effective) dependence of activation energy for slip in MgO crystals. The solid curves represent eqn. (5.3). The straight line plot is shown as a test of the impurity hardening mechanism according to Fleischer [179].

depended on the heat treatment used prior to testing.

The fact that plots of $(\sigma^*)^{\frac{1}{2}}$ versus $(T)^{\frac{1}{2}}$ and $(\sigma^*)^{\frac{1}{2}}$ versus $(\Delta H)^{\frac{1}{2}}$ in the present experiments can be represented by a straight line from 77°K to 673°K without any deviation of parabolic nature at either extremity, which would normally be expected for a Peierls type of mechanism (see e.g. Spitzig [180]), strongly supports the contention that a Fleischer type of mechanism is operative.

5.1.3 Power law approach

Basically, two important points will be considered: (i) the applicability of various methods of analyzing m^* data, and (ii) the equivalence of the power law and rate theory approaches to deformation. The first of these has been discussed in section 4.1.4 of experimental results. It has been shown that the value of m^* obtained by the Gupta-Li analysis is in good agreement with that obtained from other techniques. Since m^* remains practically constant with strain (c.f. fig. 4.12) within the experimental error limits, the influence of a drastic change in mobile dislocation density is thought to be unimportant in the temperature and strain range studied, except perhaps in the beginning stages of deformation at 293°K [181] and above.

The second problem, in particular a description of the parameter, m^* , in terms of the relevant activation parameters, has been attempted by Li [79,82], who was amongst the first to derive some physical significance of m^* and relate its temperature dependence

to thermodynamic quantity, ΔS , the entropy of activation. Using thermodynamical arguments, it was demonstrated that the behaviour of the product (m^*T) in the limit as $T \rightarrow 0$ can be analyzed and used in the studies of dislocation dynamics with a minimum of uncertainty concerning the role of entropy. Starting with the fact that the third law of thermodynamics requires that $\Delta S \rightarrow 0$ as $T \rightarrow 0$, Li suggested that for a singly-activated process, the quantity (m^*T) approaches a limiting value near 0°K . In actual examples however, (m^*T) may increase [54], decrease [49] or remain constant [182] with temperature at higher temperatures depending upon the stress dependence of ΔS and ΔH . Some of the important relationships are given below (after Li [49]):

$$\left(\frac{\partial m^*T}{\partial T}\right)_{\sigma^*} = 0 \text{ at } 0^\circ\text{K} \quad (5.7)$$

$$\left(\frac{\partial \Delta H}{\partial \ln \sigma^*}\right)_\epsilon = -m^*kT \quad (5.8)$$

and

$$\left(\frac{\partial \ln \sigma^*}{\partial T}\right)_\epsilon = \frac{\Delta H}{m^*kT^2} \quad (5.9)$$

Figure 4.14 shows plot of the parameter m^* as a function of temperature. Included in that figure is also a plot of (m^*T) against temperature. It is seen that (m^*T) values at various temperatures can be fitted on a straight line with zero slope and a constant value of $3.7 \times 10^{30}\text{K}$ for $(m^*T)_0$. Because of the limited accuracy with which $(m^*T)_0$ could be obtained from fig. 4.14, $(m^*T)_0$ was also calculated

from the slope of plots of $1/m^*$ versus T as shown in fig. 5.7 where a comparison is also made of the previous result by Phillips [183] on MgO crystals having 80 p.p.m. of Fe compared to 100 p.p.m. in the present crystals. The two results are seen to agree quite reasonably considering the difference in the amount of Fe content used.

Figure 5.8 is a graph of ΔH versus $\log \sigma^*$ [equation (5.8)] and T versus $\log \sigma^*$ [equation (5.9)] and shows that the values obtained for $(m^*T)_0$ of 3.2×10^3 °K and 3.6×10^3 °K and for σ_0^* of 4.0 kg/mm^2 and 4.1 kg/mm^2 respectively are in good agreement with the experimental values of $\sigma_0^* = 4.5 \text{ kg/mm}^2$ and $(m^*T)_0 = 3.7 \times 10^3$ °K. The agreement between these values derived from Li's formulations thus lend support to the applicability of the third law of thermodynamics to thermally-activated flow of MgO crystals and shows that results obtained here are internally consistent with one another.

Returning to the question whether the experimental results can equally well be rationalized on the basis of the power law approach, it can be argued that if the power law and the rate theory approaches to deformation are equivalent:

$$m^* = V^*\sigma^*/kT \quad (5.10)$$

and for m^* to be independent of stress, $V^* \propto 1/\sigma^*$ and $m^*T = \text{constant}$. This is the case if entropy effects can be neglected. Figure 4.12 indicates that m^* values obtained by eqn. (5.10) agree with those obtained by other techniques, and (m^*T) remains constant with

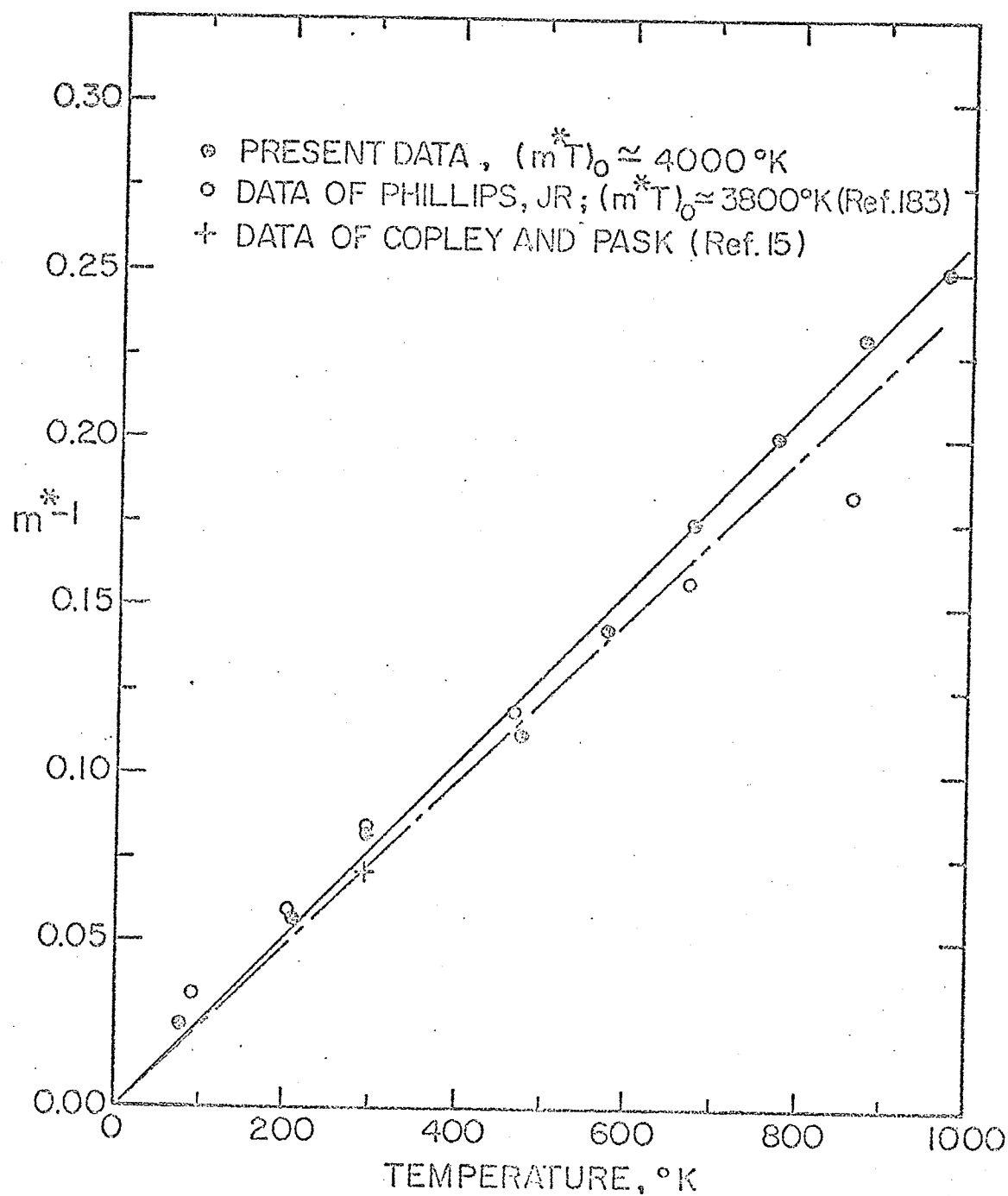


FIGURE 5.7: Inverse of the dislocation velocity-effective stress exponent, m^* , as a function of temperature. Data from literature are shown for comparison.

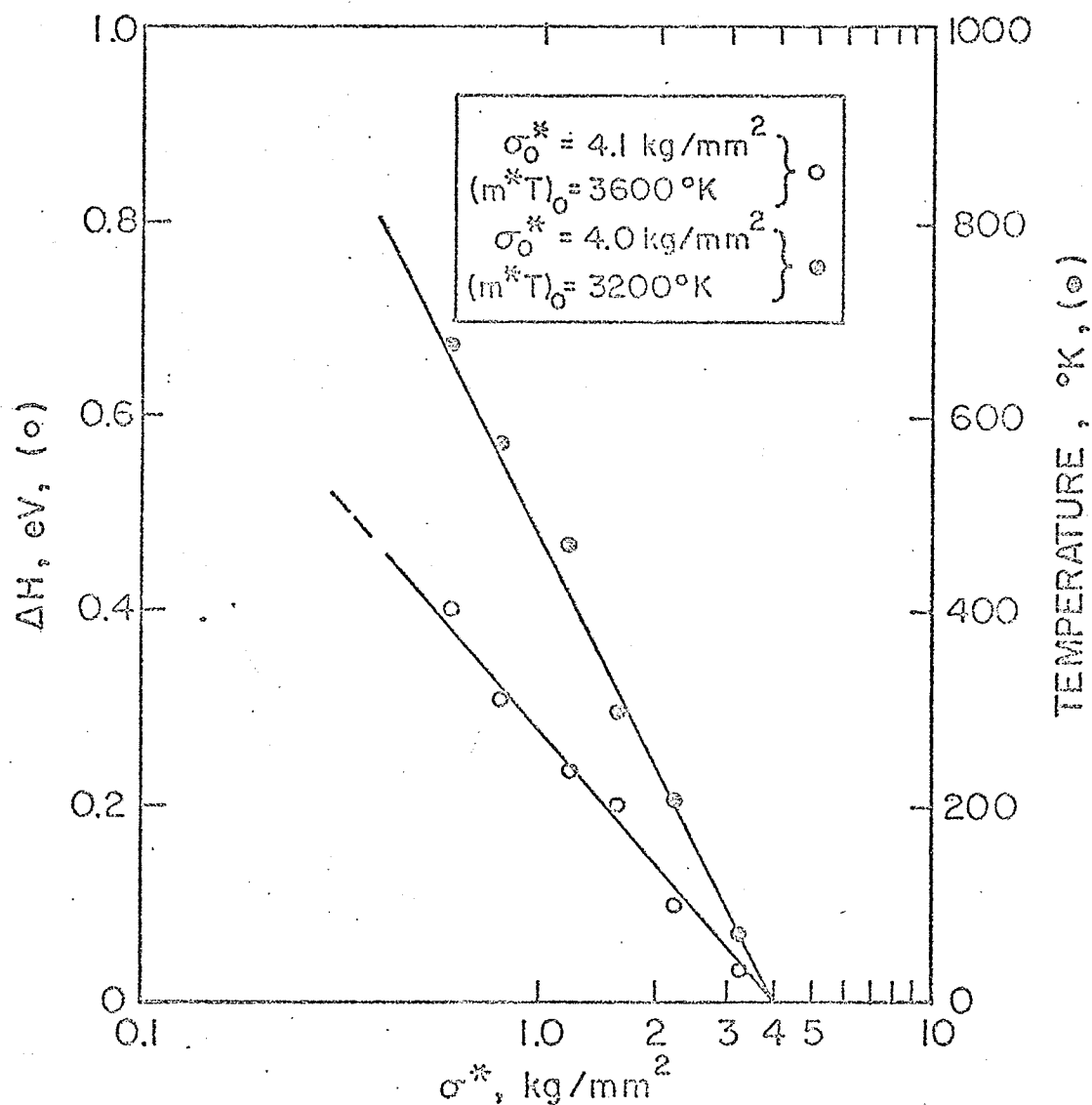


FIGURE 5.8: Activation energy (ΔH) and temperature (T) as a function of effective stress (σ^*) according to relationships (5.8) and (5.9). $(m^*T)_0$ = limiting value m^*T at low temperatures and σ_0^* = effective stress at 0°K.

temperature (fig. 4.14). The present results therefore indicate that over the temperature and strain range considered, the power law and rate equation approaches are equivalent and entropy effects are negligible in the present case. A negligible entropy term is also indicated by the linear relationship between ΔH and T shown in Fig. 4.18. Deviations from linearity would be expected if entropy effects were significant as has been shown by Arsenault and Li [86] and Arsenault [184].

5.2 Work Hardening Behaviour of MgO Single Crystals

In the absence of transmission electron microscope observations on the actual dislocation structures and because of a lack of data on the variation of dislocation density with strain, only rather general comments can be made on the work hardening behaviour of MgO single crystals. Experiments using etch pitting give evidence to the predominance of $\{110\} \langle 110 \rangle$ slip, on both orthogonally and obliquely intersecting slip systems. Below room temperature, the etch pit studies show that the major slip activities are confined on the obliquely-inclined slip systems. Considering the dependence of the dislocation energy on the Burgers vector from oblique systems (120° type, fig. 2.2), the high rate of work hardening at 77° and 208°K can be explained qualitatively as follows. Since the dislocations interacting on obliquely-inclined systems according to:

$$\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[10\bar{1}] \rightarrow \frac{a}{2}[1\bar{1}0]$$

produces a (sessile) dislocation lying on $\{112\}$ type plane which is not a plane of easy glide in MgO; the regions of intersection are likely to become sites of considerable impediment to further movement of dislocation through and hence giving rise to high rates of hardening. This reaction was proposed by Keh et al. [10] and observed in MgO crystals using transmission electron microscopy by Groves and Kelly [11]. As long as this reaction occurs, slip propagation is difficult and a sufficiently high stress will be required to undo the reaction or to bow out the dislocations between the two reaction points [13,22]. Furthermore, since the jogs resulting from the oblique intersections are charged, the high hardening rates may also be caused by the higher stress required by the formation and subsequent dragging of the charged jogs compared to the neutral jogs which form from orthogonal intersection (90° type, fig. 2.1).

The relatively low work hardening rates observed above room temperature (fig. 4.1) can also be explained on a similar basis; since the etch pitting results (fig. 4.22) show predominance of only orthogonal dislocation intersection. At higher temperatures (at and above 473°K), slip starts out with the formation of glide bands either on one or both of the equally-stressed $\{110\} \langle 110 \rangle$ slip systems, but a further increase in stress results in the lateral widening of one of the orthogonal bands. The relatively constant rate of work hardening seen in fig. 4.1 (for $T > 293^\circ\text{K}$) between about 1 to 6% of shear strain

can be hence related to the sideways propagation of active bands, since in this type of deformation, dislocation mobility is restricted only to the advancing glide band interfaces. At shear strains greater than $\sim 5-6\%$ when the whole crystal is covered with the dislocation bands, the increase in the work hardening rate (seen as the second stage of hardening, fig. 4.1) arises probably due to further deformation occurring within the bands.

5.3 Microyielding and Fracture in Polycrystalline MgO

Two points should be noted before considering the experimental results on room temperature deformation of polycrystalline MgO. All the specimens were chemically polished and microscopically examined to ensure that no surface damage was present prior to testing. Thus plastic flow and cracking is not a result of surface flaws which can have a significant effect on the deformation and fracture of polycrystalline MgO (see e.g. Evans and Davidge's [148] work). Furthermore, the microyield stress is defined as the stress at which the lattice and total strains are no longer proportional. Beyond this stress residual strains (lattice as well as plastic) is present on unloading the specimen, and since residual lattice strain is clear evidence of plastic deformation [170,171], the microyield stress is associated with plastic flow rather than crack formation. In view of the limits of accuracy with which strain measurements were made, the microyield stress represents the flow stress for about 5×10^{-6} plastic strain.

5.3.1 Slip initiation

The micrographs presented as typical examples of slip initiation in fig. 4.29 clearly show that the first evidence of slip is associated with grain boundaries, the majority of the pile ups formed having one end in contact with a grain boundary. The etch patterns are very similar to those found in Fe-3% Si alloy [134-136] and a number of other b.c.c. metal systems [137-139] stretched similarly in the microstrain range.

Several models have been suggested for grain boundary sources. Depending upon whether the operation of a source in the boundary requires or does not require grain boundary sliding, these models have been classified into two main types for convenience by Tangri et al. [132]. For a material like magnesium oxide, only the models based on the pre-existence of ledges in the grain boundaries need to be examined. This is firstly because of the fact that the grain boundary sliding at room temperature in MgO is highly unlikely and secondly that ledges at grain boundaries have been recognized [185] similar to metallic materials. The models that have been proposed to account for the grain boundary dislocation generation are due to Li [186] and Price and Hirth [187]. Li [186] suggested that grain boundary ledges can act as donors of dislocations. A grain boundary ledge in this model is considered as an absorbed edge dislocation such that under the influence of an external applied shear stress, the ledge is removed from the boundary generating a dislocation in the grain interior. It should be noted that this

kind of source is not really a dislocation mill which is capable of continuous generation of dislocations. A grain boundary ledge may be a donor of one or a few dislocations. Subsequent generation of further dislocations within the grain may take place for example by a double cross-slip mechanism [188-190]. Price and Hirth [187] have modified the ledge theory, suggesting that the ledge is sheared one Burgers unit along the slip plane thus nucleating a screw dislocation. Continued shearing of the ledge causes additional (screw) dislocation generation. Although a detailed electron microscopy investigation was not performed, the etching characteristics of some of the initial pile-ups suggested (on the basis whether etch pits emerge vertically or inclined on the $\{100\}$ faces [24,188]) that they were of edge character rather than screw. The predominance of edge dislocation etch pits was also found in polycrystalline LiF by Scott and Pask [126]. Only further work using transmission electron microscopy should be able to determine if Price and Hirth mechanism was viable. The large number of etch pits seen with initial pile-ups in fig. 4.29 should not be taken as all coming from the boundaries since they may form as a result of dislocation multiplication [189-191].

Finally, Baro and Hombogen [192] have postulated that lattice dislocations can be created at the head of a grain boundary dislocation pile-up, mainly at regions of stress concentrations such as triple point junctions. On the basis of this, they have also attributed the grain size dependence of the flow stress to the operation of grain boundary sources as:

$$\sigma_y = \sigma_{iGB} + k_{GB} \ell^{-1/2} \quad (5.11)$$

where σ_{iGB} is the stress opposing the motion of grain boundary dislocations, ℓ is the length of the grain boundary pile-up and is assumed proportional to d , the grain size, and k_{GB} is a constant involving the shear modulus of the boundary and the Burgers vector of grain boundary dislocations. Figure 4.25 shows however, that the stress to nucleate grain boundary sources is relatively independent of grain sizes larger than 10 μm . This result is again similar to that obtained on Fe-Si alloy by Suits and Chalmers [193] and Tandon and Tangri [136]. These results therefore cannot be explained on the basis of eqn. (5.11). As can be noted from above, the critical concept in the Baro and Hornbogen's model is the assumption of the free slip distance, ℓ , of the grain boundary dislocation being proportional to the length of the straight and periodic array of the grain boundary. Since slip in this model is assumed to take place in the grain boundary which forms pile-ups at the corners of grains, the Burgers vector of the grain boundary dislocation and the line of dislocation must be contained in the boundary. Thus any kink or change of direction of the boundary will limit the free slip distance over which the necessary requirements are met. In deriving eqn. (5.11) Baro and Hornbogen assumed $\ell \propto d$, however, this may not be the case. Instead, ℓ may be determined by the misorientation across the grain boundary and a simple grain size dependence of the stress for grain boundary source activation may not be the case.

Reference to fig. 4.25 indicates another interesting feature which is similar to the observations on metals. The stress at which first nucleation of dislocations occur from the grain boundaries is significantly lower than that for microflow or fracture. Recently Tangri et al. [132] have analyzed this more specifically for an analogous situation occurring in polycrystalline Cu, Ni and Fe-Si alloy. It has been shown [132] that if account is taken of the stress concentration factors, such as at the ledges due to its geometry and due to elastic incompatibility at the interface, the magnitude of stress at which dislocation emission from grain boundary is experimentally observed falls within the predicted range. It is believed that a rather similar explanation based on compatibility effects exists for the occurrence of slip at low stresses in the present work on polycrystalline MgO and those for polycrystalline LiF studied by Scott and Pask [126] who also observed local slip activity near grain boundaries at a load much lower than the predicted value.

5.3.2 Microyield

The results of fig. 4.25 show that the microyield stress obeys the Hall-Petch relationship with respect to grain size. Petch [194] postulated that dislocation pile-ups form against the grain boundary resulting in a stress concentration at the head of the pile-up nucleating slip in the adjacent grain. A similar model was suggested by Cottrell [195], both associate the grain size relationship with the

propagation of slip across grain boundaries. The etch pitting experiments show that, contrary to the above models the microyield stress is associated with slip band formation within the grains and examples of slip breakthrough of grain boundaries at the microyield stress were extremely rare. Hence, the pile-up models do not appear applicable for the microyield stress-grain size relationship.

Alternative models are the work hardening [156,157] and grain boundary source models [159]. In the work hardening type models, one invokes the experimental correlation that:

$$\sigma = \sigma^* + \alpha \mu b \sqrt{\rho} \quad (5.12)$$

where σ is the flow stress, σ^* is the thermal component of the flow stress, ρ is the average dislocation density, μ is the shear modulus, b is the Burgers vector and α is a constant usually taken as a measure of the efficiency of dislocation strengthening.

Figure 5.9 is a plot of the microyield stress against (initial dislocation density)^{1/2} and it can be seen that a straight line relationship is obtained with a gradient of 0.82 kg/mm⁻¹, corresponding to a value of $\alpha \approx 1.5$. The value of the intercept on the stress axis gives $\sigma_0 = 4.7 \text{ kg/mm}^2$ compared to a value of 4.9 kg/mm² obtained from (stress) versus (grain size)^{-1/2} plot in fig. 4.25. To be noted is that the value of α appears to be in accord with what would be predicted on the basis of several work hardening theories [196]. The main point to be mentioned however, is that in the theory of Conrad et al. the intercept of the

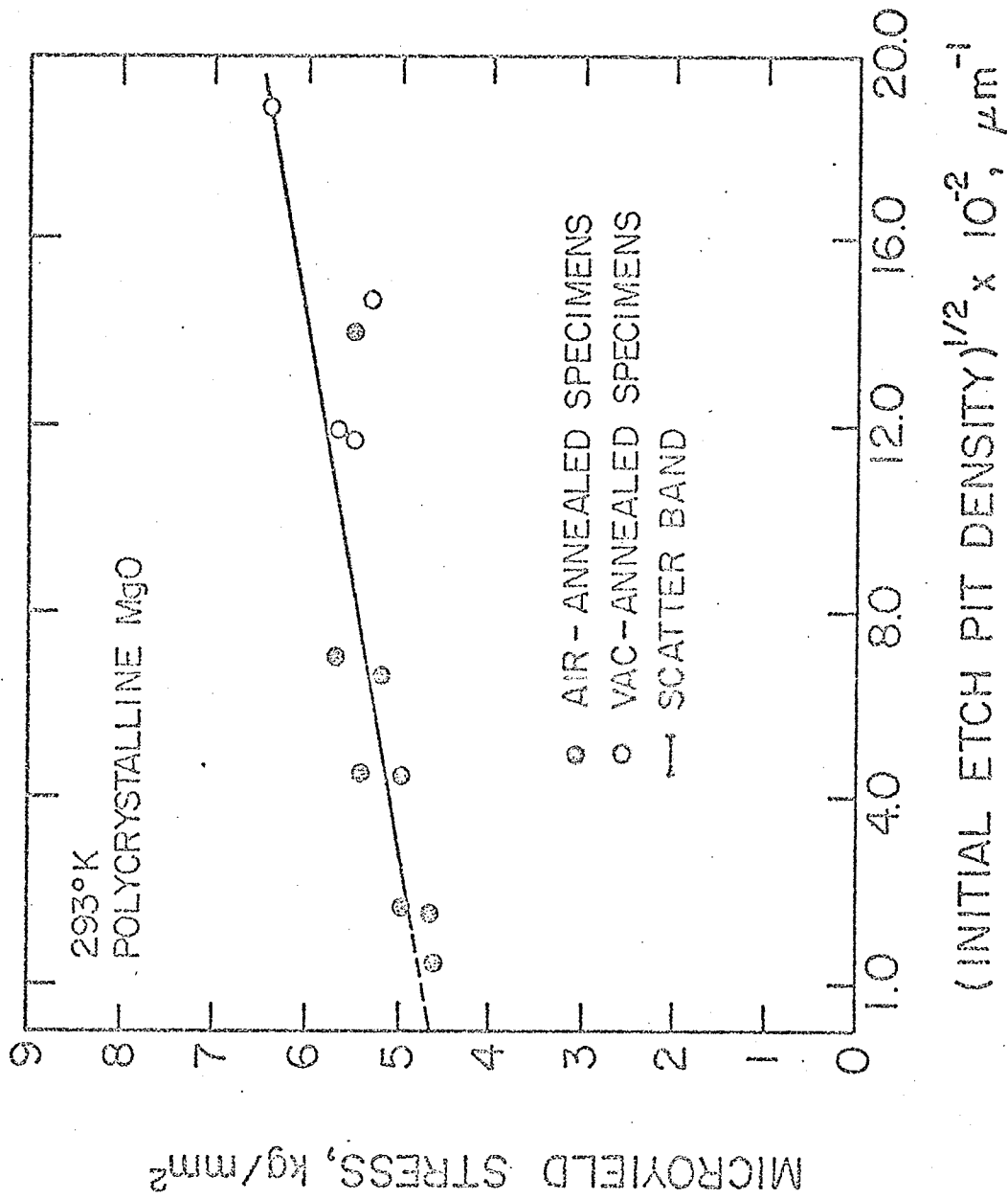


FIGURE 5.9: Variation of microyield stress against (initial dislocation density)^{1/2}.

Petch plot should be strain independent, whereas fig. 4.25 indicates that the intercept increases with strain.

An alternative way to rationalize this behaviour is based on the work by Ashby [133], who showed that a proportionality between the dislocation density and the reciprocal of the grain size follows from a consideration of the density of dislocations required to compensate for the non-homogeneous deformation which must occur in the neighbourhood of grain boundaries during polycrystal deformation. This concept has been examined by Schankula et al. [160] using a simple dimensional argument similar to that proposed by Ashby [133] for two phase materials (see also Embury [197] for a recent review). Since the physical picture of a polycrystal deformation as provided by Ashby also emphasizes the role of dislocations generated to preserve continuity of the polycrystal across grain boundaries in addition to the dislocations stored inside the grains, this model differs from that of Conrad et al. where the main emphasis on the effect of grain size is placed on the internal stress opposing the motion of dislocations only within the grains. This model then suggests that the subsequent accumulation of dislocations with continued straining is grain size dependent with $\rho \propto 1/d$.

From the experimental results obtained in the present work on polycrystals of MgO, some further agreement with Ashby's model becomes evident. The micrographs of etch pitting experiment clearly show the distinction of the dislocation behaviour near-boundary regions and in regions remote from grain boundary. Here, the existence of strain gradients in polycrystals and also the compatibility effects are

satisfied with the geometrically necessary dislocations in regions close to boundaries. With further increase in the level of straining, fig. 4.33 shows that the glide bands broaden and there is spawning of secondary bands which contribute to the storage of dislocations inside the grains. The present result thus indicates, at least qualitatively, that the accumulation model should be valid for explaining the grain size dependence of yielding in polycrystals of MgO. If we consider the increment of flow stress due to stored dislocations to be additive to the yield stress, the Hall-Petch equation for finite plastic strains becomes [197]:

$$\sigma_y = \sigma_0 + \{ k_y + \alpha \mu \left(\frac{\epsilon}{b} \right)^{1/2} \} d^{-1/2} \quad (5.13)$$

Thus, the Hall-Petch slope should increase with plastic strain as long as the rate of accumulation of dislocations is determined by the grain size. Figure 4.25 indicates this to be the case for the present work in accord with the concept described above.

Another rationale of Hall-Petch equation is that of emission of grain boundary dislocations [159]. Here, it is postulated that yielding is from grain boundary ledges and assuming a constant ledge density, the number of dislocations produced is proportional to the grain boundary surface area. Thus a Petch type relationship is again obtained. Although there is now ample experimental evidence both based on electron microscopy and etch pitting that grain boundaries act as sources of dislocations in metals; most of the evidence for ceramic materials to-date is based only on etch pit observations. Even

if grain boundary source theory is accepted, it is difficult to judge its validity throughout the deformation since the model is sensitive to whether the grain boundary dislocations essentially act as uniform sources with sufficient ease at all stages. With the limited strain range available in the present work it is not possible to decide on the operative model. The results indicate however, that the work hardening and grain boundary source models are in general agreement with the results, and that the microyield stress is controlled by the initial dislocation density.

A further point should be made regarding the microyield data of fig. 5.9. Figure 5.9 shows that irrespective of the heat treatment (that is, whether annealed in air or in vacuum), the microyield stress data always fit the same straight line; indicating that the work hardening behaviour of air-annealed or vacuum-annealed specimens is due to identical mechanisms. On the basis of the work hardening models this would signify that the higher flow stress after a given strain in finer-grained materials arises because more dislocations are created in that material for a given strain.

5.3.3 Fracture behaviour

As shown in fig. 4.25 the fracture stress-grain size data also follows a Hall-Petch type equation similar to the microyield and microflow stresses by a modification of equation, $\sigma_y = \sigma_0 + kd^{-1/2}$, in which the subscript σ_y is replaced by the fracture stress, σ_F ,

and σ_o and K become function of strain:

$$\sigma_F = \sigma_{oF} + K_F d^{-1/2} \quad (5.14)$$

where σ_{oF} and K_F are constants for the fracture criteria.

Comparison of the fracture stress-grain size plot with the microyield stress plot reveals that the intercept σ_{oF} is much larger than the intercept of the yield stress line. It is evident therefore that with relationship (5.14) as the equation for fracture stress, σ_{oF} cannot be taken simply as 'frictional' stress for dislocation motion. Although the value of σ_{oF} has not been evaluated theoretically, Ku and Johnston [124] have attempted to clarify the experimental significance of σ_o term in eqn. (5.14). In bicrystals of MgO, heat-treated to lock dislocations, they introduced fresh dislocations by making indentations at various distances from the grain boundary. The stress required for crack initiation was shown to be proportional to $d^{-1/2}$ where d was the length of the glide band. They suggested that σ_o was the stress for dislocation multiplications. A comparison of their work with the present one (both tests at room temperature) shows that the dislocation multiplication occurs at a much lower stress, in the neighbourhood of the microyield stress. The crack nucleation was observed always beyond the microflow stress curve which approximated to about 75 to 85% of σ_F , the measured fracture stress values. Since the present experimental data is consistent with eqn. (5.14) and shows that the intercept and gradient of various $d^{-1/2}$ plots tend to increase with

increase of strain, much larger σ_{oF} in the fracture stress situation reflects the extensive work hardening that the matrix has undergone following initial yield.

In view of the above and the fact that nucleation of a few cracks at random points did not result in complete fracture of the specimens, σ_{oF} appearing in fracture stress-grain size relation can be defined here more properly as a measure of the stress required to move the dislocations which produces crack rather than simply a dislocation multiplication stress as suggested by Ku and Johnston. Such a definition also takes into account the common observation that in majority of the experiments with semi-brittle ceramics, complete fracture does not always result from either dislocation multiplication or from one single crack nucleation event. In any case, it is clear that σ_{oF} represents an appreciable part of the total value of σ_F . In the case of polycrystalline MgO where only the fracture stress values have previously been measured as a function of grain size, σ_{oF} has been associated with the flow stress of single crystals [148]. The present result however, indicates that the microstrain should be possible in single crystals at a much lower stress corresponding with the intercept for the polycrystal microyield stress curve of fig. 4.25. The main point of interest is that significant plastic flow and work hardening occurs in polycrystalline MgO prior to fracture. The similarity of the present work with that of Stokes and Li [123] on polycrystalline NaCl is worth mentioning. For example, when the data of Stokes and Li on the room temperature stress-strain behaviour is replotted in terms of

(stress) versus $(d)^{-1/2}$, one finds interestingly similar behaviour. Firstly, even though the range of grain sizes used by them was above about 100 μm , it is found that the yield and fracture stresses both show a linear fit according to Hall-Petch equation. Secondly, while the intercept of the yield stress $-d^{-1/2}$ plot extrapolates somewhat close to single crystal yield (macroscopic) value on the stress axis, the intercept (σ_{0P}) and slope (K_P) of the fracture stress $-d^{-1/2}$ plot are quite different and larger than for the yield stress. This behaviour again indicates that the influence of grain size on the deformation of rock salt type polycrystalline materials is in accord with the concept that the rate of accumulation of dislocations during work hardening is dependent on the grain size. However, since the factors controlling initial yielding mechanism and its correlation with the process of dislocation accumulation is unknown, no firm quantitative comparisons can be made at the present. Obviously there is a need for more experimental evidence concerning the variation of dislocation density with grain size for a wide range of grain sizes.

6.0 SUMMARY AND CONCLUSIONS

6.1 Deformation of MgO Single Crystals

(1) The plastic deformation of MgO single crystals compressed along a cubic axis has been studied in terms of the thermal and athermal components of the flow stress over a temperature range 77° to 673°K . It is shown that the thermal component of the flow stress is independent of strain and that the athermal component is the main contributor of work hardening.

(2) The dislocation velocity-effective stress exponent, m^* , has been determined for MgO single crystals using indirect techniques. The experimental results indicate the existence of two main characteristics for m^* over the temperature range investigated; namely, that (a) m^* is strongly temperature dependent, increasing with decreasing temperature; the product (m^*T) however, remains constant with temperature, and (b) m^* is independent of strain ($>1.0\%$ strain between 293°K and 673°K).

(3) Over the temperature range investigated, the results indicate that the strong elastic interaction between dislocations and centres of tetragonal strain produced by trivalent ion-vacancy pairs is controlling the deformation. This is essentially the model proposed by Fleischer to explain hardening in monovalent ionic crystals by divalent ions.

(4) The experimental data are consistent in terms of both the thermally-activated rate equation and the power law approach to

deformation and suggest that entropy effects are negligible in the present case.

6.2 Deformation of Polycrystalline MgO

(1) The role of plastic flow occurring prior to fracture in fully-dense polycrystalline MgO with grain sizes 3 to 120 μm was studied using a microstrain measurement technique in conjunction with classical etch pit method to monitor the generation and growth of dislocation glide bands. It has been shown that in the chemically-polished specimens, dislocations are initially produced from sources in or very close to the grain boundary and at a stress level significantly lower than that of microflow or fracture stress. The stress for activation of these grain boundary sources is independent of grain size for grain sizes larger than 10 μm .

(2) The microyield stress (corresponding to a plastic strain of 5×10^{-6}) shows a Hall-Petch relationship in terms of grain size. Since slip breakthrough is rare at the microyield stress, the grain size dependence is attributed to the change in dislocation density with grain size. The analysis of the microyield stress data of air-annealed and vacuum-annealed specimens with respect to grain size indicate that the same mechanism influence the work hardening behaviour in both cases.

(3) The fracture stress also obeys a Hall-Petch relationship in terms of grain size. The intercept stress, σ_{OF} , is much larger than

the equivalent stress for yield and this is attributed to the extensive work hardening that occurs prior to fracture. The gradient of the fracture stress grain size plot is also larger than that for yield as expected on theoretical grounds.

7.0 FURTHER RECOMMENDED RESEARCH

7.1 Single Crystals

(1) A detailed investigation of the dislocation accumulation mechanisms using transmission electron microscopy and etch pitting technique is required for the understanding of work hardening behaviour.

(2) Since impurities seem to be the rate-controlling factor in the deformation of MgO crystals, an equivalent investigation to the present one, with crystals containing different solute contents would be of great interest.

7.2 Polycrystals

(1) A detailed investigation of grain boundary structure using electron transmission microscopy is necessary before the yielding process can be understood.

(2) Microstrain experiments at higher temperatures and hence, accompanied by greater ductility is required to distinguish between the different theories for the Petch relationship.

8.0 CITED LITERATURE

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