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Grain boundary sensitization and desensitization during the ageing of 316L(N) austenitic stainless steels

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Two casts of type 316L(N) austenitic stainless steel have been solution treated for 1 h at 1070 °C, air-cooled, then aged for up to 20 000 h at temperatures between 550 °C and 750 °C. Grain boundary precipitation of the $M_{23}C_6$ phase occurs, and the Cr composition profile normal to the grain boundaries has been determined at high resolution by an analytical electron microscope. The data have been fitted firstly to collector plate models, which indicated that some of the material was in the process of desensitization, or 'healing', indicated by a rise in the boundary Cr content. The data were then fitted to a model of the Cr profile as a function of ageing treatment in the 'healing' regime, and a good correlation was obtained.

1. Introduction

The phenomenon of sensitization in stainless steels refers to a susceptibility to intergranular corrosion resulting from microstructural change. It occurs either from slow cooling from a solution anneal temperature or by reheating in the temperature range 500–800 °C.

The theories proposed to explain sensitization have been critically reviewed by Wilson [1], Hanninen [2] and Cowan *et al.* [3], and it is widely held that the phenomenon arises from the local depletion of Cr due to the precipitation of Cr-rich carbides along the grain boundaries. If the Cr level falls below the required value to form a protective passive film, this leads to susceptibility to intergranular corrosion.

The object of the present work has been to apply a high-resolution analytical electron microscope to measure the depletion of Cr adjacent to the grain boundaries of two 316L(N) steels during extended periods of ageing. This would establish the temperature regimes in which sensitization occurs, and also the extent to which, at long ageing times, "healing" occurs by the diffusion back into the boundaries from the interiors of the grains at a rate higher than the rate of Cr removal from the boundary by carbide growth.

2. Experimental procedure

Two type 316L(N) steels have been studied, cast by Krupp and by Creusot Loire respectively. Their chemical analyses are given in Table I. The steels were solution treated for 1 h at 1070 °C, air cooled, then aged at temperatures between 550 °C and 750 °C for periods up to 20 000 h. Thin foils were prepared for observation in a Philips CM12 analytical electron microscope used in the STEM mode. In order to produce a Cr composition profile normal to grain boundaries, an electron probe of 10 nm diameter was used. Those grain boundaries in which the boundary plane was parallel to the electron beam direction at 20 degree tilt were chosen for the Cr composition profile normal to the grain boundaries. The probe was stepped manually on both sides of grain boundaries in increments varying from 20 nm around the grain boundary region to 100 nm in more remote regions of the matrix.

The results were quantified using the Link System RTS2 computer program. which uses a peak stripping routine from stored standard spectra, then applies the Cliff–Lorimer [4] factor which is independent of the specimen thickness and composition, and varies only with the potential of the microscope. Error bars for compositional analysis were determined by making multiple measurements at a single point. In all cases this error was less than ±0.7 wt %.

The thickness of the foil for each analysis area was determined using convergent beam electron diffraction (CBED) as described by Kelly *et al.* [5]. In view of the time-consuming nature of this technique, the following procedure was followed.

Starting from an edge of a hole in a foil, a number of points were randomly selected when traversing towards the thicker region. For each point the thickness was measured by CBED and the net integral (i.e. the integrated area without background) and the gross integral (i.e. the integrated area with background) was obtained by selecting a large window (0–20 keV) on each spectrum.

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TABLE I Chemical compositions of the steels (wt %)

Steel	C	Si	Mn	Ni	Cr	Mo	S	P	B	N	Co	Cu
Krupp	0.022	0.23	2.05	12.45	17.50	2.40	0.007	0.023	4 p.p.m[a]	0.068	0.05	0.05
Creusot Loire	0.025	0.30	1.79	12.44	17.43	2.40	0.0008	0.021	9 p.p.m[a]	0.078	0.024	0.1

[a] p.p.m. = parts per million

A linear relationship was obtained when the thickness values were plotted against integral values for each point, and this method of foil thickness measurement has been discussed fully elsewhere [6]. CBED was employed to measure the foil thickness for the Krupp samples, and the net integral method was used for the Creusot Loire samples.

3. Experimental results

The Cr concentration profile has been determined across a number of low angle grain boundaries, so that isolated carbide particles rather than continuous carbide films were present (Fig. 1). The traverse was made with a grain boundary crossing point which was at least 500 nm away from the nearest carbide.

Fig. 2(a) shows the effect of ageing time on the Cr profile for Krupp samples which had been aged at 650 °C for 16 h, 100 h, 1000 h and 5000 h, where it may be seen that the minimum Cr concentration at the boundary is below 13%. Up to an ageing time of 100 h the Cr concentration at the boundary decreases, while above this ageing time it increases. It is also noticeable that a small peak in the Cr level was detected on either side of the boundary in both the 16 h and 100 h specimens. No explanation can be offered for this effect.

Fig. 3(a) shows the effect of ageing temperature on the Cr profile across the boundary for samples aged for 1000 h at 600 °C, 650 °C, 700 °C and 750 °C. As can be seen, the width of the region containing less than 13% Cr decreases (270 nm, 120 nm and 0 nm) and the wt % Cr at the boundary increases (9.8%, 11.8% and 13.7%) with increasing ageing temperature. The worst intergranular attack might therefore be anticipated for the material aged at 600 °C for 1000 h for the range of temperatures and times studied.

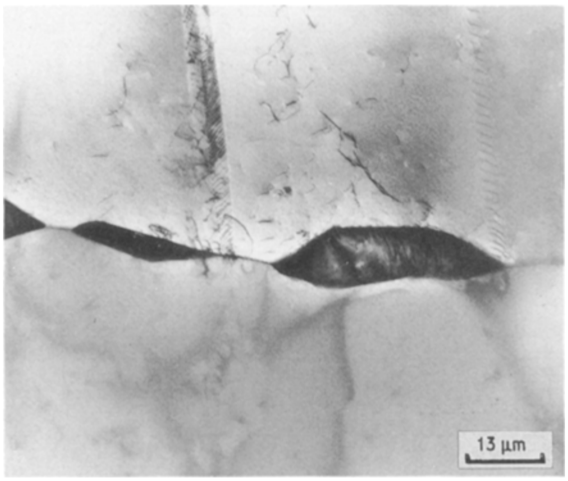


Figure 1 Transition electron micrograph showing precipitation of $M_{23}C_6$ phase in grain boundary of Krupp specimen aged at 750 °C for 1000 h.

Fig. 2(b) shows the effect of ageing time at 650 °C upon the Cr profile in the German Creusot Loire material, and Fig. 3(b) illustrates the effect of 10 000 h and 20 000 h ageing at different temperatures upon the profile. Here again, there is evidence of desensitization or "healing" becoming apparent after long ageing times.

4. Discussion

The models of grain boundary sensitization most commonly employed use the collector plate mechanism of grain boundary precipitate growth outlined by Aaron and Aaronson [7] and Brailsford and Aaron [8]. In order to render the problem amenable to analytical solution, a number of assumptions have commonly been made. These include:

1. grain boundary precipitates have a lath-like morphology, giving rise to planar diffusion fields;
2. diffusion along the boundary is sufficiently rapid for the composition at the boundary to remain constant;
3. the grain extends to infinity away from the boundary;
4. the diffusion of chromium is much slower than that of other components, so only the diffusion of this element need be considered.

Using these assumptions several workers have modelled the chromium composition profile at a grain boundary (e.g. [9, 10]). The form of equation used in these studies is the error-function solution of Fick's second law:

$$\frac{C_x - C_{gb}}{C_{bulk} - C_{gb}} = \mathrm{erf}\left(\frac{x}{2(Dt)^{1/2}}\right) \qquad (1)$$

This solution is applicable strictly to diffusion in an infinite solid of composition C_{bulk} to or from an interface of constant composition C_{gb}, and gives the composition C_x at a distance x away from the interface.

The assumption of a constant boundary composition has been critically examined using a finite difference model [11] and the results obtained indicate this assumption is approximately valid for times in excess of 3 h at 650 °C. All of the data in the present study were obtained after ageing for times sufficient for the development of an essentially constant boundary composition profile. The error-function solution has, therefore, been used in the present analysis.

The grain boundary composition has been taken from the experimental values given previously, and

Equation 1 used to generate the appropriate composition profiles, assuming the measured grain boundary compositions are correct. Smith [12] has obtained data for the volume diffusion coefficient (D) of chromium in Type 316 steel:

$$D = D_0 \exp[-Q/RT] \qquad (2)$$

where $D_0 = 6.3 \times 10^6\,\mathrm{m}^{-2}$ and $Q = 243\,\mathrm{kJ\,mol}^{-1}$. The fit to the available composition profiles using these values was, however, poor and alternative values derived for type 304 material using grain boundary chromium profile measurements [10] have been used in this analysis. These give values for D_0 and Q of $2.2 \times 10^4\,\mathrm{m}^{-2}$ and $289\,\mathrm{kJ\,mol}^{-1}$, respectively. A full comparison of the predicted and experimental data is given in Fig. 4.

The results obtained suggest that some of the material is in the process of 'desensitization' or "healing", and the Cr content is seen to rise above the minimum level. Bennett and Pickering [11] have modelled this regime approximately by stopping all carbide growth at a given point in time.

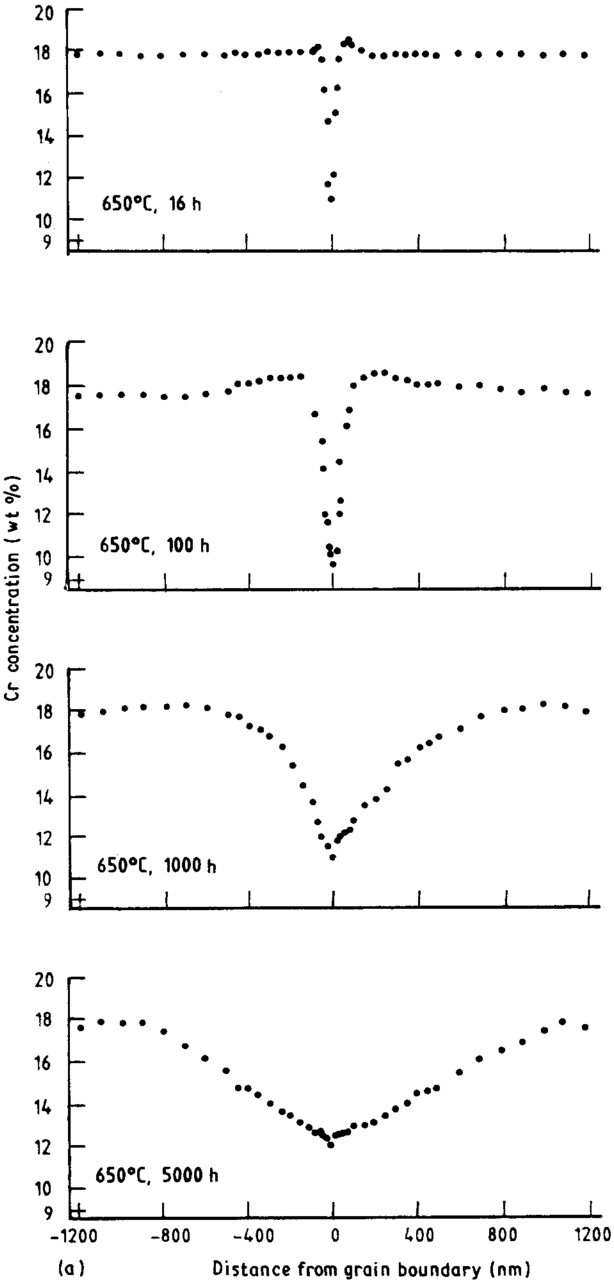
In the present work a more detailed estimation of the healing process has been derived. The equilibrium solute concentration in the boundary has been estimated as outlined by Faulkner *et al.* [13, 14] and based on solubility data obtained by Deighton [15] has been used, together with an estimation of the bulk carbon content obtained using the data of Lai [16]. The boundary solute concentration is assumed to be equal to the equilibrium concentration at the particle/matrix interface, C_i, where:

$$C_i = \left[C_{\mathrm{bulk}}^{-1} \exp\left(\frac{-120960}{RT} - 0.9\right)\right]^{6/23} \qquad (3)$$

This value is then corrected for curvature (Gibbs–Thompson) effects, and C_{gb} is obtained from:

$$C_{gb} = C_x \exp(2\sigma\Omega/RTr) \qquad (4)$$

where r is the radius of curvature of the precipitate at the advancing interface, estimated [14] as 10^{-7} m, Ω is the molar volume ($1.5 \times 10^{-5}\,\mathrm{m\,mol}^{-1}$) and R is the universal gas constant. σ is the carbide/austenite interfacial energy which assumes a value of $0.668\,\mathrm{Jm}^{-2}$ [15]. If the value of C_{gb} is then substituted into Equation 1 a complete model of the chromium profile as a



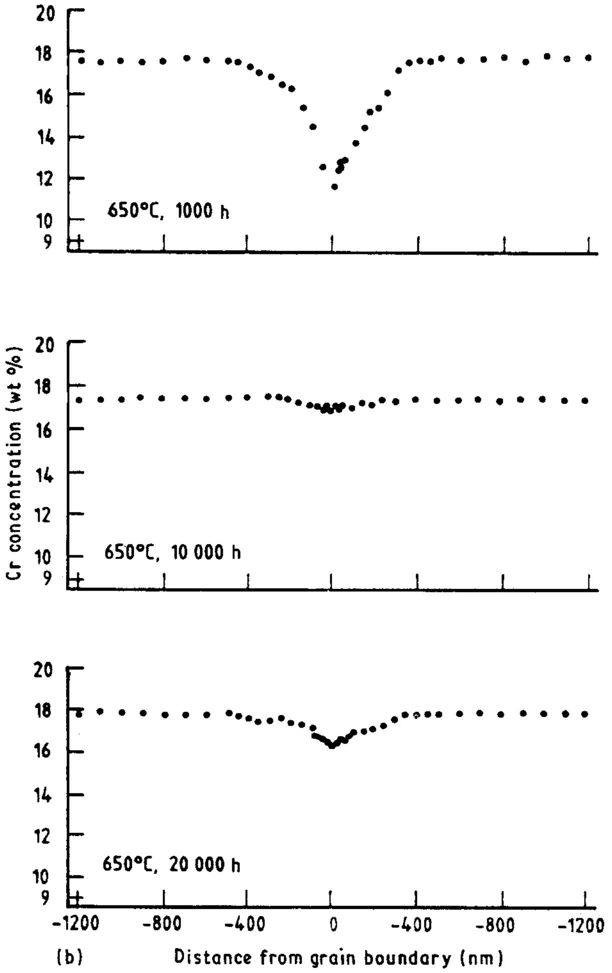


Figure 2 The effect of ageing time at 650 °C on grain boundary Cr concentration profiles in 316L(N) stainless steels, (a) Krupp, (b) Creusot Loire.

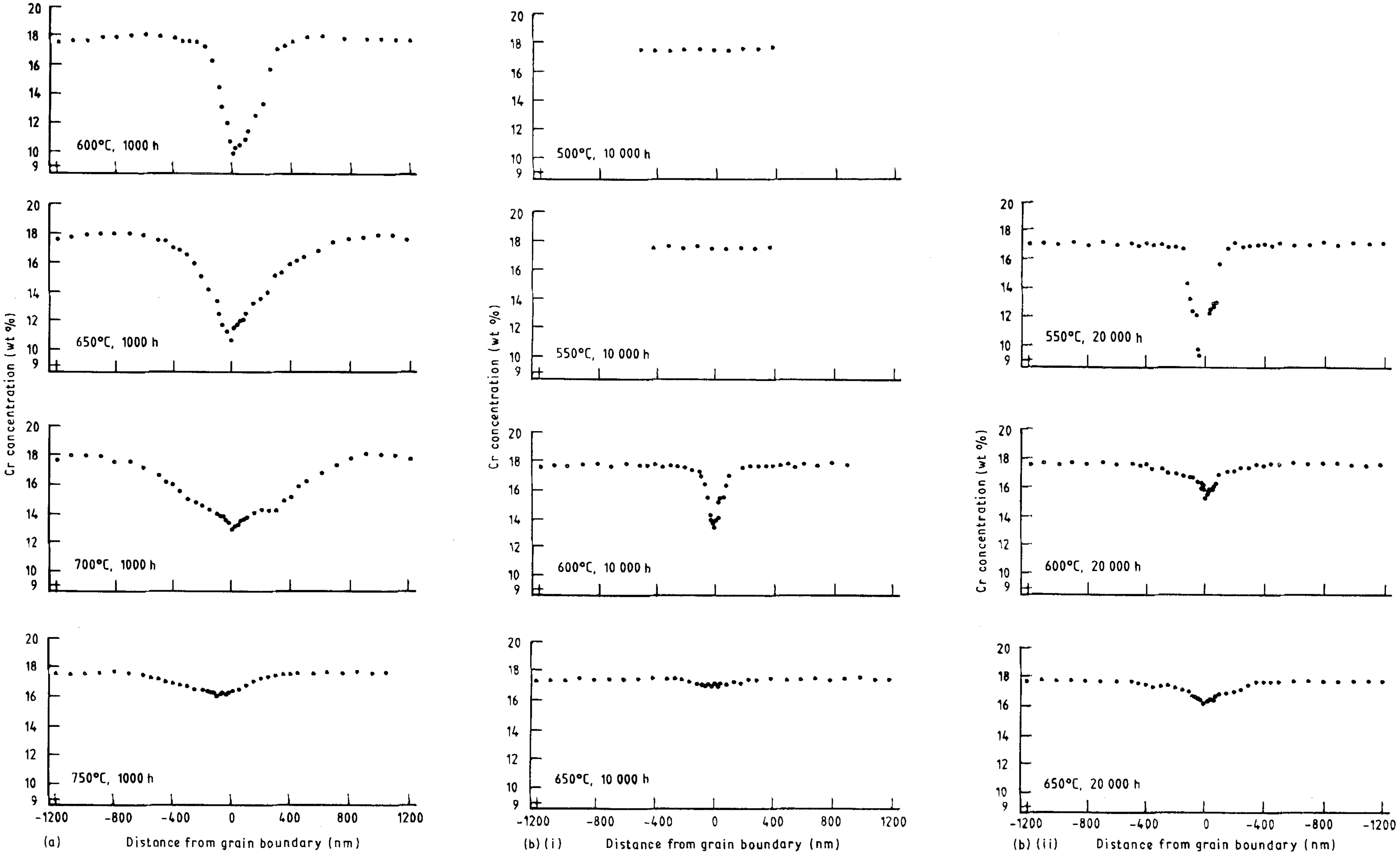


Figure 3 The effect of ageing temperature on grain boundary Cr concentration profiles in 316L(N) stainless steels, (a) Krupp, (b) Creusot Loire.

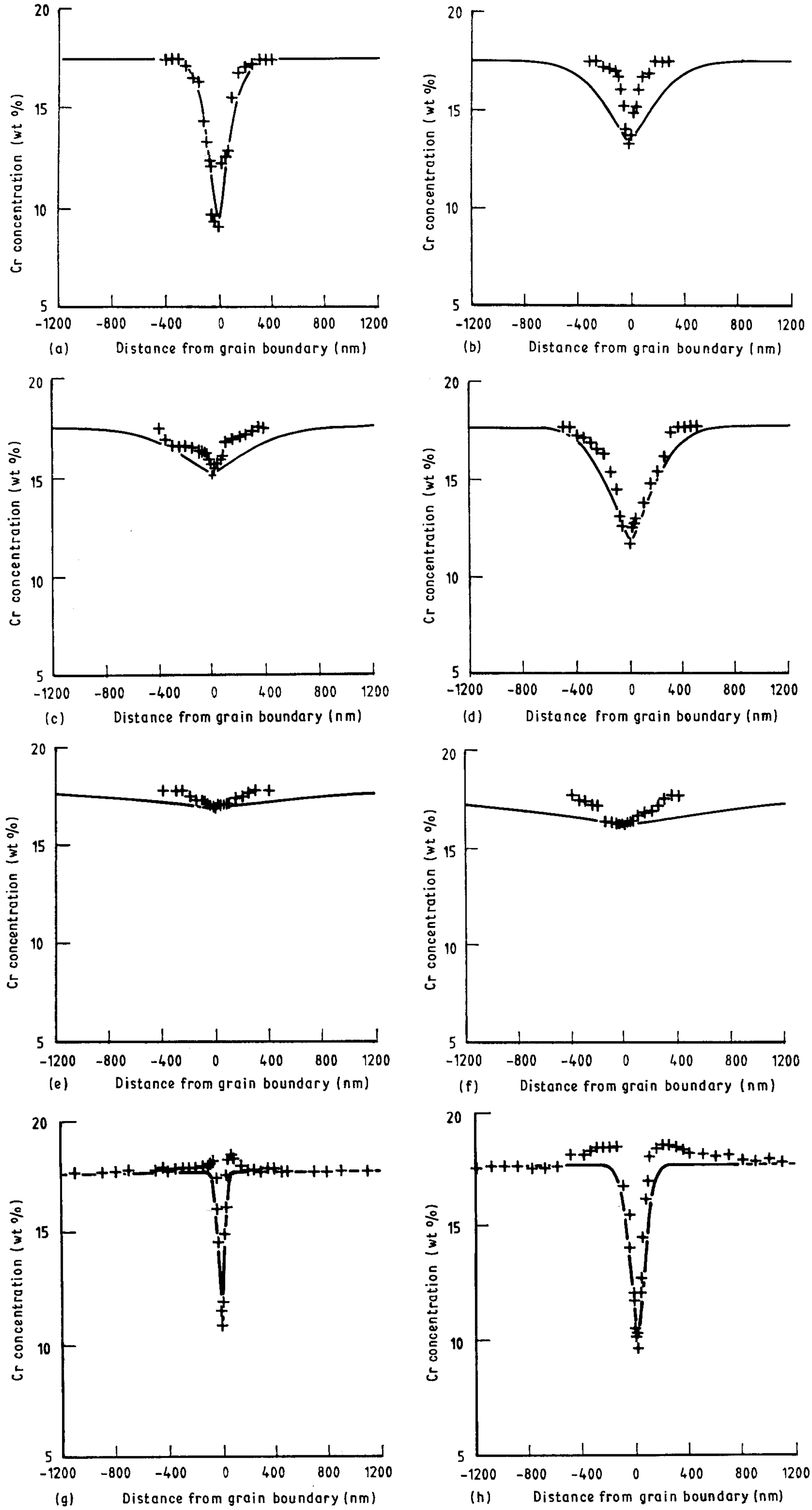
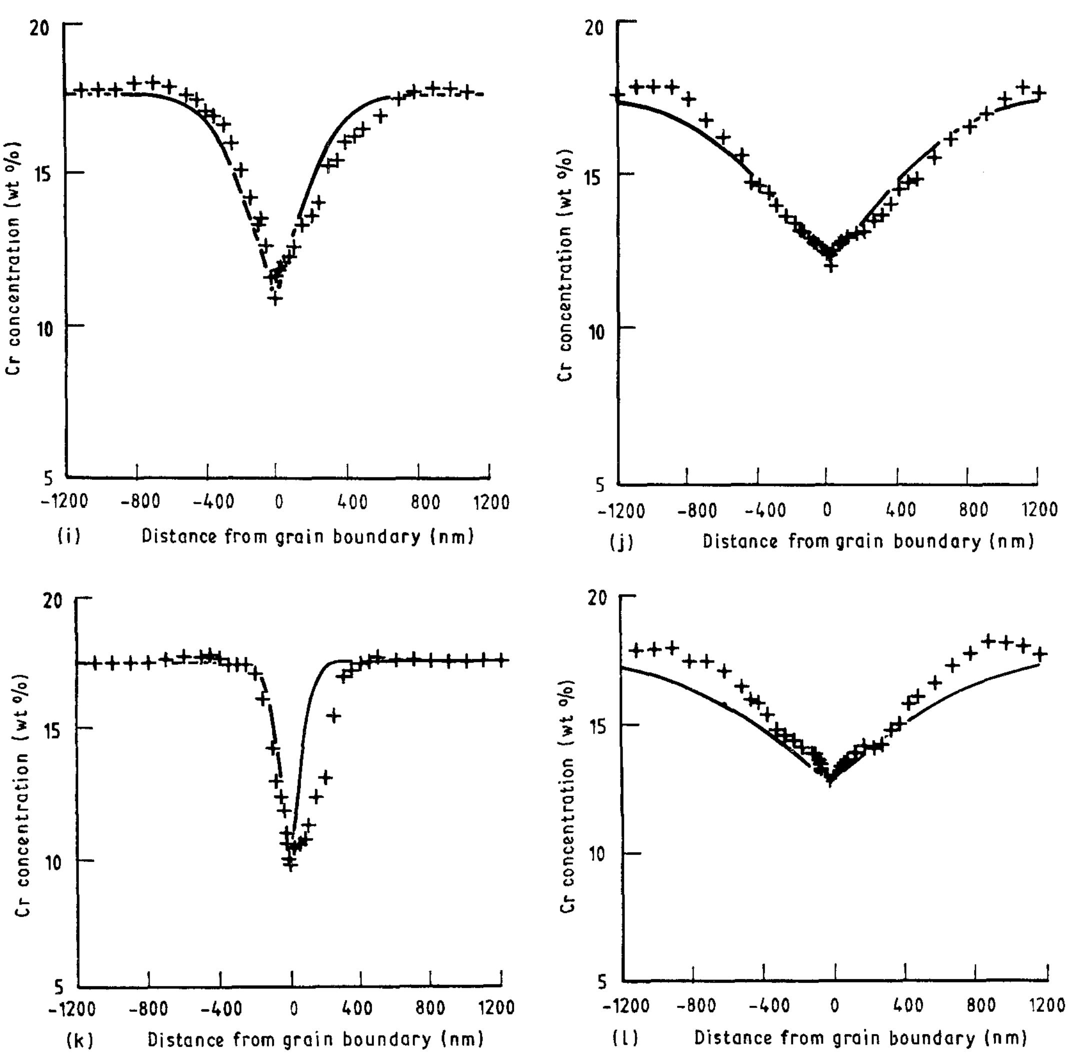


Figure 4 Comparison of measured grain boundary Cr composition profiles with those calculated according to Equation 1.



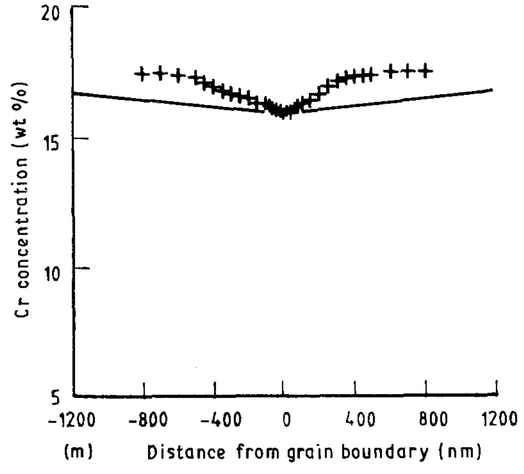


Figure 4 Continued.

function of ageing treatment in the "healing" regime is possible, provided that an indication of the rate of carbon removal from the matrix can be obtained.

Lai [16] showed that the weight fraction of $M_{23}C_6$ carbide in Type 316 steel could be approximately derived as a function of time at temperature using a Johnson–Mehl formulation, such that:

$$\text{wt. fraction } M_{23}C_6 = 1 - \exp[bt_a^n] \qquad (5)$$

where b, n are constants and $t_a = t\exp(-29347/T)$. t is the time in hours and T the temperature in Kelvin.

The data given by Lai [16] have been analysed to give values for n and b of 0.27 and 552, respectively.

The rate of carbon removal from the matrix can then be obtained directly from Equation 5 since the weight fraction of carbon removed is directly proportional to the weight fraction of $M_{23}C_6$ carbides formed (no other carbides occurring). This is then subtracted from the total amount of carbon in the steel to give the matrix carbon content.

Fig. 5 shows the results obtained, and indicates a good correlation with the data for the Krupp material. The model does, however, consistently underestimate the chromium level in the boundary of the Creusot Loire material, suggesting that the rate of $M_{23}C_6$ carbide formation is significantly higher than indicated by Lai's data [16] in this alloy. This is consistent with the experimental data which indicate the kinetics of healing are significantly higher in the Creusot Loire material than in the Krupp plate, but no explanation for this behaviour has yet been found.

The model also fails to reflect adequately the composition profile at longer times, after substantial healing has occurred. This may be attributed to the fact that the model does not attempt to explain the process of healing in detail, but rather provides an estimate of the free carbon available to form carbide and the boundary composition associated with this

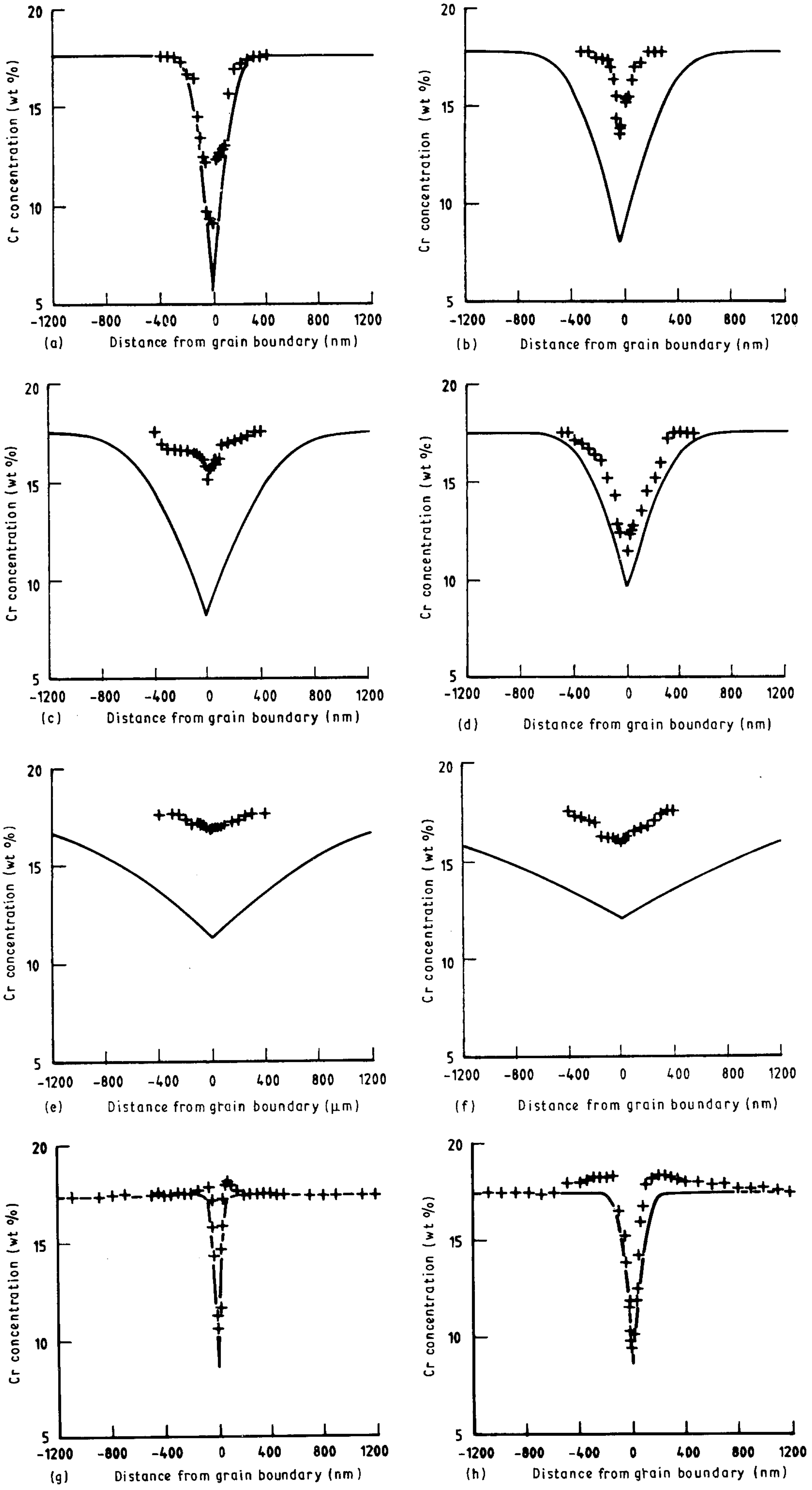
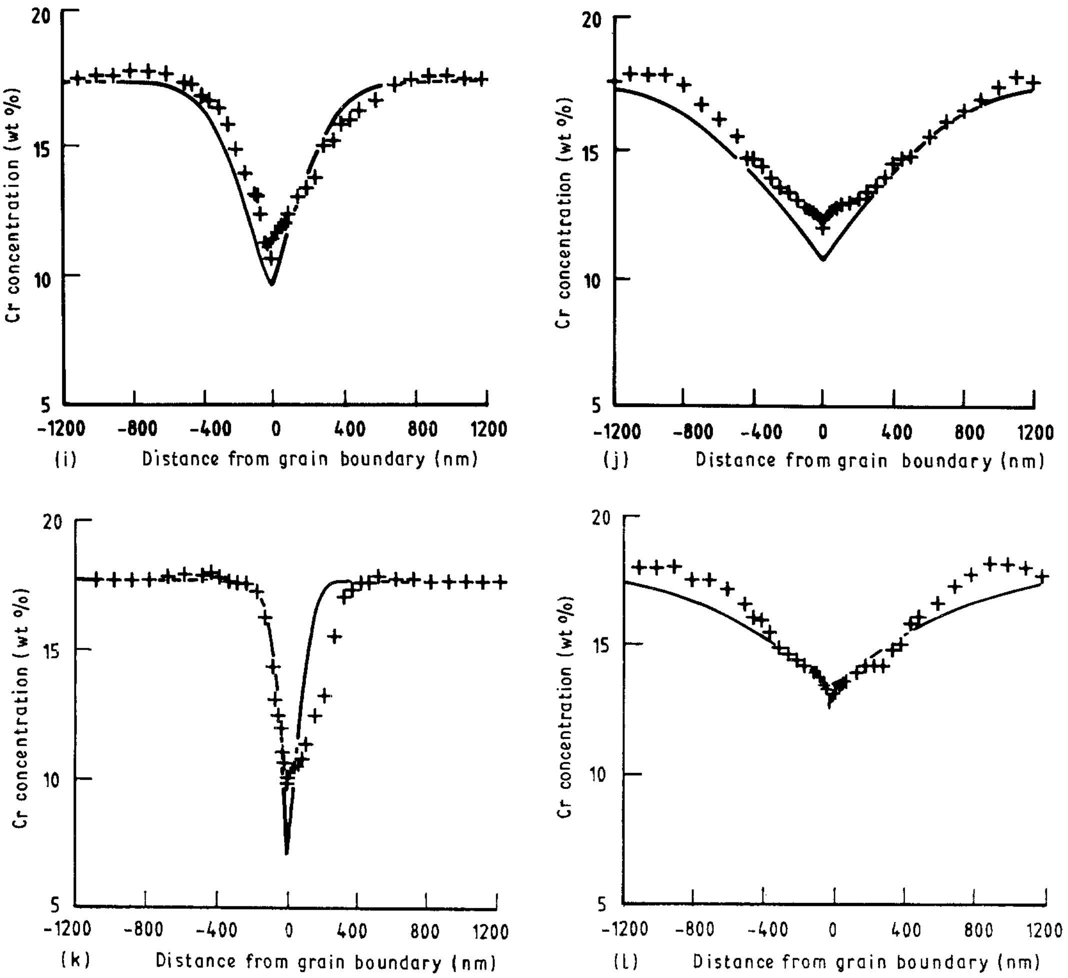


Figure 5 Comparison of measured grain boundary Cr composition profiles with those calculated according to Equation 1 modified by Equations 4 and 5.



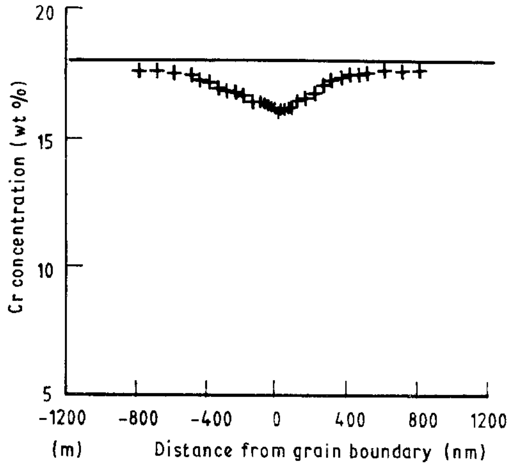


Figure 5 Continued.

level of carbon. The error function employed has been shown to apply to the early stages (but not initial [11] stages of sensitization [17] but may not be strictly applicable to the healing process, in which the grain boundary chromium content is continuously increasing and the composition profile may be affected by previous gradients.

5. Conclusions

1. The Cr composition profile normal to the grain boundaries has been determined at high resolution in two 316L(N) steels as a function of ageing time and temperature. Ageing at 650 °C, the grain boundary Cr concentration decreases up to an ageing time of 100 h, while above this ageing time it increases.

2. For samples aged for 1000 h, the width of the region containing less than 13% Cr decreases and wt % Cr at the boundary increases with increasing ageing temperature, owing to 'healing' processes.

3. The data have been fitted to a collector plate model, and a good correlation has been obtained.

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References

1. F. WILSON, *Brit. Corr. J.* **6** (1972) 100.
2. H. HANNINEN, *Int. Met. Rev.* **24** (1979) 87.
3. R. L. COWAN and C. S. TEDMON, in "Advances in corrosion science and technology", Vol. 3, edited by M. G. Fontana and R. W. Staehle (Plenum, New York, 1973) p. 293.
4. G. CLIFF and G. LORIMER, *J. Microsc.* **103** (1975) 203.
5. P. M. KELLY, A. JOSTSONS, R. G. BLAKE and J. G. NAPIER, *Phys. Status. Solidi.* **31a** (1975) 771.
6. A. TEKIN, A. UGUZ and J. W. MARTIN, *Materials Characterization* **25** (1990) 99.
7. H. B. AARON and H. I. AARONSON, *Acta Metall.* **16** (1968) 789.
8. A. D. BRAILSFORD and H. B. AARON, *J. Appl. Phys.* **40** (1969) 1702.

9. E. P. BUTLER and M. G. BURKE, *Acta Metall.* **34** (1986) 557.
10. T. THORVALDSEN and A. SALWEN, *Scripta Metall.* **18** (1988) 739.
11. B. W. BENNETT and H. W. PICKERING, *Acta Metall.* **36** (1988) 539.
12. A. F. SMITH, *Metal Sci.* **9** (1975) 375.
13. R. A. CAROLAN and R. G. FAULKNER, *Acta Metall.* **36** (1988) 257.
14. R. G. FAULKNER and J. CAISLEY, *Met. Sci.* **11** (1977) 200.
15. L. E. MURR, "Interfacial phenomena in metals and alloys" (Addison-Wesley, Reading, Mass, 1975).
16. J. K. L. LAI, *Mater. Sci. Engng* **58** (1983) 195.
17. T. THORVALDSSON and G. J. DUNLOP, *J. Mater. Sci.* **18** (1983) 793.

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