

GRAIN BOUNDARIES IN METALS

BY

D. McLEAN

NATIONAL PHYSICAL LABORATORY

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PHYSICS AND CHEMISTRY OF
MATERIALS

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WILLIS JACKSON H. FRÖHLICH N. F. MOTT
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PREFACE

GRAIN boundaries exist in metals because the grains on either side of the boundary are different or differently oriented. Some of the effects of grain boundaries are due to this change and not to the boundary as such; for example, part of the difference between the plastic properties of pure single crystals and pure polycrystals is due to the changing orientation in the polycrystals. But the boundary itself is a region physically distinct from the grains on either side, and many of its effects are due to this: for example, preferred precipitation at boundaries, fast diffusion along boundaries, and the yield point in polycrystalline mild steel and similar metals. A grain boundary has a dual character, and either aspect may have important effects.

The influence of grain boundaries may be large and not always simple. Thus, suitable boundaries can make metals that glide easily as single crystals strain harden rapidly as polycrystals, or turn ductile single crystals into brittle polycrystals. Diffusion can be so much faster along boundaries than through the grains that under certain conditions the grain boundaries transport more material than the grains do in spite of their thinness. Such effects prevent many of the properties of polycrystals from being simply the average of those of single crystals of all possible orientations. In the field of plastic properties particularly, the dominant thing is the *interaction* between the grains and grain boundaries.

Many properties of metals are affected by grain boundaries. Some are affected more or less directly, while others are affected indirectly, as for example, when precipitation along boundaries is a serious matter. I have tried to make this book fairly complete within the limits suggested by the fact that it is addressed primarily to metallurgists and may also interest physicists working on metals. The chief omissions are probably that there is no discussion of the chemical effects of grain boundaries or of the effect of liquid surface active environments. There are many loose ends; above all, although there are theories that

explain particular properties of grain boundaries with varying degrees of satisfactoriness, there is no comprehensive theory that accounts for all properties with a good degree of numerical precision.

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CONTENTS

CHAPTER I. HISTORICAL INTRODUCTION

1.1 Definition	1
1.2. Are metals amorphous or crystalline ?	1
1.3. The amorphous cement theory	5
1.4. The transition lattice theory	11

CHAPTER II. MODERN THEORIES OF GRAIN BOUNDARIES

2.1. Survey	15
2.2. Width of grain boundaries	16
2.3. The 'island' model	17
2.4. Kê's model	21
2.5. Dislocation model: simple tilt boundary	22
2.6. Definitions: tilt and twist boundaries	23
2.7. Dislocation model: extension to arbitrary boundary	24
2.8. Energies of dislocation boundaries	28
2.9. Smoluchowski's model	35
2.10. Friedel <i>et al.</i> 's model	36
2.11. Coherent boundaries	37
2.12. The bubble model	38
2.13. Conclusions concerning the structure of boundaries	42

CHAPTER III. ENERGIES OF INTERFACES

3.1. Introductory	44
3.2. Numerical equality of interfacial tension and free energy	44
3.3. Grain boundary triangle of forces: dihedral angle	46
3.4. Line tension at grain boundary junctions	49
3.5. Methods of measuring interfacial free energy	50
(a) Methods for grain boundaries	50
(b) Methods for other interfaces	58
3.6. Influence of orientation on interfacial free energy	62
3.7. Influence of impurities on interfacial free energy	68
3.8. Measured values of interfacial free energy	69
3.9. Temperature dependence of interfacial free energy	72
3.10. Thermodynamic formulae for small particles	73

CHAPTER IV. ENERGY OF GRAIN BOUNDARIES AND MICRO-STRUCTURE

4.1. Shapes of grains in three dimensions	81
4.2. Shapes of grains in two dimensions	87
4.3. Grain growth	88
4.4. Range of grain sizes	92
4.5. Distribution of small amounts of a second phase	94
4.6. Embrittlement of brass by mercury	99
4.7. Melting at grain boundaries	100
4.8. Continuous and discontinuous precipitation	107
4.9. Numerical relations	110
4.10. Stereoscopic microradiography	114

CHAPTER V. SOLUTE CONCENTRATION AT GRAIN BOUNDARY—EQUILIBRIUM SEGREGATION

5.1. Introduction	116
5.2. Reason for equilibrium segregation	116
5.3. Zener's platelets	122
5.4. Driving force for segregation	124
5.5. Total solubility and lattice solubility	126
5.6. Solubility at grain boundaries	131
5.7. Approach to equilibrium	131
(a) Magnesium in aluminium	133
(b) Carbon in alpha iron	133
5.8. Experimental evidence for equilibrium segregation at grain boundaries	138
(a) Experiments using a radioactive tracer	138
(b) Metallographic effects at grain boundaries	139
(c) Miscellaneous	142
5.9. Influence of other solutes	143
5.10. Thermodynamics of grain boundaries	143
5.11. Method for the experimental determination of grain boundary concentration	148

CHAPTER VI. INFLUENCE OF GRAIN BOUNDARIES DURING DEFORMATION

6.1. Hindrance to slip by grain boundaries	151
6.2. The complexity effect	157
6.3. Experiments on bi-crystals and on slip near boundaries	161
6.4. Local elongation and hardness	166

CONTENTS

ix

✓ 6.5. Strain-hardening in different polycrystalline metals	172
✓ 6.6. Yield stress of polycrystals	179
✓ 6.7. Influence of grain size on creep strength	195

CHAPTER VII. SUB-BOUNDARIES

7.1. Dislocation structure of sub-boundaries	200
✓ 7.2. Effect of purity on etching of sub-boundaries	201
✓ 7.3. The formation of sub-boundaries during freezing, cold work, annealing, creep, and transformation	203
7.4. Movement of sub-boundaries under stress	211
✓ 7.5. Effect of sub-boundaries on mechanical properties	214
7.6. Smialowski structure	215
✓ 7.7. Deep-etching patterns	217

CHAPTER VIII. DIFFUSION ALONG GRAIN BOUNDARIES

8.1. Depth of penetration along grain boundaries	219
✓ 8.2. Measurements of grain boundary diffusion	224

CHAPTER IX. MIGRATION OF GRAIN BOUNDARIES

9.1. Direction of and driving force for migration	231
9.2. Influence of boundary type on mobility	234
9.3. Mechanism of migration	236
9.4. Influence of impurities	239
9.5. Comparison between theoretical and experimental rates of migration	242
9.6. Recrystallization	251
(a) Primary recrystallization	251
(b) Secondary recrystallization	252
(c) Recrystallization textures	254
✓ 9.7. Migration during creep	256
✓ 9.8. Migration of boundaries between phases	256
✓ 9.9. Vibration of grain boundaries	257

CHAPTER X. SLIDING AT GRAIN BOUNDARIES

10.1. Theory of Kê-type measurements	258
10.2. Results obtained in Kê-type tests	264
(a) Agreement with theory	265
(b) Results for pure metals	270
(c) Effect of impurities	272
(d) Background relaxation	275
(e) Grain boundary viscosity	276

10.3. Sliding in bi-crystals and polycrystals	279
10.4. The mechanism of sliding	286
10.5. Role of sliding in creep	288
~ 10.6. Yield strength of grain boundary	292
Appendix	293

CHAPTER XI. INTERGRANULAR BRITTLINESS

PART A. LOW-TEMPERATURE BRITTLINESS

11.1. Types of brittle fracture at low temperature	296
11.2. Tough-brittle transition in iron	299
11.3. Occurrence and extent of low-temperature brittleness	303
11.4. Theories of low-temperature brittleness	308
~ 11.5. Overheating and burning	321

PART B. INTERCRYSTALLINE FRACTURE AT ELEVATED TEMPERATURE

~ 11.6. Experimental observations	322
~ 11.7. Theories	328

AUTHOR INDEX	339
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SUBJECT INDEX	345
---------------	-----

FIGS. 3.4, 5.7, 5.8, 5.9, 6.1, 6.2, 7.2, 7.3, 7.7 *a* and *b*, and 11.9 appear as plates facing pages 50, 140, 141, 150, 204, 205, 212, and 330

CHAPTER I

HISTORICAL INTRODUCTION

1.1. Definition

A GRAIN boundary in a piece of metal is the boundary separating two crystals (or 'grains') that differ either in crystallographic orientation, composition, or dimensions of the crystal lattice, or in two or all of these properties.

This definition of a grain boundary excludes the uncontaminated surface of a single crystal from being classed as a grain boundary. How correct it is to exclude an uncontaminated free surface is a matter for argument. It is obviously a boundary in a spatial sense, and has a higher free energy than a grain boundary, but it does not affect the mechanical behaviour as a grain boundary does. Contaminated surfaces, on the other hand, may affect the mechanical behaviour like a grain boundary; where the contamination takes the form of a distinct layer, e.g. of oxide, the interface is a grain boundary according to the definition given here.

1.2. Are metals amorphous or crystalline?

In a pure metal the differences between adjacent crystals are usually differences in crystallographic orientation. Consequently a clear idea of the nature of a grain boundary could not arise until it had been realized that metals are crystalline. This happened at about the turn of the century.

Earlier, ideas had been confused. The plasticity of metals when compared with the flowability of viscous solids and the brittleness of substances known to be crystalline made it seem that metals were also viscous solids, i.e. amorphous. The eminent metallurgist Roberts-Austen expressed this view. In 1886, comparing the extrusion of lead to the extrusion of treacle, he concluded that 'the lead proves by its behaviour that it is really a viscous solid, as it flows readily through the orifice'.¹

¹ W. C. Roberts-Austen, Royal Institution Lecture, 26 March 1886.

But metals are not always deformable. Sometimes instead they behave in a brittle way. Brittle metals not infrequently break along the grain boundaries, and the fracture looks 'crystalline'. This gave rise to the idea, still occasionally met with, that metals, although normally amorphous, could crystallize under certain conditions and might then be brittle instead of deformable. As Roberts-Austen put it, 'The crystallisation of metals is of great importance, as the formation of crystals, due to continued vibration, intense cold, sudden alterations of temperature, or the presence of impurities may render a metal absolutely useless'.¹ The conditions referred to are conditions which sometimes induce brittle behaviour. Another point of view was put forward by Mellor. He allowed that pure metals were crystalline, 'But in studying the structure of alloys, the crystals are usually so ill defined and imperfect that it is impossible to decide from their external shape whether they be true crystals or simply amorphous grains'.²

About the same time as the first of the two quotations above from Roberts-Austen, a study of micro-structures had made Sorby support the idea that metals are crystalline. In 1887 he wrote, 'It seems . . . nearly certain that the separate grains . . . are separate, though imperfectly developed, crystals'.³ In the same paper he said, 'It was at one time supposed that by continual vibration a bar of so-called fibrous iron became crystalline. To test this question, a bar . . . (was vibrated) . . . for fifteen hours, until it broke with a crystalline fracture. A longitudinal section of the broken end showed that the structure was no more crystalline than iron in its natural state. . . . In any case, when studying such questions, we must not look upon iron as a homogeneous substance, but simply as a mass of small crystals, which cohere less strongly than separate parts of individual crystals'. Two years later Ewing and Rosenhain⁴ wrote that

¹ W. C. Roberts-Austen, *An Introduction to the Study of Metallurgy*, 5th ed., 1902.

² J. W. Mellor, *The Crystallisation of Iron and Steel*, 1905, p. 68. (See also W. C. Brannant, *Metallic Alloys*, 1908, p. 94.)

³ H. C. Sorby, *J. Iron Steel Inst.*, 1887 (1), p. 255.

⁴ J. A. Ewing and W. Rosenhain, *Proc. Roy. Soc. A*, 1899, 65, 85.

metal 'grains are, in fact, crystals, except that each of their bounding surfaces is casually determined by the meeting of one grain with another. This is, we believe, the view usually accepted by metallurgists'. Stead¹ held a similar view.

Strong evidence for the crystallinity of metals was put forward by Ewing and Rosenhain in 1900.² They studied the form of slip lines and etch pits in several metals. They thought that 'The occurrence of such geometrical (etch) pits in surfaces of metals that have never been polished or etched may be taken as very strong evidence in support of the view that the crystalline grains of metals are built up of crystalline elements which are similarly oriented throughout the mass of each grain'—a very fair statement of the modern viewpoint. They found that slip lines were straight and etch-pits straight sided after, as well as before, deformation. The concept that the atoms are arranged in definite layers which slide over each other during plastic deformation, leaving the crystalline perfection essentially unimpaired, seemed to provide the only explanation of these observations, and they therefore regarded it as support for the idea that metals are normally crystalline: 'The writers believe that they have established the fact that the structure of metals is crystalline even under conditions which might be supposed to destroy crystalline structure. . . . The distinction which is often drawn between crystalline and non-crystalline states in metals appears to be unfounded.'² Indisputable proof of this was eventually secured when it became possible to measure the crystal lattice dimensions with X-rays.

Nevertheless, the idea that metals could be amorphous lingered on, and Guertler thought it appropriate to write in 1912 'Schweder had of course already correctly recognised the parallel between the crystallisation of alloys from the melt and that of salts from solution in 1877, but his work remained unnoticed. . . . Even in 1898 Andrews could say as though it were a novel statement "an analogy seems to exist between the freezing of

¹ J. E. Stead, *J. Iron Steel Inst.*, 1898, 53, 145. (Also *J. Iron Steel Inst.*, 1898, 54, 137.)

² A. Ewing and W. Rosenhain, *Phil. Trans. Roy. Soc. A*, 1900, 193, 353.

ice and the crystallisation of molten metals''¹ and 'First, the following must be emphasised: 1. All metals and alloys crystallise on freezing'.² On the next page he writes 'One frequently finds in the literature the remark that this or that alloy crystallises on annealing, or is crystalline after certain procedures but not after others. This description is inaccurate. All metals are inherently crystalline'.³

The stubborn persistence, which these quotations show, of the idea that metals can exist in the amorphous condition below their melting-points made it plausible to explain particular behaviours in terms of the transformation of small parts of a mass from the crystalline to the amorphous state, much as Roberts-Austen explained some cases of brittleness by the reverse transformation of the whole mass. Beilby accounted for the 'Beilby layer' produced by polishing in this way. While modern research supports the idea that the Beilby layer is amorphous, or at least consists of crystals too small to detect, the stability of the more or less amorphous condition is ascribed to the intimate entrapment of oxide, etc.⁴ Consequently the deduction which Beilby drew from his discovery, namely that with sufficiently rapid chilling a metal could be made to remain in the amorphous condition, was incorrect. But it assisted his theory that work hardening was due to the transformation of a layer of metal along each slip plane into amorphous metal.⁵ He likened the friction on slip planes during deformation to that on an exterior surface during polishing and, as the latter circumstances gave birth to an amorphous film so, he thought, did the former. It also assisted his theory that the greater hardness of solid solutions compared with pure metals was due to their being amorphous; they were held to be amorphous because of the supposed difficulty of explaining how two or more sorts of atoms could lie on the same crystal lattice over large regions.⁵ Implicit in both these theories were two conceptions important

¹ W. Guertler, *Metallographie*, Berlin, 1912, p. 5.

² Loc. cit., p. 13.

³ Loc. cit., p. 14.

⁴ e.g. F. P. Bowden, *Inst. Metals Symposium*, 'Properties of Metallic Surfaces', 1953, Discussion, p. 334.

⁵ G. Beilby, *J. Inst. Metals*, 1911, 6, 5.

in the development of ideas about the grain boundary. One was that a substance could be amorphous or crystalline, but not 'in between'—in other words, an absence of the modern conception of the existence of degrees of perfection of the crystal lattice. The other was that at temperatures too low for there to be appreciable atomic vibration, amorphous substances deformed less easily than crystalline ones because they could possess no lattice planes of easy slip.

The situation at the turn of the century was therefore that metals were considered to be normally crystalline, that the grains seen under the microscope were separate crystals of different orientation, and that it was possible for portions of a piece of metal to exist in the amorphous condition below the melting-point.

1.3. The amorphous cement theory

In the words of its chief protagonist, Rosenhain, 'The theoretical conception (of the amorphous cement theory) is to the effect that the crystals of a pure metal are surrounded and cemented together by a very thin layer of the same metal in amorphous condition, whose properties correspond to those of the liquid metal subjected to extreme undercooling. The amorphous metal thus defined corresponds with the amorphous phase of Beilby. . . .'¹ A similar point of view was put forward simultaneously by Sears,² Osmond,³ and Bengough.⁴

Although the general circumstances of the times described in the preceding section were the real reason why this theory of the grain boundary was conceived, the particular experimental evidence that supported it and was its chief prop for many years came from studies of mechanical properties at elevated temperature. Rosenhain and Humphrey¹ obtained micrographs showing quite clearly that in steels slowly stretched at high temperature the individual grains slid bodily over each other, but did not

¹ W. Rosenhain and J. C. W. Humphrey, *J. Iron Steel Inst.*, 1913, 87, 219.

² J. E. Sears, *Trans. Camb. Phil. Soc.*, 1908-12, 21, 105.

³ F. Osmond, Discussion on 'Transformation of Steel', *J. Iron Steel Inst.*, 1911, 84, 61.

⁴ G. D. Bengough, *J. Inst. Metals*, 1912, 7, 168.

do so at low temperature. They explained this as being due to the difference of the change in behaviour of crystalline and amorphous metal with rising temperature. At low temperatures the amorphous grain boundary cement would be hard but the crystals would be comparatively soft and would deform easily. With rising temperature the amorphous cement would soften more rapidly than the crystals, as is characteristic of amorphous materials, and would eventually become the softer component. In tests at high temperature, deformation would therefore occur mainly along the grain boundaries. In the same paper it was reported that the maximum tensile stress increased with rate of strain. This was explained by the amorphous cement theory as follows: 'A very viscous liquid will extend slowly under a comparatively low stress, but it will behave like a brittle solid under one rapidly applied. The familiar example of pitch, which will flow readily but slowly, while it may easily be broken by a blow, illustrates this property clearly. The observations of the authors, demonstrating the large influence of the rate of straining or stretching on the results of tensile tests in their experiments, are thus readily explained by the amorphous cement theory.'

The work was extended to non-ferrous metals by Rosenhain and Ewen,¹ who heated specimens of lead, tin, aluminium, and bismuth to a temperature 50° C below the melting-point, at which point they applied a light load (of 72 lb./sq. in.) and then slowly heated until fracture occurred. This happened 3–20° C below the melting-point, and the fractures were intercrystalline. Hence, it was concluded, at high temperature the grain boundaries are weaker than the crystals. (It may be noted that in neither of these papers was a distinction drawn between shear strength and fracture strength.) The situation was represented as in Fig. 1.1. In Fig. 1.1, at the temperature T_1 , the strengths of the crystals and boundaries are equal. This temperature was later called the 'equi-cohesive temperature'.² Rosenhain and Ewen argued that intergranular fracture in these experiments was not due to a thin grain boundary film of eutectic as the

¹ W. Rosenhain and D. Ewen, *J. Inst. Metals*, 1913, 10, 119.

² Z. Jeffries, *J. Amer. Inst. Metals*, 1917–18, 11, 300. (Also *Science of Metals*, McGraw-Hill, 1924, p. 167.)

materials were too pure for such a film to be present. Perhaps a more cogent point was that a lead-tin alloy which contained much eutectic broke at a temperature about 100°C below the melting-point of lead, instead of $3\text{--}20^{\circ}\text{C}$, the actual temperature of fracture being 0.5°C below the eutectic temperature.

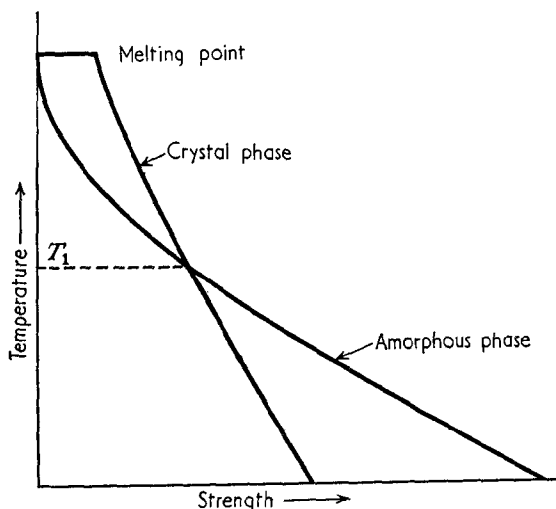


FIG. 1.1. Effect of temperature on strength of crystalline and amorphous phases (after Rosenhain).

This paper contains an account of the mechanism of sliding which supposes that a thick grain boundary is temporarily, but not permanently, necessary for sliding to occur. '... it is not supposed that the layer of intercrystalline cement is thick enough to allow the more or less irregularly shaped crystals to slide past one another freely; the softness of the cement merely removes the boundary support from the crystals, and deformation consequently occurs almost entirely at or near the grain boundaries. As a result of this deformation, fresh quantities of amorphous material will be formed in consequence of molecular disturbance, and from the thickened amorphous layer thus temporarily formed during deformation the excess quantity will recrystallise as soon as the metal comes to rest. At the end of the straining process, therefore, we should expect to find signs of great disturbance at or near the boundaries, and the crystals