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**GRAIN
BOUNDARIES
IN
METALS**

D. McLEAN

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BY

D. McLEAN

NATIONAL PHYSICAL LABORATORY

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**MONOGRAPHS ON THE
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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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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. Brannnt, *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 $3\text{--}20^{\circ}\text{C}$ 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. 187.)