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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Concluding Remarks

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Concluding remarks

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This conference has performed one historic function. Professor Westbrook took us well towards the earliest civilized use of materials with his account of the Babylonian merchant Nanni's complaint, only recently deciphered, about the harmful effects of residuals in metal that he had been sold. Since that date 4000 years ago, knowledge has not only grown, but has become increasingly particularized along separate channels which, as a consequence of our modern specialization, have ceased to communicate with each other. The unrestrictive, thoughtful nature of the conference theme has had the effect that these specialized channels have been brought into communication again.

Many effects of residuals were, so to speak, put on display for all to inspect. Thus, on the practical side: (*a*) in polycrystals, on the cohesion at grain boundaries, usually a weakening effect; (*b*) on the efficiency of surfaces which promote a catalytic action; (*c*) on the rate of corrosion of single-crystal or polycrystalline metal; (*d*) on the cracking of polycrystalline metal during hot rolling. All of these effects arise because residuals may concentrate at the location in question and, since the factor of concentration may be as great as 10^6, sometimes a very large effect is produced by a very small overall concentration. The various scientific reasons for a localized concentration were also publicized: (i) the atoms of residual elements have lower energy when sited at the interface or surface than in the interior; (ii) the scaling of a surface, before or during hot rolling, preferentially absorbs certain elements, the remainder therefore accumulating at the interface between scale and metal; (iii) interfaces are the best sinks for vacancies that drag residual element atoms with them to these locations; (iv) residual atoms combine with other elements to form precipitates. Of these, (ii) and (iii) involve a dynamic equilibrium, and therefore a quantitative theoretical treatment of the equilibrium concentration achieved is more difficult than in (i) or (iv), which involve a thermodynamic equilibrium; indeed, there is not yet any such treatment for (ii). Most of the effects embraced by the conference can therefore be defined as those which are caused by segregation to surfaces or interfaces, which are also those whose study has been given an enormous fillip in recent years because powerful experimental methods, such as examination with the Auger spectroscope, have produced a great quantity of information. These effects have existed for a long time, and it would have been mainly with these that, without knowing it, the Babylonian merchants were concerned.

Probably the only effects little touched on by the conference are those arising from segregation to dislocations (which scientifically is an example of (i) and which affects the flow properties of some metals at low temperature), and also electrical effects in semiconductor materials which, in essence, arise from the non-stoichiometry generated by residuals.

To have held such a conference for the first time has been very profitable. It has provided knowledge which is timely, because historical factors are at work which are inexorably causing residual contents to increase. The pressures for recycling of metal are one such well publicized

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factor. A less publicized but perhaps equally relentless factor is the steadily diminishing metal content of the ores that are being exploited. The harmful results that residuals may have are therefore bound to cause increasing concern. There is also, however, a potential benefit in a greater supply of residuals, as Dr Naylor pointed out, in that there is the possibility of using some of them as the cheapest of alloying elements. To avoid the harmful effects and to secure any good that is possible, the first requirement is extended knowledge. Consequently, a quite general benefit from the conference is the guidance to all those concerned in planning scientific strategy. The conference has shown that over a wide and definable front, which for a long time had remained relatively stagnant, a steady advance is now in progress because precise and direct experiments have become possible. Consequently, for some time to come, effort placed at any point in this definable front will yield considerable gain. For all those involved in any way, this is clearly useful knowledge, because it helps to plan the future.

A more particular benefit may accrue from the ability to inspect the various specialist channels side by side. In each channel, it is evident that experimental facts are being equally well quantified by the experimental techniques currently available. It is also evident that the degree of scientific comprehension, by contrast, varies a great deal from one channel to another, especially with regard to quantification. One can hope that the side-by-side comparison, and the stimulation to be derived from the channels that are in front, will encourage development of better scientific comprehension in the channels that lag.

To emphasize this point, reference can be made to a specific comparison. Temper brittleness is a malady that has recurred for decades. It was one of the first to be studied with the techniques for surface examination, and its theory has recently seen the prodigious advance described in Dr Guttmann's paper. Consequently Dr Seah and Professor McMahon were able in some degree to finalize their own distinguished contributions by drawing up a specification for tolerance limits to residual contents based on scientific comprehension, in the sense that they were derived from an examination of experimental data in the light of quantitative theory, so that, for example, they take account of interactions between the different residual elements as well as of temperature sensitivity. Overheating and burning are maladies with equally long histories, and many experimental facts have recently been quantified with the same surface techniques. Using these data, Dr Hartley and Dr Yamaguchi were also able to draw up specifications for tolerance limits to residual contents. However, the theory of these effects is not well quantified, perhaps because the dynamic equilibrium referred to above is involved, and consequently these specifications remain empirical. *Ipso facto*, they have the merit of immediate applicability within the composition range already investigated, but even within this range there is no guarantee that nothing important has been overlooked, and that no unnecessary but expensive limitation has been included. There is a long history of theoretical advances which make possible more reliable judgements of what to do next – from the efficiency of steam engines improving continuously after Carnot provided the correct scientific guide, to energy extraction per kilogram increasing enormously where it is possible to follow Einstein's theoretical guide concerning the equivalence of mass and energy. There seems no reason why this good principle should not apply in the modest domain under consideration to provide the best promise of efficiency, reliability and cheapness. Especially should quantitative theory be valuable where phenomena such as temper brittleness, overheating and burning are all presumptive ailments, so that it is necessary to chart a narrow course as regards the composition and treatment which avoids them all.

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Of such a conference, the first ever of its kind, it is pertinent to ask: Has anything substantial been omitted? Has all progress been recorded?

As regards the first question, one significant omission has been the large body of Japanese work, the only representative of which was the very competent paper by Dr Yamaguchi mentioned above. The high cost of travel between Japan and Europe may have much to do with this omission. During a recent visit there I offered to mention some of this substantial body of relevant work and accordingly was given material to show. For these written remarks I have selected from this material two items which lie in my own field of interest, and have chosen them because I can appreciate them best. They are both concerned with the variability in behaviour among grain boundaries in a given metal, a factor potentially significant for segregation and precipitation at grain boundaries, though so far it has not been explored much.

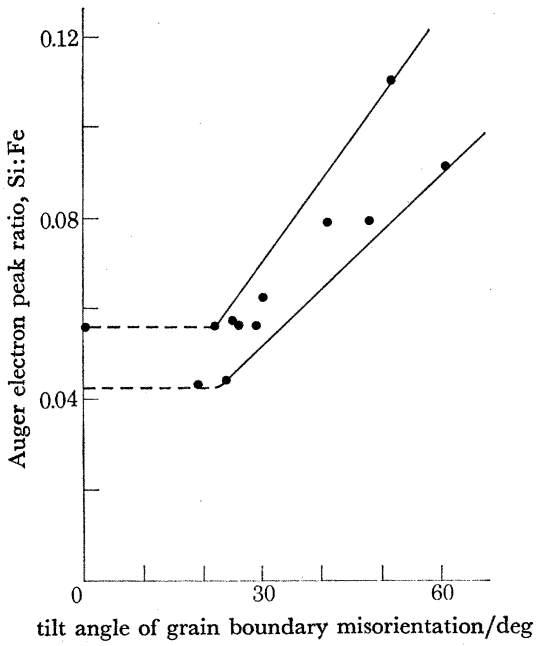

FIGURE 1

Figure 1 shows the results of measurements made by Kokawa *et al.* (1978) of Si in grain boundaries of Fe, as a function of misorientation. The measurements were made on bi-crystals, and show segregation continuing to increase with misorientation angle up to the large angles characteristic of ordinary polycrystals; therefore, with silicon dissolved in polycrystalline iron, one would expect substantial variation of the segregation from one boundary to another. Ogura (personal communication) has a good deal of qualitative evidence pointing in the same direction for the segregation of phosphorus in a Ni–Cr ferritic steel, the principle of his method being that on suitably etching a sample of the steel in the segregated condition, different grain boundaries etch to widely differing degrees. Figure 2 shows results of measurements of grain boundary self-diffusivity in iron polycrystals made by Y. Ishida (private communication). The abscissa is the relative diffusivity, and the ordinate is the number of times that each diffusivity was encountered in the area examined. In this figure there is a wide spread of diffusivities, amounting to at least 20:1. These results therefore demonstrate that grain

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boundaries in a given polycrystal are far from identical. If some are less dangerous than others with regard to a particular behaviour, e.g. segregation or precipitation, there arises the possibility of a useful means of property control.

Regarding the second question, a single domain in the wide field spanned by this conference served as my own particular test of the progress registered. The domain in question is the influence on mechanical properties of segregation at grain boundaries; it is a domain I have followed closely for many years. Here, it is very clear that the wealth of accurate experimental information provided by the surface techniques now available has proved to be a great stimulus, since there are new ideas in circulation which were adequately vented, e.g. Guttmann's theory of multi-component segregation, described in his lucid and comprehensive paper. Again, theories of grain boundary cohesion and the effect of segregation were discussed by Dr Hirth and Dr Asaro with a degree of precision scarcely thinkable only a few years ago. However, to understand properly the influence on mechanical properties, it is necessary to know whether

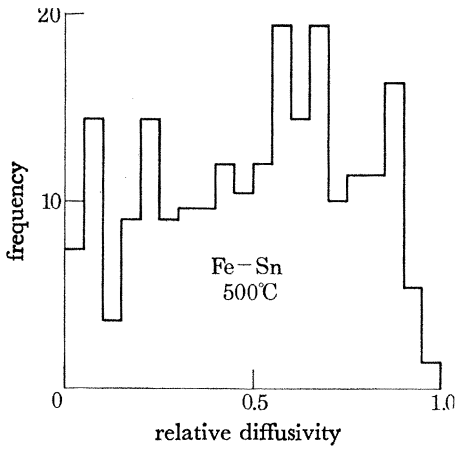

FIGURE 2

segregation affects dislocation glide in the vicinity of grain boundaries since difficulty of glide as well as reduced cohesion can induce brittle behaviour. Hitherto there has been no experimental means of study, but Dr Dingley's new X-ray technique for measuring elastic strains over distances of the order of 1 μm promises to open a door to such studies. As far as this test goes, therefore, the answer to the second question is that the conference in fact registered hitherto unrecorded progress.

How should this conference be followed up? Few would be rash enough to suggest that it be the start of yet another international series of conferences. In any event, a more specific follow-up seems appropriate, suited to the state of affairs revealed. Here there are two items: first, the near certainty that there will be rapid scientific progress in an area containing industrial problems that are already significant, and which are growing; second, concerning this whole area, there exists a spirit of empiricism in industry, whereas in detached centres such as Government and University laboratories there exists a substantial level of scientific comprehension. The former is cautious about the latter, knowing from experience that clearly predicted improvements are often accompanied by unexpected side-effects, while the latter is nevertheless impatient to try out its knowledge on the industrial scale. Instead of organizing further conferences, it is better to recall a precedent that will resolve these differences and result in the

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quickest progress. In the past, the British metallurgical societies have set up temporary committees to deal with particular matters, e.g. the Ingots Committee in the 1930s, the Alloys in Iron Committee of the 1940s; metallurgical societies in other countries follow this practice today. Judging by these examples, the equivalent temporary body might be the most helpful form that any future organization might take.

In Britain certainly, and in some other countries also, the state of the subject, the prevailing intellectual climate, and the nature of the people who are interested, all augur well for the success of any such body concerned with residuals, additives and materials properties.

Reference (McLean)

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