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A SEM (scanning electron microscopy)-based method to evaluate impurity segregation to prior austenite grain boundaries in high strength steels

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The depth of grain boundary grooves on the etched surface of high strength Cr–Ni steels has been determined as a measure of P-segregation to prior austenite grain boundaries by a SEM (Scanning Electron Microscopy)-based grain boundary etching method (GEM). The mean depth and distribution of the depth can be decided by stereoscopy on the SEM micrographs of the replica of the etched surface. The results showed that the cast steel has less, but non-uniform P-segregation and the high temperature austenitization reduced the P-segregation on prior austenite grain boundaries in both steels.

1. Introduction

It is well known [1–3] that the impurity segregation to prior austenite grain boundaries has a significant influence on the mechanical properties of high strength steels. Therefore, a quantitative evaluation of this segregation is necessary for clarifying the origins of the variation of mechanical properties of steels with composition, processing and environment etc. Auger Electron Spectroscopy (AES) can be applied to detect the impurity atoms existing in the extreme thin layer of grain boundary directly. However, AES can not be used to analyse the grain boundary segregation in the case where the steels do not break intergranularly. In addition, there are some questions about the validity of AES results due to the change in nature and quantity of surface atoms during the preparation and transfer of AES specimens. As stated below, a meaningful result could not be obtained by AES in materials with non-uniform distribution of impurity. It was discovered [4–6] that the channel-like grain boundary grooves will appear in steels with impurity segregation on prior austenite grain boundaries after etching the polished specimens in suitable solutions and the depth of grain boundary grooves can be a measure of intergranular impurity segregation. Based on these observations, a simple grain boundary etching method (GEM) [7, 8] has been developed to analyse the intergranular P-segregation in iron-base alloys. The mean grain boundary groove depth was determined as the quantitative measurement of intergranular P-segregation, either by electroplating nickel on the etched surface and then measuring the penetration of nickel into the grooves [7] or by metallographically polishing the etched specimen and measuring the change of the dimension of hardness indentation, which was made before polishing, when the grain boundary groove disappeared [8]. All the procedures, however, are very time-consuming, particularly when an accurate result is desired.

This paper will present a SEM (Scanning Electron Microscopy)-based grain boundary etching method. The variation of P-segregation to prior austenite grain boundaries with received states (as-cast and forged) and austenitizing temperature in a Ni–Cr high strength steel will be examined by this method. The influence of this segregation on the fracture, fatigue and stress corrosion cracking behaviour of these steels has been thoroughly discussed in our other papers [9–12].

2. Experimental procedures

A high strength Ni–Cr steel was used in this study with following compositions (wt.%): C (0.28), Ni (2.20), Cr (1.05), Mn (0.80), Si (0.60), S (0.011), P (0.01).

This steel was made by air induction melting. Half of each heat was investment cast into the specimen blanks for mechanical property tests directly, and another half into an ingot which was hot forged to the specimen blanks. The specimens of cast and forged steels were austenitized at 900, 1000, 1100 and 1200° C for 1 h, then quenched into a salt bath at 180° C for 1 h before cooling to room temperature and finally tempered at 200° C for 6 h. The details of melting and heat treatment of these steels can be found in references [9, 11].

The metallographic samples were cut from the broken testpieces for mechanical property measurement. The mechanically polished samples were etched in a saturated aqueous solution of picnic acid with some wetting agent (sodium tridecylbenzene sulphorate) at

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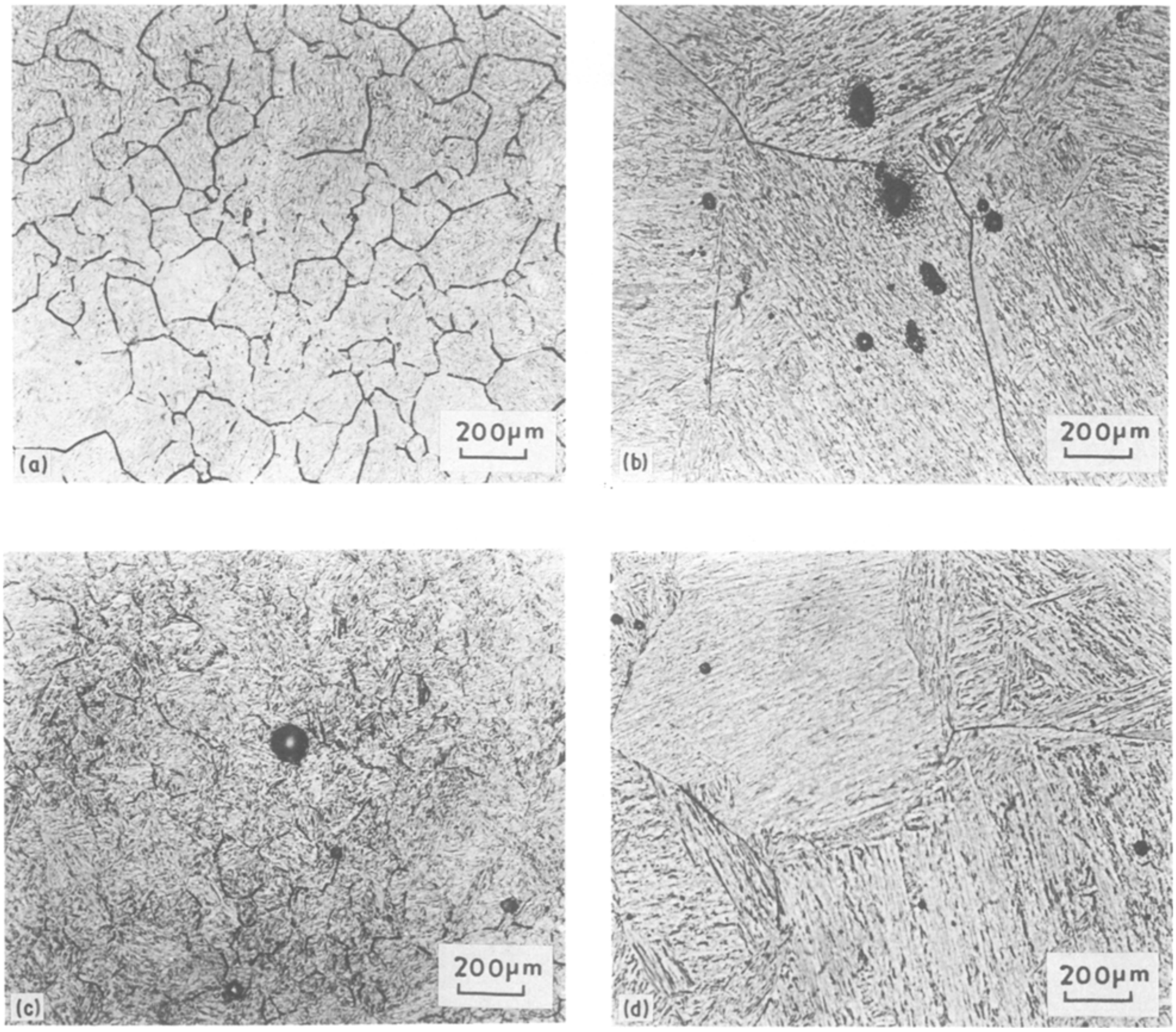

Figure 1 Optical micrographs of grain boundary morphology of forged (a), (b) and cast (c), (d) steels. Austenitizing temperature: (a), (c) 900° C and (b), (d) 1200° C.

a ratio of about 1 g per 100 ml solution. It was proved [6–8] that this solution is very efficient to reveal the P-segregation to prior austenite grain boundaries of high strength steels. The etching was proceeded under the action of ultrasonic vibration in an ultrasonic cleaner (50–80 kHz, 50 W) with the aim of increasing the etching rate (etching time will be reduced from 30 min without ultrasonic vibration to 2–3 min with ultrasonic vibration) and reducing the deposits of etching products in the grain boundary grooves.

A single-stage plastic replica technique was utilized to copy the profile of grain boundary grooves. To remove any possible deposits of etching products in the grooves, the sample should be cleaned several times by pressing on and stripping off the plastic film on the etched specimen surface before taking a replica of grain boundary grooves. The Formvar (polyvinyl formal dehyde) plastic film about 0.25 mm thick was softened in acetone and then firmly pressed on the surface of the etched specimen. After drying, the plastic film was pulled off with adhesive tape which was fixed on a flat substrate, e.g. a piece of steel plate. The surface of plastic film contains the negative of the sample surface, i.e. the grain boundary groove shows up as a ridge. To make the film electric conductive and increase the contrast of SEM pictures, the plastic film was shadowed with carbon in the vacuum evaporator at an oblique angle of about 30 degrees. The thickness of the carbon layer was about 100 nm, but the thickness has almost no influence on the measurement of groove depth (ridge height on replica surface) due to the simultaneous increase in the heights of grain interior and grain boundary ridges. The height of grain boundary ridges can be determined in SEM by stereoscopy [13, 14]. Two sequential SEM micrographs were taken with the replica at two tilted angles, usually $+10$–$15°$ and -10–$15°$ relative to horizontal position. The difference in height between any two points, Δh, can be given by

$$\Delta h = \frac{\Delta x}{2M \sin \alpha} \tag{1}$$

where Δx is the difference in distance between two points in sequential micrographs, α is the tilted angle relative to horizontal position, and M is the magnification of micrographs. The calculation of Δh can be easily carried out by computer.

If one is at the top of ridge and another one at grain interior near grain boundary, the Δh will be the depth of grain boundary groove. Due to possible non-

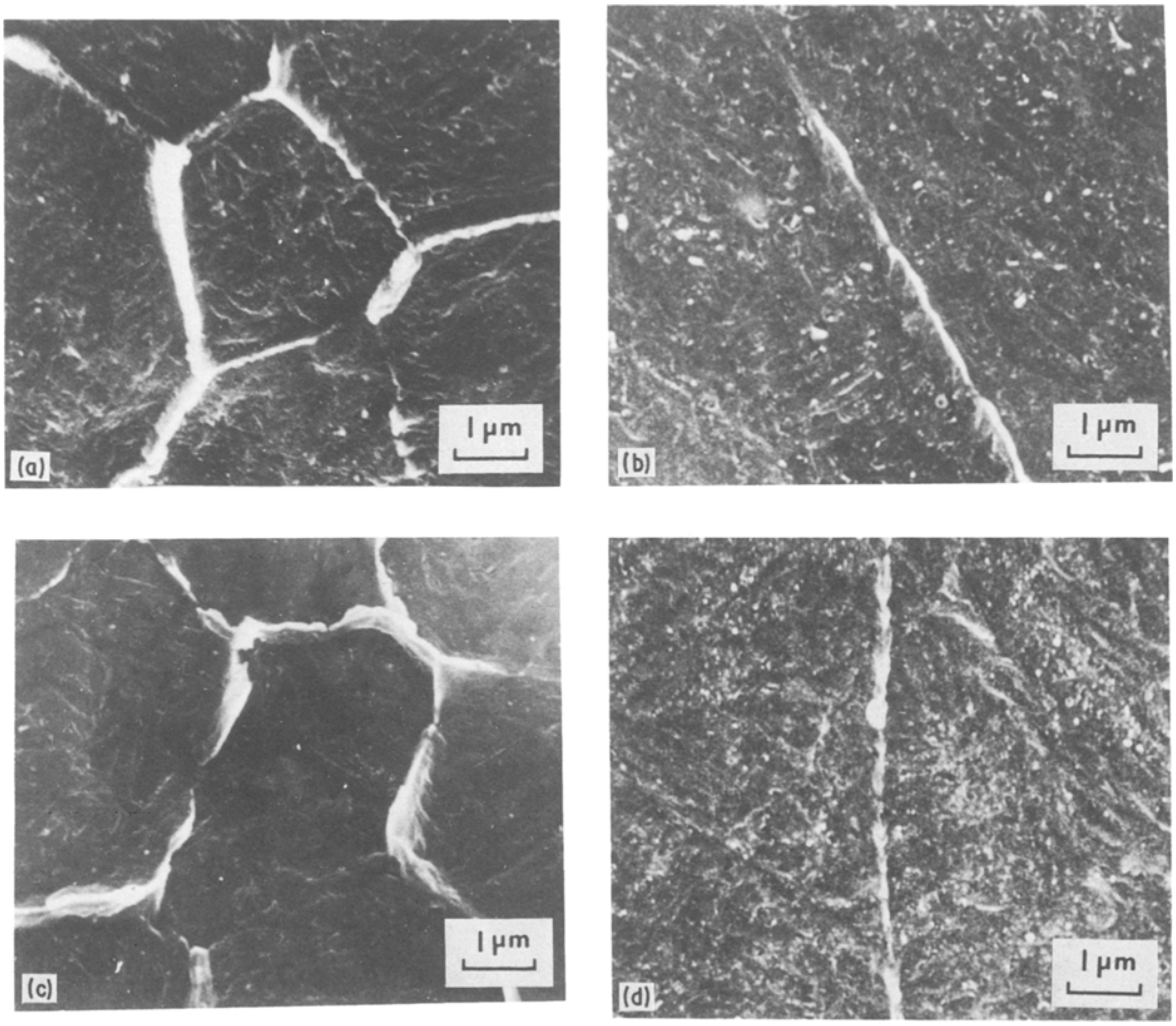

Figure 2 SEM micrographs of the structures shown in Fig. 1. Forged steel (a) 900° C (b) 1200° C and cast steel (c) 900° C (d) 1200° C austenitization.

uniform groove depth along grain boundaries, a mean depth should be measured. Three points were selected along any segment of grain boundary between two triple intersections of grain boundaries and the mean values of heights of these points relative to a specific point in the grain interior was calculated as the mean depth of this segment of grain boundary groove. The mean depth of grain boundary grooves of whole sample is given by

$$\Delta h = \frac{\sum_i \Delta h_i}{N} \qquad (2)$$

where N is total number of measured grain boundary segments, usually $N = 100$ in this study, Δh_i is the mean groove depth of a grain boundary segment. For grain boundary segment without groove, Δh_i is taken as zero.

It is worth noting that the operation voltage of SEM should be kept as low as possible to avoid any distortion or damage of plastic replica. In this study, operation voltage was 5 kV in most cases.

3. Results and discussion

Fig. 1 shows the optical micrographs of prior austenite grain structures of cast and forged steels austenitized at 900 and 1200° C. It can be seen that the prior austenite grain boundaries were delineated by etching much clearly in forged steel than in cast steel and became narrower with increasing austenitizing temperature. The grain boundaries were revealed very non-uniformly in cast steel austenitized at 900° C; only the grain boundaries in the interdendritic regions were clearly revealed. The SEM micrographs of the same samples showed a trend identical to that of optical metallography, but the profile of grain boundaries can be clearly identified, see Fig. 2. A channel-like grain boundary groove (ridge in SEM picture) does exist. Fig. 3 shows an example of the stereo-pair of grain boundary ridges through which the mean depth of grooves was determined. The measured mean depth of grain boundary grooves are listed in Table I. These data quantified the qualitive observations by optical microscopy and SEM. The logarithmic mean depth of grooves was plotted in Fig. 4 as a function of the reciprocal austenitizing temperature. The variation of

TABLE I Mean depth of grain boundary grooves, μm

Steel	Austenitizing temperature (° C)			
	900	1000	1100	1200
Forged	0.84	0.59	0.44	0.29
Cast	0.63	0.47	0.31	0.21

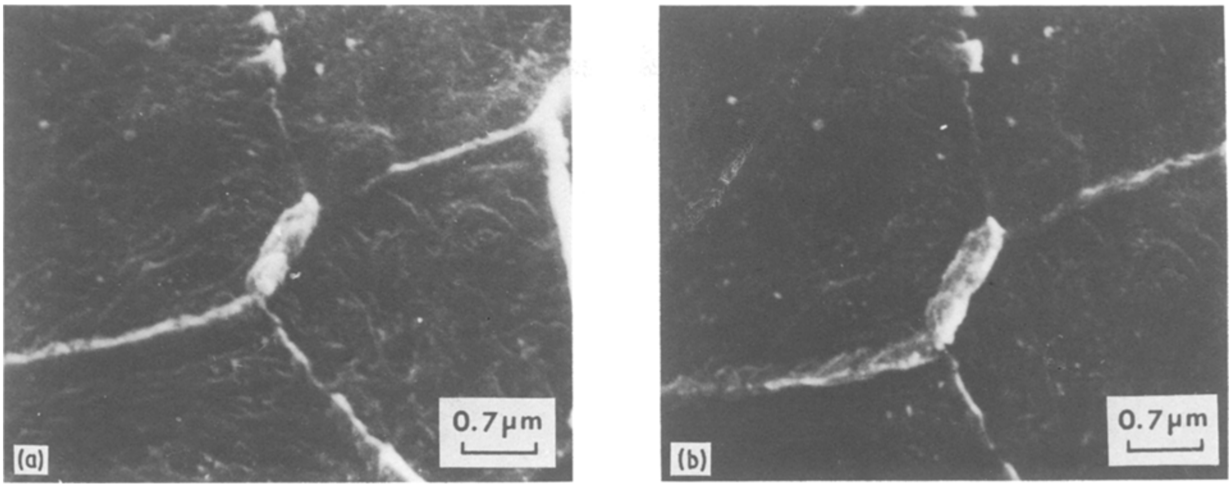

Figure 3 Stereo-pair of the grain boundary grooves in cast steel austenitized at 900° C, (a) + 10° and (b) − 10° tilted angles.

groove depth with austenitizing temperature in both steels can be described by an Arrhenius type of equation with the activation energy of about $42\,\mathrm{kJ\,mol^{-1}}$ which is in good agreement with self-diffusion activation energy of phosphorus in γ-iron [15]. This result demonstrated that the occurrence of grain boundary groove results from P-segregation to prior austenite grain boundaries in both forged and cast steels. The P-segregation on austenite grain boundaries is less severe in cast steel than in forged steel, which could partly explain the difference in mechanical behaviour between the two kinds of steel [10, 12, 13]. Probably, the impurity trap other than prior austenite grain boundaries, e.g. the interface between non-metallic inclusion particles and grain matrix, plays an important role in cast steel [9]. The increased austenitizing temperature reduced the P-segregation on austenite grain boundaries of both steels, which is an important reason for the change in mechanical properties of high strength steels with austenitizing temperature [10–12].

It is worth noting that the mean groove depth can not indicate the difference in the distribution of P-segregation of cast and forged steels. As shown in Figs 1 and 2, the distribution of phosphorus on grain boundaries is very non-uniform in cast steel, especially austenitized at low temperature. Fig. 5 shows the distribution frequency of groove depth of 900° C austenitized cast and forged steels. The groove depth of grains located at interdendritic regions in cast steel has

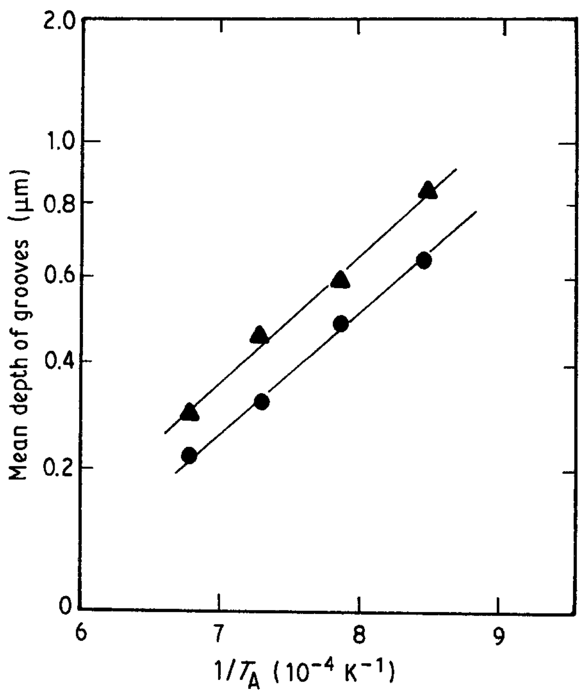

Figure 4 Plot of mean depth of grain boundary grooves vs reciprocal austenitizing temperature. (▲ forged steel, ● cast steel).

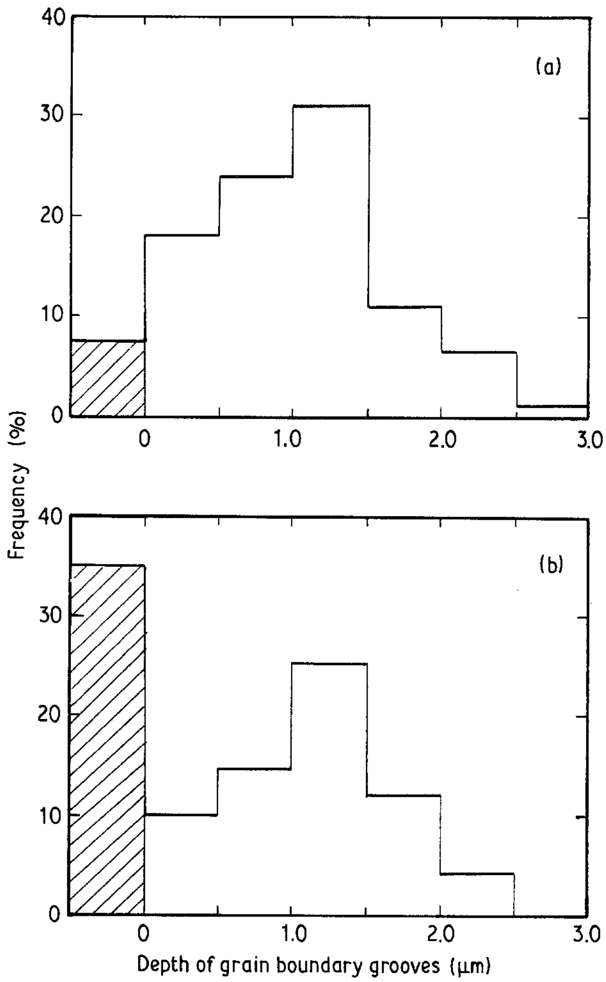

Figure 5 Distribution of grain boundary groove depth of (a) forged and (b) cast steels, 900° C austenitization.

almost the same magnitude as that of most grains in forged steel, but a lot of grains in the dendrite arms have negligible groove depth. The non-uniform distribution of P-segregation has significant influence on mechanical properties of cast steel. Therefore, the information about the distribution of impurity segregation is equally important in some cases. The SEM-based GEM can easily complete this kind of measurement, but it is very difficult for AES to obtain this information. The cast steel tends to be prone to intergranular fracture at low temperature preferentially along the boundaries of grains in interdendritic regions, thereby the AES measurement could overestimate the severity of impurity segregation in cast steel.

4. Conclusion

A rapid SEM-based grain boundary etching method (GEM) has been developed to evaluate P-segregation to prior austenite grain boundaries in high strength steels. Not only the mean depth of grain grooves, but also their distribution can be easily measured by this method.

Cast steel has less severe, but more non-uniform P-segregation on austenite grain boundaries than forged steel. The high temperature austenitization will reduce the P-segregation to austenite grain boundaries in both cast and forged steels.

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