Some Aspects of Grain-Boundary Embrittlement in High Purity Iron

This short report concerns the occurrence of an extreme case of grain-boundary embrittlement encountered when 13 mm diameter rods of Ferrovac "E" iron were heat treated to obtain a range of grain sizes. The residual impurities in weight percent for this high purity iron were:

C 0.008	Si 0.005	Sn 0.002	Mo 0.001
O_2 0.0012	P 0.002	Cr 0.001	Co 0.004
H_2 0.00006	S 0.005	V 0.004	Cu 0.001
N_2 0.00015	Ni 0.025	Al 0.01	W 0.01

In order to obtain a range of grain sizes, the specimens were initially austenised for 20 min at 1000°C and then quenched. When these samples were subsequently annealed at temperatures below Ac_1, rapid grain growth occurred.

The initial grain growth treatment was a 24-hour anneal in vacuum at 850°C, followed by furnace cooling. This treatment resulted in total grain-boundary embrittlement in these samples which, after the austenising and quenching treatment, had shown a very high ductility. Fig. 1 is a scanning electron micrograph, at low magnification, of one of the embrittled samples, showing the fracture face with cracks following the boundaries.

Throughout this presentation, brittle fracture is defined as room temperature fracture occurring almost entirely along the ferritic grain boundaries with no macroscopic evidence of plastic deformation. Such a fracture could be initiated simply by dropping the specimens, or overtightening the grips before tensile testing.

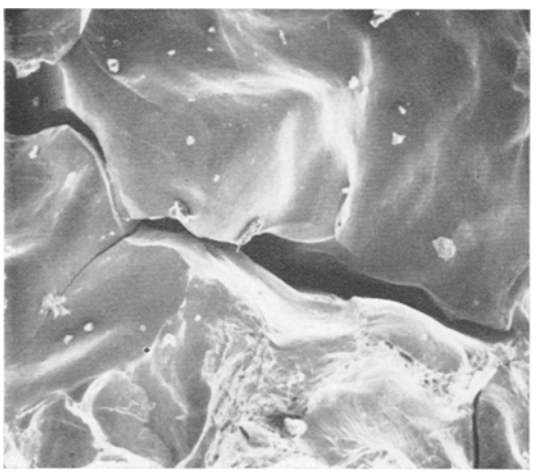

Figure 1 Scanning electron micrograph of embrittled iron specimen (× 60).

Ductile fracture is defined as fracture at room temperature after severe necking and considerable elongation, as expected for high purity iron. The assessment of brittleness or ductility was made by monotonic tensile tests at room temperature on an Instron Testing Machine.

In a first attempt to understand the nature of this embrittlement, a series of quenched samples were annealed for various times at different temperatures. Because it was known that grain growth in the as-received specimens was much slower than in the quenched specimens, a number of the as-received bar samples were also included in the heat treating to assess the grain-size effect. Table I summarises the results.

Table I allows the following remarks to be made:

(i) A time and temperature dependent process is effective in causing the boundary embrittlement.

(ii) The embrittlement does not take place during cooling from the annealing temperature since quenching or furnace cooling did not influence the results.

(iii) The grain size appears to be a factor in the embrittlement process. It is seen that the anneal for 6 h at 850°C of the as-received specimens, giving a grain size of 340 μm, did not embrittle the boundaries while the anneal of 2 h at 850°C on the quenched material, yielding a 1400 μm grain size, caused complete embrittlement.

Since equilibrium adsorption involves the enrichment of solute in the boundary, whose width is of atomic dimensions, it is difficult to rationalise the relatively long times and high temperatures required if Gibbsian adsorption underlies the embrittlement. Furthermore, if equilibrium adsorption is controlling this observed phenomenon, then a strong dependence on the rate of cooling from the annealing temperature would be expected and relatively slow cooling (furnace cooling in this case) would accentuate the brittleness. This was not apparent.

In view of these observations, it appeared that long range diffusion was involved in the process of grain-boundary embrittlement. Consequently, optical and scanning electron microscopy were used to examine the fracture faces for the presence of precipitates or voids. Neither was detected. This suggested that if, indeed, grain boundary precipitates were responsible then they must have been either very small, since they remained unresolved by the scanning electron microscope, (resolution $\sim$ 300 Å) or in the form of an extremely thin continuous film which is

TABLE I Isothermal heat treatments of high purity iron

	Temperature of anneal (°C)	Time of anneal (h)	Cooling mode after anneal	Grain size after anneal (μm)	Condition
Previously austenised at 1000°C and quenched	—	—	—	100	ductile
	700	2	quenched	200	ductile
	800	2	quenched	1200	ductile
	800	22	quenched	1600	brittle with slight elongation
	800	40	quenched	2000	brittle
	850	2	quenched	1400	brittle
	850	2	furnace-cooled	1400	brittle
	850	24	furnace-cooled	2200	brittle
No previous heat treatment	700	1	furnace-cooled	100	ductile
	800	48	furnace-cooled	220	brittle
	850	6	furnace-cooled	340	ductile
	850	42	furnace-cooled	350	brittle

difficult to detect by the techniques used. However, the results given in table I do suggest some diffusion controlled solute(s)-boundary interaction underlying the embrittlement phenomenon, as previously mentioned, with the consequence that strong consideration must be given to an alternative solute transport mechanism. Bercovici *et al* [1, 2] have demonstrated that solute may be transported to the boundary by a vacancy flux during cooling. Also they showed that this process was particularly effective during the first stage of cooling, i.e. over a short temperature range whose upper limit was the holding temperature. Chopra [3], using these concepts, was able by cycling between 110 and 290°C, to induce grain boundary precipitation in a lead-silver alloy whose silver concentration was less than 0.7 of the solubility limit at the lower cycling temperature.

On the basis of these considerations, it appeared that the present embrittlement may have been initiated by a cyclic pumping of solute to grain boundary regions due to a cyclic vacancy flux to boundaries because of temperature fluctuations in the furnace during the high temperature "isothermal" annealing. To test this hypothesis, quenched samples were annealed under conditions of continuously rising temperature from 700 to 880°C, the temperature transient being of various durations. The results of these tests are shown in table II.

It is seen that in this case all specimens remained ductile. Particularly noteworthy is the fact that the specimens subjected to the $7\frac{1}{2}$ and 12 h temperature transients were above 850°C for a much longer time than required to induce brittleness under "isothermal" conditions. Consequently, we tentatively conclude that the present embrittlement is caused by a mechanism in which a coupled vacancy-solute flux to the boundary occurs because of the temperature fluctuations. At the moment, experiments are in progress using controlled temperature cycles, in the hope that an attempt will be made to identify the solute(s) transported to the boundaries and the mechanism of solute-boundary interaction which causes the embrittlement.

TABLE II Continuous heating of iron specimens quenched from 1000°C and heated continuously from 700 to 880°C

Time of heating	Grain size (μm)	Fracture
45 min	1200	ductile
60 min	1500	ductile
155 min	2000	ductile
$7\frac{1}{2}$ h	—	ductile
12 h	2500	ductile

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