A Study of Intergranular Fracture in Iron Using Auger Spectroscopy

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Low temperature impact tests on three fairly pure irons have shown that the propensity for intergranular fracture is largely independent of prior heat treatment. Furthermore, the effects of carbon and oxygen contents and carbon:oxygen ratio were found to be opposite to those previously reported. Examination of fracture surfaces by Auger Spectroscopy showed that sulfur was strongly segregated to grain boundaries but showed no evidence of oxygen segregation. The fracture behavior of specimens previously tested in creep or high temperature fatigue differed from that of untested specimens in that fracture was predominantly by transgranular cleavage.

IT has long been known[1,2] that iron can exhibit intergranular embrittlement at low temperatures but the detailed mechanism for this behavior is not understood. The embrittlement seems to be dependent on small variations in carbon content and on heat treatment.[3] Rellick and McMahon[4] have suggested that the embrittlement may be due to oxygen segregated to the grain boundaries whilst carbon is dispersed within the grains, this being achieved by quenching from about 970 K. Quenching from successively lower temperatures resulted in increasing ductility which was attributed to carbon segregating to the boundaries and interacting with the oxygen. It was also shown that the addition of aluminum prevented embrittlement irrespective of quenching temperature, presumably by acting as an oxygen scavenger. Jolly and Goux[5] have observed similar effects but show evidence that sulfur rather than oxygen was the embrittling element. Honda and Taga[6] investigated the effect of carbon and oxygen on the fracture of electrolytic iron, slowly cooled from 973 K. The tensile properties were independent of oxygen content in the range 0.002 to 0.016 pct but the fracture changed from transgranular to intergranular below a critical carbon content of 0.002 pct.

Embrittlement can result from the adsorption of minor impurities at grain boundaries, with consequent reduction of the interface energy. The subject has recently been reviewed by Hondros.[7] Changes in the grain boundary and surface energy can also lead to reduced creep fracture resistance since the nucleation and growth of cavities depends on the energy required to create new surfaces. For instance Tipler and McLean[8] have shown that the addition of 0.3 at. pct antimony to copper halved the creep fracture elongation of that material.

Until recently it was difficult or impossible to obtain direct evidence of grain boundary segregation, but the technique of Auger electron spectroscopy can now be used for this purpose. This technique, for example, has demonstrated the segregation of antimony and phosphorus to grain boundaries in steels.[9,10] The availability of an Auger analysis system equipped with a fracture stage operating in UHV, and a fine focus electron gun, which permits the chemical analysis of the surface of individual grains on the fracture surface, has made it possible to identify unambiguously impurities segregating to the grain boundaries.

The present study arose originally from a wish to exploit low temperature intergranular embrittlement in iron in order to study the morphology of cavities produced on grain boundaries during creep and fatigue at high temperatures. This technique was used successfully by Taplin and Wingrove[11] on BISRA AH iron but attempts to use it on an iron of similar composition, namely "Ferrovac E," were only partly successful.

EXPERIMENTAL

The present work is mainly on "Ferrovac E," but two other irons have also been studied and the compositions, together with those of the two alloys used by Rellick and McMahon[4] are shown in Table I. In view of the reasonable similarity in composition of all the alloys together with the large range of carbon:oxygen ratios in our materials, it was decided to investigate the effect of heat treatment on subsequent low temperature fracture.

Specimens of the three alloys were machined into cylinders 12 mm long by 3 mm diam and subjected to the heat treatments shown in Table II. These treatments were selected in view of the creep and fatigue testing program which involved testing over the temperature range 723 to 973 K. Following the work of Rellick and McMahon, it was thought that slow cooling from the test or annealing temperature would permit carbon to segregate to the grain boundaries and prevent embrittlement. Reheating for $\frac{1}{2}$ h at 983 K followed by quenching, however, by dispersing and retaining the carbon within the grains, was expected to produce embrittlement. On this basis, Treatments 1 and 4 were expected to result in embrittlement whereas Treatments 2 and 3 should not.

Treatments were under vacuum of nominally 1 Pa but slight oxidation did occur. The quenched specimens were annealed in evacuated Vycor capsules, the quench being achieved by breaking the capsules under water.

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Table I. Chemical Composition of Materials

	Alloy	Composition, wt pct C	O	C O Ratio	S	N	Others
Rellick & McMahon	F5	0.0056	0.0023	2.44	N.A.*	0 008	–
	F5-Al	0.0062	0 0025	2 48	N.A *	0 0021	0 047Al
Present Work	Ferrovac E	0 007	0.010	0.70	0.005	0.003	0 010Al
	A.H	0.005	0.042	0.12	N.A.*	0.05	–
	N.P.L.I	0.0023	0.0008	2.88	0.0014	0 0003	0.005 (total)
	N P.L. II	<0.001	0.004	<0 25	0 01	N A.*	0.002Al 0.004 Si

*Not available.

Table II. Heat Treatments for Impact Specimens

Treatment 1	24 h at 983 K–furnace cooled + ½ h at 983 K, quenched
Treatment 2	24 h at 983 K–furnace cooled
Treatment 3	24 h at 983 K–furnace cooled + 24 h at 773 K, slow cooled
Treatment 4	24 h at 983 K furnace cooled + 24 h at 773 K, slow cooled, + ½ h at 983 K- quenched

Table III. Heat Treatments for the Auger Specimens

Treatment 5	1 h at 973 K in vacuum tube. Vacuum tube then air cooled
Treatment 6	1 h at 973 K in vacuum tube Vacuum tube then furnace cooled.
Treatment 7	1 h at 973 K in evacuated Vycor capsule. Capsule then broken under water.

Table IV. Heat Treatments to Produce Larger-Grained Specimens of "Ferrovac E" for Auger Analysis all Furnace Cooled

Heat Treatment 8	½ h at 973 K in air.
Heat Treatment 9	24 h at 973 K in vacuum.
Heat Treatment 10	½ h at 973 K in air + 24 h at 973 K in vacuum.

After heat treatment the specimens were notched, immersed in liquid nitrogen and fractured by impact. Fracture surfaces were then examined in a Cambridge scanning electron microscope.

The cylindrical impact test specimens could not be dealt with in the Auger system. Therefore, another set of specimens 2 sq mm in cross-section, 15 mm long were prepared for the fracture surface analysis. In view of the impact results, a simplified heat-treatment schedule was adopted for these specimens for all three compositions (see Table III). The results obtained with these specimens caused us to prepare a further set of specimens of "Ferrovac E," which had a larger grain size and permitted the analysis of individual grains on the fracture surface (see Table IV). The specimens in the Auger apparatus were notched and fractured in 3-point bending at temperatures down to 153 K.

The Auger apparatus used initially was a three-grid LEED system operated as a retarding field analyzer.[12] Either an oblique incidence electron gun giving a current of 10 μA or a normal incidence gun (giving 2 μA within a circle of 200 μm) could be used. Both guns were normally operated at 1500 V. The background pressure in the vacuum system was typically 2×10^{-8} Pa, the residual gas being mainly CO. To achieve this vacuum the apparatus had to be baked for 24 h at 520 K with the specimens in position. The Auger analysis specimens therefore received a further heat treatment which would allow the carbon to diffuse significantly.

The variation of chemical composition of the fracture surface as a function of position was studied by taking spectra with the normal incidence gun at 0.25 mm intervals across the fracture surface by moving the specimen with micrometer drives on the specimen manipulator. In this way the whole of the fracture surface was analyzed and the spectra obtained compared with subsequent scanning electron micrographs of the surface.

Subsequently results were obtained with a cylindrical mirror analyzer Auger system,[13] but with this system the high spatial resolution was not available.

RESULTS

It was expected that the different heat treatments would result in different proportions of intergranular: cleavage fracture. In the case of the "Ferrovac E" and N.P.L. I iron, however, fracture seemed to be largely indpendent of heat treatment. "Ferrovac E" subjected to Treatment 1 showed completely intergranular fracture. Specimens subjected to Treatments 2, 3, and 4 showed some cleavage areas but in all cases, fracture was estimated to be at least 90 pct intergranular. The N.P.L. I iron exhibited slightly more cleavage area than "Ferrovac E" but again the ratio of intergranular:cleavage was very high with no significant dependence on treatment. In the case of the AH iron, the specimen subjected to Treatment 1 showed slightly more cleavage than intergranular area. Specimens subjected to Treatments 2, 3, and 4 showed increasing proportions of intergranular area but the increase was not regarded as very significant.

The heat treatments 5, 6, and 7 for the specimens tested in the Auger system were chosen to simulate the testing and cooling conditions experienced by the creep and fatigue specimens. Not all the specimens could be fractured successfully because of limitations in the force that could be applied. Interpretation of results from specimens that did show areas of intergranular fracture was complicated by the difficulty of ensuring that the electron beam was hitting only the fracture surface, and by post fracture contamination from the residual gas. However, none of the specimens showed unambiguously oxygen segregated to the fracture surface. The N.P.L. I iron after heat treatment 7 gave a fracture surface which was mainly intergranular and this specimen also clearly showed sulfur in the fracture surface composition.

In other experiments with "Ferrovac E" it was found that only in specimens that had suffered some (accidental) oxidation during heat treatment prior to creep testing, was the fracture predominantly intergranular on subsequent low temperature fracture; oxidation alone or vacuum annealing alone was insufficient. In view of this a further set of specimens was prepared for Auger fracture surface analysis, as detailed in Table IV.

These treatments were expected to produce specimens showing intergranular fracture after treatment 10, but not after 8 or 9. Useful results were obtained from specimens subjected to treatments 9 and 10. In

both cases specimens were fractured at 153 K. The grain size of these specimens was considerably larger (about 500 μm) than those previously prepared, so that Auger spectra could be obtained from individual grains using the normal incidence gun. Separate analyses of intergranular and transgranular (cleavage) surfaces were therefore obtained.

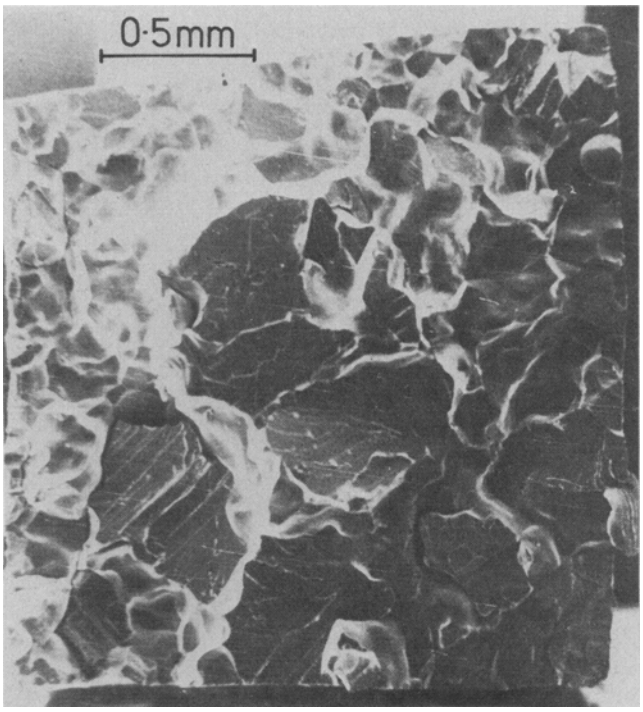
Fig. 1(*a*) shows a scanning electron micrograph of "Ferrovac E" after heat treatment 10. Specimens given heat treatments 9 and 10 gave similar results. Auger spectra from a cleavage and an intergranular area from a specimen given heat treatment 9 are shown in Fig. 2. As expected, all the cleavage surfaces gave pure iron spectra[14] immediately after fracture (*e.g.*, curve II in Fig. 2). The ambient atmosphere was such that 6 h after fracture carbon and oxygen which had adsorbed from the residual gas could just be detected on the cleavage areas. The intergranular fracture surface immediately after fracture gave a spectrum (curve I in Fig. 2) with a large peak from sulfur and smaller peaks from carbon and nitrogen, as well as the iron peaks. A plot of the peak to peak height of the sulfur Auger peak across the fracture surface shown in Fig. 1(*a*) is shown in Fig. 1(*b*). The correlation of a large sulfur peak with intergranular regions is clearly shown.

Argon ion bombardments, calculated to remove the top six atom layers from the fracture surface, removed more than 95 pct of the sulfur peak in the Auger spectrum. This shows that the sulfur was segregated uniformly at the boundaries and was not in the form of sulfide particles.

A repeat of the experiment, on a specimen given heat treatment 9, using the more sensitive cylindrical mirror analyzer gave a spectrum from a sulfur rich area on the fracture surface as shown in Fig. 3. This spectrum shows strong sulfur and carbon peaks and also peaks due to nitrogen and oxygen. However, the oxygen peak was small and showed no correlation with the sulfur peak when the electron beam was moved across the fracture surface whereas the carbon and nitrogen peaks did. This fracture was performed in a somewhat poorer vacuum (2×10^{-7} Pa) so it is probable that the oxygen peak and perhaps also some of the carbon is due to post fracture contamination.

Accurate quantitative estimation of surface composition from Auger spectra is difficult, but Hondros and Seah[15] have recently reported a spectrum from an intergranular fracture of an iron containing 44 ppm sulfur which shows a sulfur peak which agrees well with that shown in Fig. 3. Hondros and Seah estimate this peak height to represent 0.5 monolayers of sulfur and we also estimate the mean sulfur concentrations on the intergranular fracture surfaces to be 0.5 monolayers. The amount of oxygen present is even more difficult to estimate but comparison spectra obtained from a deliberately oxidized clean iron surface suggest that the retarding field analyzer results would detect an oxygen concentration greater than 2 pct of a monolayer.

In view of the strong indication of sulfur as the impurity responsible for segregation an alloy containing 0.01 pct S was prepared by N.P.L. (Alloy N.P.L. II in Table I). Specimens of this alloy were tested in creep at 973 K at a constant stress of 5.6 MN per sq m. The fracture strain was very low (0.17 pct elongation) and the specimen showed greatly increased cavity nucleation. A micrograph of such grain boundary cavities is shown in Fig. 4. The results with this alloy provide further evidence that sulfur is the dominant impurity with regard to grain boundary segregation and embrittlement for iron. These results may be compared to



(*a*)

41	13	106	45	108	108	90	10
15	121	126	95	68	123	82	80
100	173	0	0	48	133	111	112
123	137	0	0	53	0	103	87
94	92	49	4	0	0	116	135
113	0	0	16	125	52	44	13
63	106	60	0	24	108	0	91
107	125				54	98	111

(*b*)

Fig. 1—(*a*) Scanning electron micrograph of the fracture surface of a "Ferrovac E" specimen fractured at 150 K after heat treatment 10. The areas of intergranular and transgranular failure are easily distinguished. (*b*) Relative sulfur Auger peak heights across the fracture surface shown in (*a*).

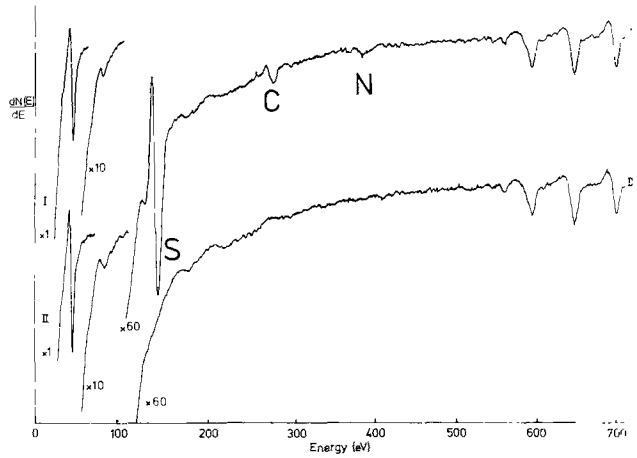


Fig. 2—Auger spectra obtained from intergranular (curve I) and transgranular (curve II) areas of a "Ferrovac E" specimen fractured at 150 K after heat treatment 9. The non-iron peaks on curve I are labelled with the chemical symbol of the elements producing them. Incident beam energy 1.5 keV. Modulation voltage above 100 eV, 5 V r.m.s., below 100 eV, 2 V r.m.s.

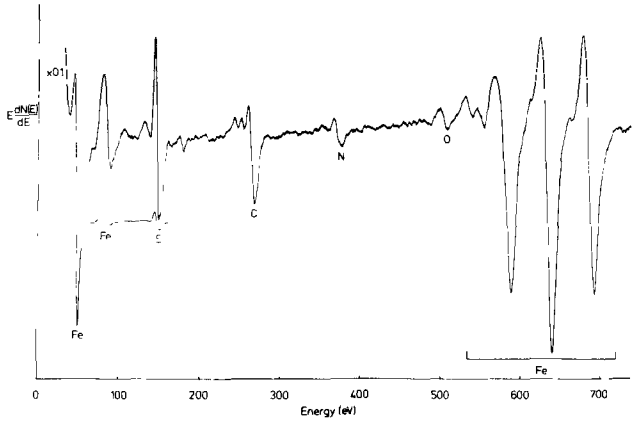


Fig. 3—Auger spectrum obtained with a hemicylindrical mirror analyzer from a "Ferrovac E" specimen fractured at 150 K after heat treatment 9. (Note: Y-axis measures $E\,dN(E)/dE$ in arbitrary units). Incident beam energy 2.5 keV. Modulation voltage, 3 V r.m.s.

those of Beevers and Kirby[17] who have found that the presence of phosphorus in similar N.P.L. iron alloys seems to reduce cavitation during creep at 973 K.

DISCUSSION

The initial experiments indicated that the low temperature fracture behavior of the three alloys was fairly independent of heat treatment both in terms of annealing temperature and cooling rate. This was unexpected in view of the work of Rellick and McMahon[4] who found that slow cooling from about 973 K could prevent embrittlement. Also surprising was the fact that N.P.L. iron fractured intergranularly. This relatively pure iron had both a very low oxygen content and a high carbon:oxygen ratio. The AH iron, however, having both the highest oxygen content and the lowest carbon: oxygen ratio showed rather more cleavage than intergranular fracture. These results are in direct conflict with the explanation for embrittlement proposed by Rellick and McMahon. The impact fracturing technique differed from that of Rellick and McMahon who used tensile testing. It might be expected, however, that impact loading would increase the likelihood of cleavage fracture whereas the reverse appears to be the case. In the same context, it may be that the fracture mode is sensitive to variations in specimen geometry.

The results of the Auger spectroscopy are perhaps the most important to emerge from this work. The evidence of sulfur segregation to the grain boundaries is unequivocal, particularly in the case of the specimens which gave Auger scans from both cleavage and intergranular regions. This result is supported by that of Hondros and Seah.[15] These results, however, are somewhat in opposition to those reported by Rellick *et al.*,[16] who show Auger spectra from a Ferrovac iron fracture surface and from an Fe-0.15 pct Ti alloy fracture surface which show no sulfur but some oxygen, carbon, and nitrogen. Rellick *et al.* suggest that the oxygen may be due to post-fracture contamination and our results taken under similar conditions would tend to confirm this. The absence of sulfur in their traces indicates that in this case sulfur is not the embrittling species

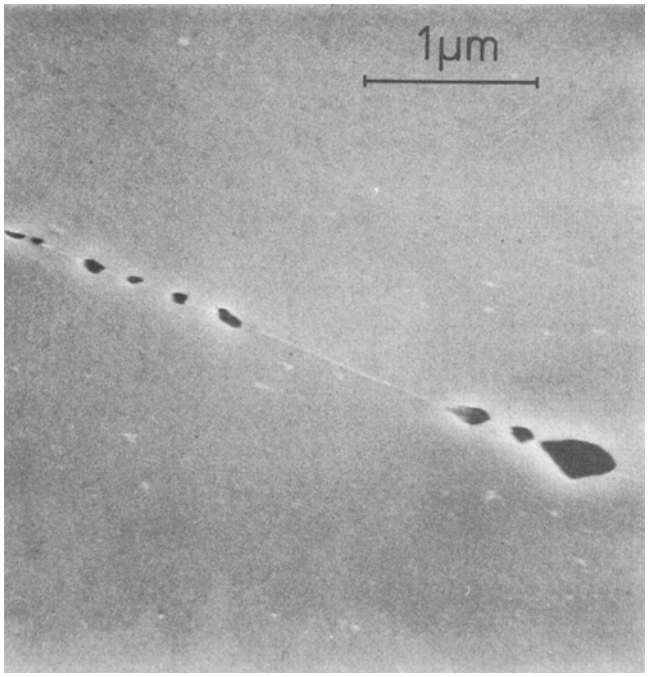


Fig. 4—Scanning electron micrograph of longitudinal microsection of Alloy N.P.L. II after creep at 873 K at a stress of 5.6 MN/m^2 for 1 h showing grain boundary cavities. The fracture strain was 0.17 pct. (Micrograph courtesy of G. Leone).

and that perhaps nitrogen is responsible. The presence of carbon, on the ideas of Rellick and McMahon, would be de-embrittling.

Unfortunately no sulfur contents are available for the irons used by Rellick *et al.*, so no comparison with our results is possible. Taking the grain boundary concentration of sulfur from our measurements to be one monolayer (*i.e.*, twice 0.5 monolayers on each fracture surface) and a grain boundary width of 2 at. diam, this represents a grain boundary sulfur concentration which is 10^4 times the bulk value for "Ferrovac E" and about 3×10^4 times the bulk concentration for N.P.L. I, which agrees with the results of Hondros and Seah.[15]

Honda and Taga[6] have attributed intergranular embrittlement of iron solely to carbon content. It is note-

worthy, however, that the carbon and oxygen concentrations in their iron were very similar to those of other impurity elements; in particular, sulfur (0.004 pct) and phosphorus (0.002 pct) were present, both of which are known to embrittle iron. No Auger spectroscopy was performed in this work.

Despite the evidence for sulfur at the grain boundaries the embrittlement phenomenon is still not fully explained. In particular, specimens of "Ferrovac E" previously tested in creep or fatigue at 973 K did not generally fracture along the grain boundaries when subsequently notched and impacted under liquid nitrogen. Early unsuccessful attempts were attributed to large grain size but later tests on materials having comparable grain size to that used for the embrittlement specimens ($\simeq 80\,\mu$m mean diam) also resulted in predominantly cleavage fracture. After creep or fatigue testing, "Ferrovac E" has a pronounced dislocation subcell network within the grains and the grain boundaries often become serrated because of interactions with sub-boundaries. It is possible that this may influence the low temperature fracture mode so that cleavage fracture becomes more likely. It is also possible that the vacancy flux to the grain boundaries under creep conditions may have some effect on the boundary region composition.

CONCLUSIONS

1) The low temperature fracture behavior of the three irons, in terms of relative proportions of intergranular:cleavage areas was relatively independent of annealing temperature and cooling rate.

2) The tendency for intergranular fracture appeared to increase with increasing carbon:oxygen ratio and with decreasing oxygen content. This behavior is opposite to that previously reported.[4,18]

3) Auger spectroscopy showed that sulfur was heavily segregated to grain boundaries. No clear evidence of oxygen at grain boundaries was found suggesting that sulfur is responsible for the intergranular embrittlement.

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REFERENCES

1. J. R. Low and R. G. Feustel *Acta Met*, 1953, vol. 1, pp 185-92.
2. W. P Rees and B. E. Hopkins *J. Iron Steel Inst*, 1952, vol. 172, pp 403-09
3. C. J McMahon: *Acta Met.*, 1966, vol 14, pp. 839-45.
4. J. R. Rellick and C. J. McMahon, Jr.. *Met. Trans.*, 1970, vol 1, pp 929-37.
5. P. Jolly and C. Goux *Mem. Sci Rev. Met.*, 1969, vol 66, pp 605-17.
6. R. Honda and H. Taga *Met Sci J*, 1968, vol. 2, pp. 172-76
7. E D Hondros. in "Interfaces Conference, Melbourne 1969", pp. 77-100, R C Gifkins, ed., Publ. Butterworth, Sydney, 1969
8. H. R. Tipler and D McLean. *Met. Sci. J.*, 1970, vol. 4, pp. 103-07.
9. P. W Palmberg and H L Marcus *Trans. ASM*, 1969, vol. 62, pp 1016-18
10. H. L. Marcus and P. W. Palmberg *Trans. TMS-AIME*, 1969, vol. 245, pp 1664-66.
11. D. M. R. Taplin and A. L. Wingrove *J. Mater. Sci.*, 1969, vol. 4, pp. 789-96.
12. R E. Weber and W T. Peria *J. Appl. Phys*, 1967, vol. 38, pp. 4355-58.
13. P. W. Palmberg, G. K. Bohn, and J C. Tracy *Appl Phys Lett*, 1969, vol. 15, pp. 254-55.
14. T W. Haas, J. T. Grant, and G. J. Dooley: *Phys. Rev. B*, 1970, vol. 1, pp. 1449-59.
15. E. D. Hondros and M. P. Seah *Scr. Met.*, 1972, vol. 6, pp 1007-12
16. J. R. Rellick, C. J McMahon, Jr., and H. L. Marcus *Met. Trans.*, 1971, vol 2, pp. 342-43
17. C J. Beevers and B. Kirby: private communication, University of Birmingham, Department of Physical Metallurgy, Birmingham, England.
18. D. S. Tomalin and D. F. Stein *Trans TMS-AIME*, 1965, vol 233, pp 2056-62.