SEGREGATION OF BORON TO GRAIN BOUNDARIES IN IRON AND A STAINLESS STEEL

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Résumé. — Nous avons étudié l'effet du bore sur les énergies de joint de grains et les énergies de surface du fer à 900 et 1 000 °C et de l'acier inoxydable AISI 316 entre 950 et 1 250 °C. Il est montré que le bore réduit ces énergies comme le font les éléments à faible solubilité.

Abstract. — The effects of boron on the grain boundary and surface energies in iron at 900 and 1 000 °C and AISI 316 stainless steel in the temperature range 950-1 250 °C were investigated. It was found that boron reduced these energies in a manner typical of an element with low solubility in the matrix.

It has been found that boron improves the grain boundary strength of iron at low temperatures [1] and increases the creep rupture life and ductility of austenitic steels and nickel alloys at high temperatures [2]. Measurements of grain boundary and surface energies were used to determine whether equilibrium segregation of boron to these interfaces occurs in iron and AISI 316 stainless steel. The techniques used were the standard ones of measuring the ratios of twin and grain boundary energies to the surface energy from the profiles formed during vacuum annealing at the intersections of these boundaries with the surface. By assuming that the boron content of the materials did not affect the twin boundary energy, its effect on the relative surface and grain boundary energies was assessed. The multiphase equilibration technique [3] was used to obtain a value of surface energy for one of the steels and this and a literature value of surface energy for boron free iron were used to estimate the absolute values of all the interfacial energies. Details of the energy measurements are given elsewhere [4].
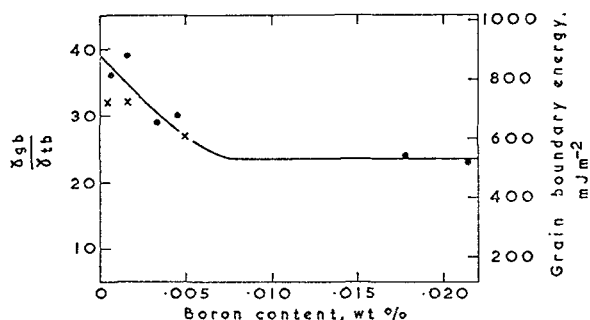
Figure 1 shows the effect of boron additions on

FIG. 1. — Grain boundary energies in iron boron alloys at 1 050 °C.

the grain boundary energies of iron samples equilibrated at 1 050 °C. Additions of boron caused a progressive decrease in the grain boundary energies until the boundaries had apparently become saturated with boron. Similar effects of boron additions were found at 950 °C and for the surface energy values at both temperatures. Measurements on pairs of 316 steel samples with different boron concentrations showed comparable reductions in the grain boundary energies. The data obtained are summarised in the table below with some results taken from Hodgson [5] for nickel-boron alloys, showing similar behaviour to the iron-boron alloys. The right hand figure in column 3 for the iron and nickel alloys is the approximate bulk concentration at which the interfaces became saturated with boron.

The similarity between the results in the iron, 316 steels and nickel, both in the size of the effect and the bulk concentration of boron at which the minimum value of the interfacial energy was reached, is marked despite a wide variation in the impurity content of the alloys. The large reductions in grain boundary and surface energies caused by additions of boron indicate that it segregates to these interfaces at the annealing temperatures used. For the iron and nickel alloys the type of behaviour observed is typical of that for solutes of low solubility. Hondros and McLean [6, 7] found a reasonable correlation, figure 2, between the *interfacial activity*, the initial steep slope of the interfacial energy versus bulk concentration curve, and maximum atomic solubility — solutes with a very low solubility having a very high interfacial activity. The activity values calculated for boron in both iron and nickel were high and fitted well with the general trend.

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TABLE I

*Reductions in grain boundary and surface energies
with increasing boron concentration*

Material	Temp. °C	Change in B concn, ppm	Reduction in γ_{gb}		Reduction in γ_{sv}	
			%	mJ m^{-2}	%	mJ m^{-2}
Fe alloys	950	0 — 40	26	240	12	280
	1 050	0 — 70	40	350	22	380
316 steel	950	10 — 60	12	45	— 6	— 35
containing	1 050	10 — 60	34	210	29	255
0.05 wt %	1 150	10 — 60	39	310	18	180
carbon	1 250	10 — 60	20	130	9	70
316 steel	950	10 — 65	16	55	12	70
containing	1 050	10 — 65	29	160	0	0
0.12 wt %	1 150	10 — 65	29	200	20	220
carbon	1 250	10 — 65	25	150	— 8	— 53
Ni alloys	900	0 — 100	35	360	20	400
	1 000	0 — 100	50	420	35	700

Seah and Hondros [8] have defined a grain boundary enrichment factor, β, which is the ratio of the monolayer fraction of solute at the grain boundary to the bulk atomic concentration :

$$\beta = \frac{X_{gb}/X_{gb}^0}{X_c} = \frac{\partial\gamma_{gb}/\partial X_c}{X_{gb}^0 . RT}$$

where $\partial\gamma_{gb}/\partial X_c$ is the grain boundary activity. Their correlation between β and the limit of solubility at the temperature of the measurements is shown in figure 3. The values of β for boron in iron at

1 050 °C and in nickel at 1 000 °C are in reasonable agreement with this correlation.

These correlations cannot be extended to the 316 steel measurements because of the lack of data for boron free steel. However, the similarity of the effect of boron on the grain boundary energies in 316 steel to that in iron and nickel suggests that it acts in much the same way in the chemically more complex steel at the temperatures used, where it has a single phase fcc structure. In other words its segregation behaviour in all three materials is typical of a low solubility solute.
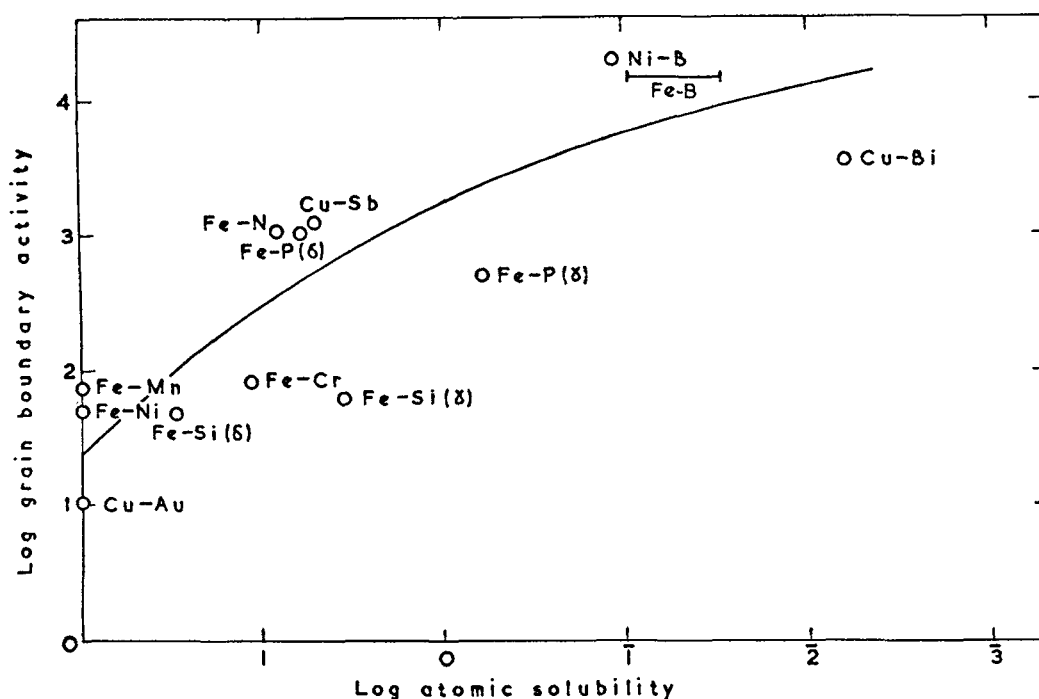

FIG. 2. — Grain boundary activity as a function of maximum atomic solid solubility.
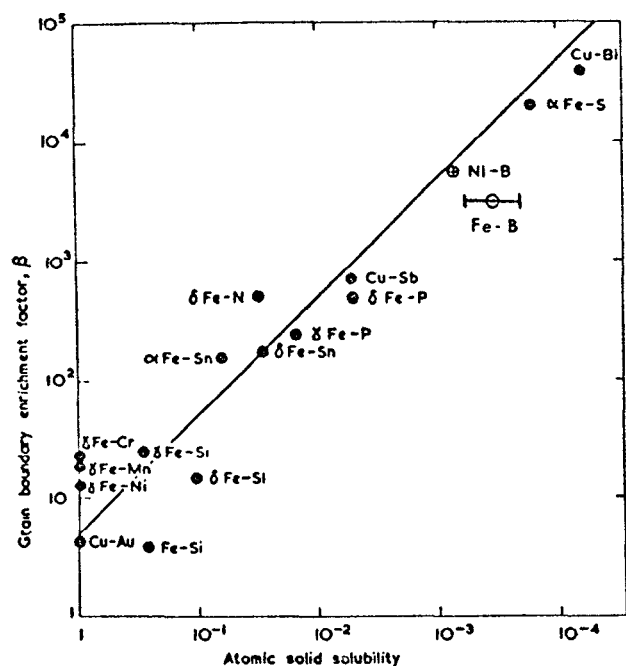
FIG. 3. — Correlation of grain boundary enrichment factor with atomic solid solubility.

Segregation of solutes to grain boundaries is usually associated with grain boundary embrittlement. This effect is explained by the reduction in the free energy $2 \gamma_s - \gamma_b$ which must be supplied to produce unit area of new surface by fracture at a grain boundary. Calculations [9] based on this simple criterion indicate that boron should cause grain boundary embrittlement in iron and nickel alloys. The fact that this is not found to be the case stresses the importance of taking into account the many other factors involved in deformation and fracture processes. In systems where impurities are associated with embrittlement, correlations have been found between interfacial energy changes and a reduction in grain boundary strength or cohesion. However, by studying systems in which an interfacially active solute is associated with apparent strengthening of the boundaries it has been possible to show that such changes in interfacial energy are not necessarily sufficient to produce grain boundary embrittlement. Instead, the embrittling tendency can be overcome by other effects of the solute, such as interaction with carbide precipitates in 316 steel or interaction with other impurities in iron.

References

[1] TAGA, H. and YOSHIKAWA, A., Proc. ICSTIS, Suppl. Trans. ISI Japan 11 (1971) 1256.

[2] WILLIAMS, T. M., HARRIES, D. R. and FURNIVAL, J., J. Iron Steel Inst. 210 (1972) 351.

[3] ALLEN, B. C., Trans. Met. Soc. AIME 236 (1966) 903.

[4] MORTIMER, D. A., Ph. D. Thesis, University of Warwick (1973).

[5] HODGSON, B. K., Ph. D. Thesis, University of Warwick (1972).

[6] HONDROS, E. D. and MCLEAN, D., SCI Monograph 28 (1968) 39.

[7] HONDROS, E. D., Interfaces Conference, Melbourne (1969).

[8] SEAH, M. P. and HONDROS, E. D., Script. Metall. 7 (1973) 735.

[9] MORTIMER, D. A., 4th Bolton Landing Conference « Grain Boundaries in Engineering Materials » (1974).

DISCUSSION

S. HOFMANN : Is not the relation between grain boundary enrichment and ambrittlement you assume only valid if the Griffith theorem is applicable ? If the segregated element may enhance microductility in the grain boundary, this is not the case in a strengthening effect should occur.

D. MORTIMER : Yes, this is so, and it is precisely because of the possibility of effects such as the one you describe that I feel caution should be exercised when interpreting mechanical property effects in terms of interfacial energy charges.

B. MICHAUT : Dans vos expériences, avez-vous fait la différence entre la ségrégation du bore et la précipitation de borocarbures ?

D. MORTIMER : Nous avons fait toutes nos expériences dans un domaine de température où on peut supposer que les matériaux ont une seule phase. C'est-à-dire pour les aciers, nous avons utilisé des températures supérieures à 950 °C.

E. D. HONDROS : I do not think that anyone will clain dogmatically that there is necessarily a connection between high enrichment factor and a propensity for intergranular weakness. The evidence at present is that generally it is so, among the many systems studied, with the exceptions of carbon and boron in iron, which appear to ameliorate an already embrittled condition. There may be other exceptions : the reason for the specific behaviour of these elements is not altogether clear althought there are many speculations.

E. d'HEURLE : Is it not to be anticipated for grain boundary embrittlement as for g. b. diffusion that

adsorption of solute atoms may increase or decrease either one of these two phenomena ? Some adsorbed solutes are knewn to decrease g. b. an diffusion in Al ; people interested in enhancing the sintering of powders select solutes to increase the rate of autodiffusion, e. g. addition de (MgO-CaO) to Al_2O_3.

D. MORTIMER : The diwing force for equilibrium segregation to grain boundaries is a decrease in their free energy γ_b. However, the presence of the segregated element will also affect the surface energy, γ_s of a grain boundary fracture surface. In a completely brittle system it is the difference 2 $\gamma_s - \gamma_b$ which determines whether the segregation causes embrittlement or strengthering. As γ_s is probably not the equilibrium surface free energy it cannot readily be measured, thus making predictions of the mechanical effect of segregation difficult, even in a completely brittle situation where the Griffith criterion is applicable. In fact, in real systems, there are usually other complicating factors and one can of course anticipate that either boundary embrittlement or strengthening will occur according to the interaction of the variouseffects of the solute elements.

G. MARTIN : Un problème me préoccupe quand on utilise le critère de Griffith dans les solutions solides fragiles :

— L'énergie d'interface qu'on récupère lorsque la fissure progresse le long du joint est sans contestation possible l'énergie intergranulaire du joint abaissée par la ségrégation intergranulaire.

— L'énergie de surface que l'on doit dépenser pour créer les deux faces de la fissure, quelle est-elle : l'énergie de la surface abaissée par la ségrégation superficielle d'équilibre ? ou l'énergie d'une surface de l'alliage en présence d'une ségrégation superficielle incomplète ?

Il doit en fait y avoir une compétition entre la vitesse de propagation de la fissure et la vitesse de formation de la couche adsorbée sur la surface fraîche.

Ce point ne peut-il pas expliquer vos observations ?

D. MORTIMER : Si ce type de mécanisme agit dans le cas du bore dans le fer et dans les aciers inoxydables, il doit agir aussi dans les cas des autres solutions solides. Il n'explique pas donc pourquoi le bore a une action *anormale* sur les propriétés mécaniques en même temps qu'il semble avoir un effet *normal* sur les énergies des joints de grains.

J. PLATEAU : Il ne faut pas oublier que la formule de Griffith est valable dans le cas d'un solide idéal non susceptible de se déformer plastiquement. Les extensions qui en ont été faites à des cas concrets supposent que l'on prenne en compte dans le taux d'« énergie superficielle » celle qui correspond à la déformation locale qui accompagne la propagation de la fissure.

D. MORTIMER : Je suis tout à fait d'accord sur ce point. C'est pour une telle raison qu'on peut être surpris qu'il y ait tant d'accord entre les prédictions des effets utilisant le critère de Griffith et les propriétés mécaniques mesurées dans les autres systèmes.