ATOM PROBE ANALYSIS OF BAINITIC PHASE BOUNDARIES IN
A LOW ALLOYED Cr Mo STEEL*

Bach P.W., Beyer J. and Verbraak C.A.
Twente University of Technology, Department
Mechanical Engineering, Materials Section,
Enschede, the Netherlands.

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Introduction.

The transformation behaviour of steel is greatly influenced by addition of alloying elements. This effect on the transformation kinetics, at least at isothermal conditions, is indicated in a TTT-diagram. By suitable alloying the pearlite and bainite regions can be separated completely. The bainite transformation is described as a shear transformation comparable to the martensite transformation. The stepwise growth of bainite, as observed in the hot-stage microscope suggests the existence of a diffusion involved part of the transformation (1). This indicates one of the reasons, why the bainitic transformation cannot be described completely by the IPS-theory of the martensitic transformations.

The bay forming in the TTT-diagram of Mo or Cr containing steels has been postulated to be a result of a kind of impurity drag (3, 4, 5) or an inhibition of ferrite formation caused by small alloying elements clusters in the austenite (6). In order to obtain a better understanding of the role of Mo and Cr in the austenite-bainite transformation this paper reports a preliminary study of the distribution of these elements near the phase boundaries.

Experimental procedure.

The material used in the present investigation is a commercial Cr Mo steel (AISI H10, DIN 1.2365), with a composition of 1.4 at.% C, 2.8 at.% Cr, 1.6 at.% Mo, 0.6 at.% Si, 0.5 at.% V, 0.3 at.% Mn. In a magnetic TTT-apparatus of own design (7) a rod of 5 mm diameter was solution treated for 10 minutes at 1100°C. To avoid martensite nucleation because of the small difference between M_s and B_s temperature (55°C) the rod is firstly quenched to 435°C and subsequently cooled at a rate of 3.5°C/min. to 400°C and then water quenched. The resulting very fine microstructure is bainite, partially martensite.

To study the solute distribution in detail an atom-probe (A.P.) was constructed (8), basically the same design as described elsewhere (9, 10). The specimens were spark eroded from the heat treated rod in the form of rectangular bars with cross sections of 0.3 x 0.3 mm. and electro-chemically polished in 6 % perchloric acid in acetic acid and finally prepared as an A.P. specimen by zone polishing with a 1 % perchloric acid in butyloxyethanol, a method also developed independently by Melmed (11). The liquid nitrogen cooled specimens were imaged by means of neon ions at $6 \cdot 10^{-3}$ Pa and with a background pressure of less than $6 \cdot 10^{-8}$ Pa. The A.P. analyses were carried out with a pulse fraction of 10 % and a low pulse rate (< 0.1), in $2 \cdot 10^{-5}$ Pa Ne, which is sufficiently high to inspect the FIM image and to follow the evaporation process and is sufficiently low to have a low background noise level. Special care has been taken in the detector circuit to minimize the extraneous signals. The local solute concentrations were calculated from an A.P. spectrum such as shown in fig. 1, containing usually between 250 and 600 detected ions.

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The iron and chromium ions appear in the double charged state, the molybdenum as Mo^{2+} , Mo^{3+} and some Mo^{4+} and the carbon somewhat more complex as C^{2+} , C^+ , or C_2^{2+} , C_3^{2+} , C_2^+ and sometimes C_3^+ on the m/n ratio's of respectively 6, 12, 18, 24 and 36. There is some ambiguity in the assignment of the carbon peak at m/n = 12. In the present analysis it is taken as completely C^+ , but taking it as completely C_2^{2+} will enhance the carbon concentration with 7-15 % relatively.

Results and discussions.

In the FIM image of the as-quenched microstructure (fig. 2), a phase boundary between the ferrite matrix of the bainite and martensite is shown. The bainite is clearly imaged showing the typical ring pattern and the martensite is rather irregular with bright spots. At several places across the interphase A.P. analyses were taken resulting in the solute concentration profile of fig. 3. In this figure, two concentration profiles across the same interface are combined. In the region of the interface, the analysis includes contributions of both phases because of the finite dimension of the probe aperture. The probe aperture corresponds to a circle with a diameter of about 1.5 nm at the emitter surface. The low carbon part in fig. 3 is taken from the bainite, the high carbon region belongs to the martensite.

Generally the martensite formed during water quenching will have the same composition as the austenite from which it was formed, and this concentration profile reflects that of the original austenite/bainite interface. The carbon apparently diffuses into the austenite at the front of the bainite interphase. This higher carbon austenite layer will be stabilized by the high carbon concentration and will be retained after quenching to ambient temperature (12). Cooling to liquid nitrogen temperature this austenite will transform to martensite. Although partitioning of Cr and Mo was not observed by micro-probe analysis by Aaronson et al. (17) short range diffusion of the elements at the interphase could be expected from the stepwise growth of bainite observed in the hot stage microscope (1). The FIM image of fig. 4 shows a wedge shaped phase boundary between bainite and martensite. The concentration profile of fig. 5 is taken across the interface at approximately 30 nm from the point of the wedge, while the profile of fig. 6 is situated about 3 nm from this edge of the bainite plate.

Both in fig. 3 and 5 the higher Cr and Mo contents on both sides of the interface and the low Cr and Mo content in the interface are remarkable. This means that there exists no true para-equilibrium at this low transformation temperature, as proposed by Hultgren (13) and Hillert (3), for this model assumes that the alloying elements Cr and Mo diffuse too slowly to redistribute at all. The higher Cr and Mo contents on both sides of the interface can perhaps be ascribed to the small "spike" of the slow diffuser in front of the interface in the Negligible Partitioning under Local Equilibrium (NPLE) model (6), although the calculated spike thickness is less than the lattice parameter for the lower temperature range (14). The NPLE also assumes that there will be no partitioning of the slow diffuser outside the interface region with the spike. In the concentration profiles of fig. 3 and 5 the Cr is somewhat enriched in the martensite, so the NPLE conditions are not fulfilled. On the other hand the carbon profile conforms to the NPLE model with a higher carbon content in front of the interface, necessary for the up-hill diffusion.

The concentration humps in the profiles can perhaps be attributed to an impurity drag mechanism as proposed by Aaronson (4), Cahn (5) and Hillert (3) as a possible origin for the bay forming in the TTT-diagram of Mo and Cr containing steels. The important free-energy loss, necessary for the retarding effect can be caused by a strong tendency of Mo and Cr to segregate to the γ/α interface.

The low Cr and Mo content in the boundary is unexpected, but can be in agreement with the existence of a coherent phase boundary, because it seems unlikely that they would reduce the coherent interface energy. Although the FIM image of fig. 2 is not clear enough to decide whether or not it is coherent, the $\{123\}_\alpha$ type boundary plane can act as a (semi) coherent habit plane in the bainite transformation process (15).

The difference between the concentration profiles of the side of the bainite plate (fig. 3) and the edge of the plate (fig. 6) might be due to a difference in migration behaviour caused by the dislocation structure involved at the bainite transformation, regarding a bainite plate as a disc in a Frank type model (18). The migration possibilities of substitutional alloying elements at the side of the disc, where screw dislocations are involved, differs from the edge, where edge dislocations are situated.

The FIM image of fig. (7) shows an about 15 nm thick martensite plate with rather sharp boundaries in a bainitic matrix. The concentration profiles across the plates at two different places (fig. 8 and 9) show a rather high carbon content, but not enough for a carbide, which indicates, that this plate again was retained austenite at room temperature. This is in accordance with the electron microscope observations of about 20 nm thick retained austenite films by Thomas (16) in 0.3 % C, 1 % Cr, 1 % Mo weight per cent steel. The distribution of the alloying elements is rather symmetrical for fig. 8 but the Mo profile in fig. 9 which is taken from the same plate is asymmetric. Again this might be due to a difference in the migration behaviour caused by the dislocation structure of a Frank type bainite disc. The boundary planes are approximately of the $\{123\}_\alpha$ type, which can act as a habit plane in the γ - α transformation (15), so the retained austenite plate can be regarded to be situated between two Frank type bainite discs.

Conclusions.

The atom probe is able to measure the short range diffusion of C, Mo and Cr, which is until now not observed with other analytical techniques. The observed distribution is probable non-equilibrium for the slow diffusers Mo and Cr, while the carbon as fast diffuser is in agreement with a local equilibrium model. This indicates that there is some diffusion of Mo and Cr involved in the bainitic transformation, which is an important matter for the transformation kinetics. It also indicates that the para equilibrium model is not valid for the bainitic transformation at about 420°C. The atom probe analyses show the existence of small retained austenite plates in the bainitic transformation, which may have an important effect on the fracture properties.

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FIG. 1

Mass spectrum of the martensite. The horizontal axis represents the mass to charge ratio, the vertical axis the number of ions in a mass channel divided by the total number of ions.

FIG. 2

Field ion micrograph of a phaseboundary in a low alloyed Cr Mo steel. The clearly imaged area with the typical ring pattern is bainite. The martensite appears irregular with bright spots. The boundary plane is approximately $\{123\}_\alpha$ (bainite).

FIG. 3

A combination of 2 solute concentration profiles across the same bainite-martensite interface. The horizontal axis indicates the approximate distance in nm, the vertical axis the concentration in atomic percent. The vertical bars represent one standard deviation ($\pm \sigma$) of the measured local composition. The horizontal thin lines indicate the bulk composition, the high carbon concentration is measured in the martensite, the low carbon concentration in the bainite.

FIG. 4

Field ion micrograph of a wedged-shaped phase boundary between bainite and martensite. The boundaries are indicated by white stripes.

FIG. 5

Solute concentration profile across the bainite phase boundary at about 30 nm from the point of the wedge of fig. 4. The high carbon part belongs to the martensite.

FIG. 6

Solute concentration profile across the bainite phase boundary at about 3 nm from the point of the wedge. The high carbon part belongs to the martensite.

FIG. 7

Field ion micrograph of a martensite plate in a bainitic matrix. The boundary planes are approximately $\{312\}_{\alpha}$ (bainite).

FIG. 8

Solute concentration profile across the martensite plate of fig. 7.

FIG. 9

Solute concentration profile across the martensite plate of fig. 7 at a distance of approximately 50 nm from the profile of fig. 8.