

AN ISOTHERMAL EMBRITTLEMENT STUDY OF A COMMERCIAL 4% Ni 1% Cr STEEL

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INTRODUCTION

Pre-requisites for the phenomenon of reversible temper embrittlement in steel are the presence of trace impurities [1] (Sn, P, Sb or As) and major alloying elements [2] (Ni, Cr or Mn). The presence of carbon is not a necessary factor but has been shown to increase the degree of embrittlement attained [2]. On heating within or slowly cooling through a critical temperature region (typically 325° - 575°C) the alloying and impurity atoms segregate to the high angle boundaries thus reducing their cohesive strength. Embrittlement manifests itself by an upward shift in the ductile brittle transition temperature with a change in the low temperature fracture mode from cleavage to intergranular. Guttman [3] has shown that the thermodynamics of segregation are consistent with the alloy - impurity interaction being greater than the respective alloy - matrix and impurity - matrix interactions and hence the chemical potential of the system can be reduced by the segregation of these elements to the high angle boundaries. It is generally considered [3,4] that the segregation is of an equilibrium type.

A non equilibrium, transient type of embrittlement was observed by Rellick and McMahon [5] in doped Fe 0.04%C alloys and was explained by a carbide rejection model in which the impurities were rejected from growing carbides into the ferrite/carbide interface, due to their low solubility in Fe₃C. During prolonged ageing treatments, these impurities had sufficient time to diffuse away from the ferrite-carbide interface, thus removing the embrittlement. Ohtani et al [6] have extended this hypothesis to low alloy steels and have suggested that segregation is due to solute re-distribution during carbide precipitation rather than an equilibrium segregation.

In this paper, an Auger Electron Spectroscopy (AES) study of grain boundary segregation, in a commercial 4% Ni 1.2% Cr (EN 30A) steel, as a function of ageing time is described.

EXPERIMENTAL PROCEDURE

Heat Treatments and Mechanical Testing

The alloy studied was a commercial 4.0 wt% Ni 1.20 wt% Cr steel (EN 30A), the composition of which is presented in Table 1. The embrittlement experiments were carried out on specimens in the fully heat-treated condition, which consisted of austenitising for 30 minutes at 950°C followed by oil quenching and then tempering for 1h at 650°C followed by waterquenching. This resulted in a tempered martensite structure and the specimens were the so-called unembrittled state. Subsequent

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temper embrittlement was induced by isothermal ageing for times up to 1000h at 500°C, followed by waterquenching. The degree of embrittlement was monitored using substandard Charpy impact samples to determine the ductile-brittle transition temperature.

AES Measurements

In situ impact fracture, at pressures ~13n Pa and temperatures ~-100°C, was performed using the Harwell impact stage [7]. A Vacuum Generators CMA Auger Spectrometer [8] was used for AES with an integral electron gun providing a spot size on the sample of ~20 µm. Differential spectra were recorded at a modulation of 3V peak to peak, a primary energy of 2.5 KeV and specimen current of 4 µA.

Argon ion bombardment (at 3kV) was used to determine the compositional profiles of segregated species as a function of distance from the grain boundary. For these bombardment conditions, 10 µA min may be approximated to a removal of ~5 monolayers.

Quantification of AES Spectra

To a good approximation the amplitude of an Auger peak in the $dN(E)/dE$ spectrum is proportional to the atomic concentration of the element producing that peak [9]. Quantification was achieved by expressing the peak height as a percentage of the prominent matrix peak (i.e. the Fe 703 eV) and converting to atomic concentrations from a knowledge of the relative elemental sensitivities. The electron sensitivity ratios were discussed in a previous publication [10] and are 0.56; 1.12 and 2.07 for Sn, Ni and P respectively.

RESULTS

Impact Testing

Ageing at 500°C produced rapid embrittlement of the alloy, as shown in Figure 1. The 20 ageing treatment exhibited at 250°C shift in the ductile-brittle transition temperature (T_D) together with a decrease in the upper shelf energy. For longer embrittlement treatments an "over-ageing" effect was noted, namely a decrease in T_D and an increase in the upper shelf energy. The hardness of the material was found to remain constant (~307 V.H.N.) throughout the ageing sequence.

AES Measurements

In situ impact fracture produced an approximately 100% intergranular mode of fracture, with failure occurring along the prior austenite grain boundaries. The AES measurements made on the fracture surfaces showed a much higher concentration of Sn, P and N compared to the bulk values. The Ni concentration was also enhanced but to a lesser degree. A quantification of the grain boundary concentration as a function of ageing time (Figure 2) illustrates the following important features:-

- The grain boundary concentration of Ni and Sn increased to a maximum value, with a subsequent desegregation of both elements for longer ageing times.
- The grain boundary concentration of P increased to a maximum segregation level which remained constant on further ageing.

- The maximum in the Ni and Sn concentrations corresponded to the maximum T_D and hence the "over-ageing" effect in the impact transition curves may be attributed to the desegregation of Ni and Sn from the prior austenite grain boundaries.
- The ratios Ni : P and Ni : Sn at the grain boundaries did not correspond to the expected stoichiometric ratios if they were present as the compounds Ni_3Sn_2 , Ni_3P . This suggests that the elements concentrate at the boundaries independently.

Ion Beam Profiling

The spatial distribution of the segregated species is shown in Figure 3, for the material aged 1000h at 500°C. The P and Sn segregation was confined to the first few monolayers of the grain boundary, whereas the Ni signal gradually approached that of the bulk over a distance of ~30 nm from the boundary.

A significant feature of the profiling was the presence of a maximum in the C concentration approximately ~7.0 nm from the fracture surface. Similar increases in C were noted for other ageing treatments (Figure 4) but the maximum appeared to increase in magnitude and to shift to a greater distance from the fracture surface with increasing ageing time. This increase in the C signal was too large to be attributable to the removal of impurities from the carbide interface. It should be noted that ion bombardment under identical experimental conditions on a ductile fracture surface produced no significant increase in the C concentration (Figure 4).

DISCUSSION

The over-ageing effect observed in the transition curves was due to the desegregation of Ni and Sn away from the grain boundary, indicating that a non equilibrium segregation had been produced. One explanation of these observations is the carbide rejection model [5,6] which postulates that grain boundary (or carbide interface) enrichment of Ni is produced by its rejection from the growing carbides. This enhanced Ni concentration provides the driving force for segregation of the trace impurities, thus reducing the chemical potential of the system. Alternatively, carbide rejection of the trace impurities could also be argued. These observations of non equilibrium segregation does not preclude an equilibrium component and it is postulated that this value would be approached on prolonged ageing.

In contrast to Ni and Sn, the P concentration was apparently stable, indicating an equilibrium form of segregation.

A significant result of the present study was the identification of a maximum C concentration in a region displaced from the fracture surface. This observation suggests that the crack did not follow the carbide/ferrite interface but propagated in a zone adjacent to it. This C redistribution as a function of ageing time could play an important role in the temper embrittlement mechanism and is being examined in greater detail.

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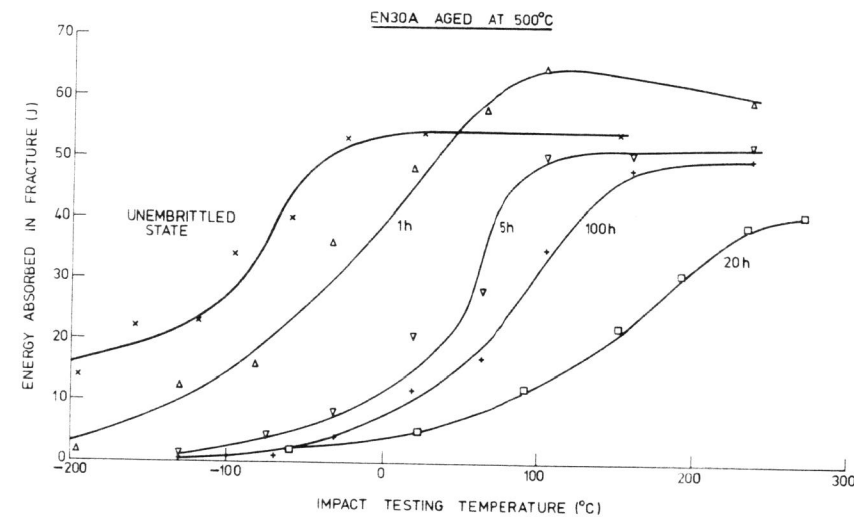


Figure 1 Impact transition curves of EN 30A as a function of ageing time at 500°C

Table 1 Composition of EN 30A Steel

Element	wt%	Element	ppm
Ni	4.06	S	<150
Cr	1.20	Sb	40
Mn	0.58	P	130
C	0.28	Sn	140
Si	0.32	As	240
Mo	0.11	N	100
Ti	<0.001		
Fe	balance		

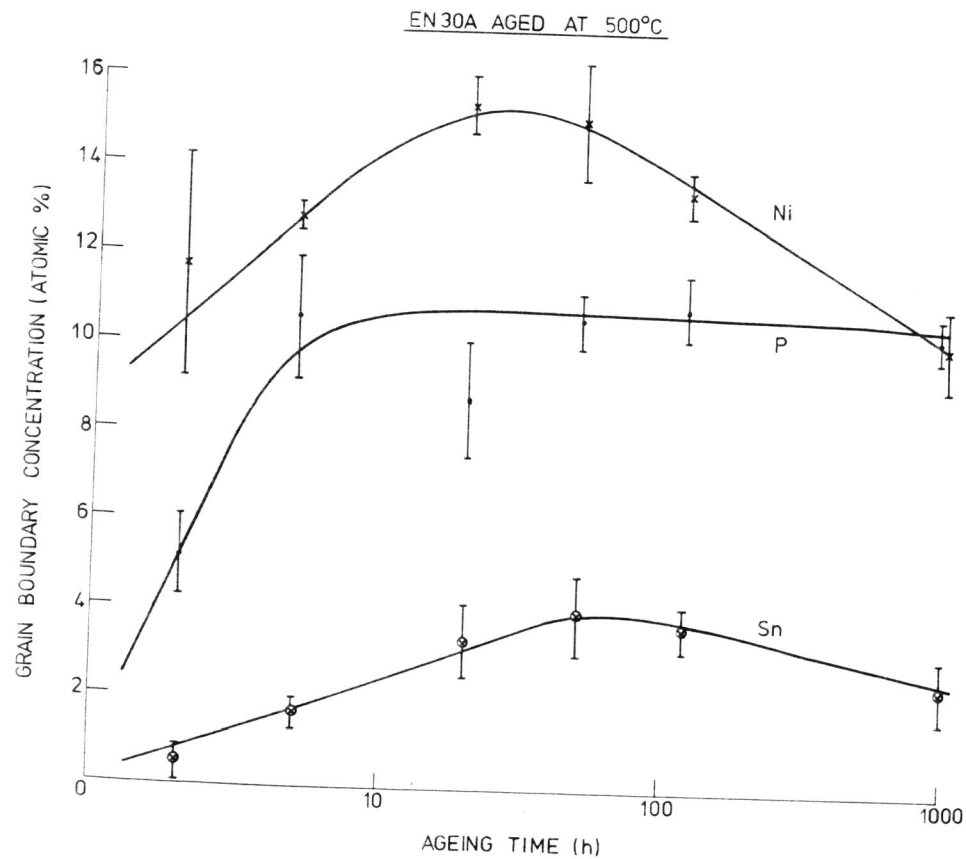


Figure 2 Grain boundary concentration of Ni, P and Sn as a function of ageing time at 500°C

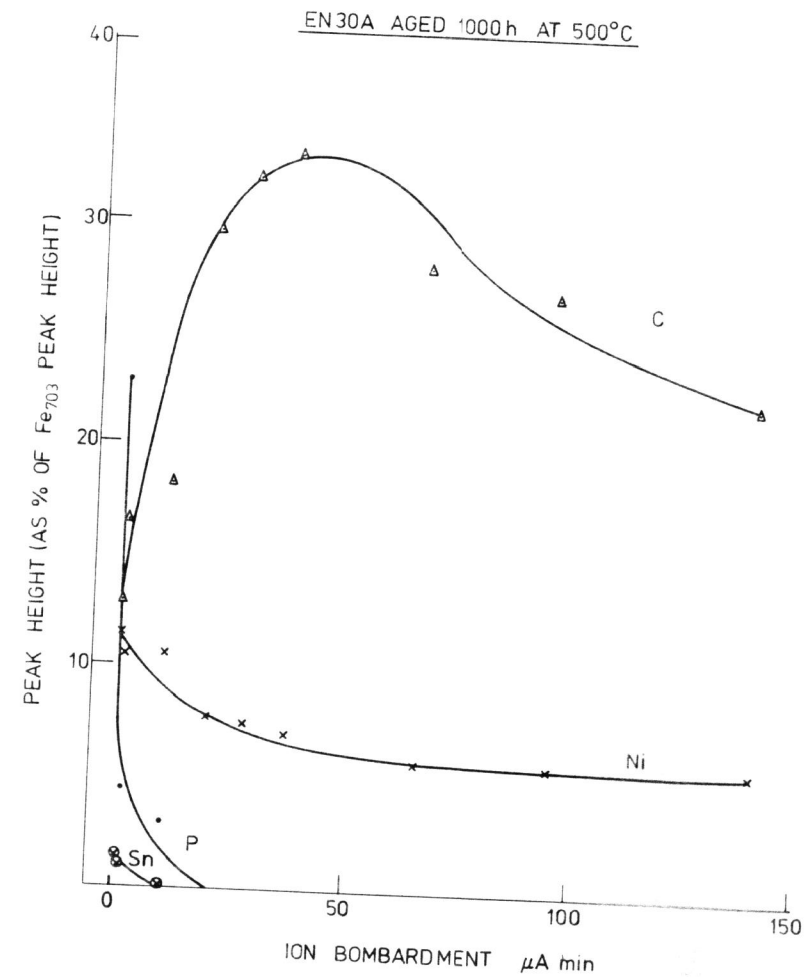


Figure 3 Composition profiles of C, Ni, P and Sn as a function of distance from the fracture surface, for the material aged for 100h at 500°C, (10 μA min approximates to a removal of 5 monolayers)

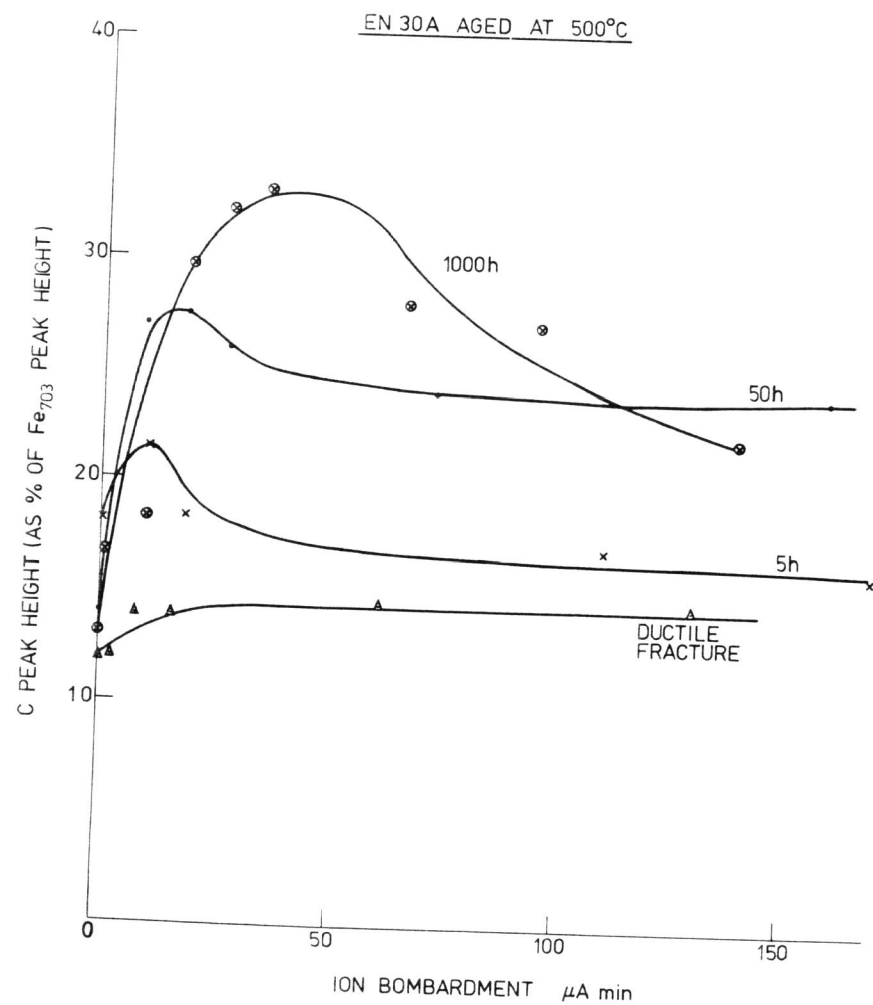


Figure 4 Compositional profile of C distribution as a function of ageing time at 500°C