Intergranular embrittlement in ferrous alloys

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Summary

Recent work on alleviation of oxygen-induced embrittlement in ferrite by aluminum additions and on the phenomenology of interface embrittlement by antimony, phosphorous, tin and arsenic is reported. The relevance of the latter to temper brittleness and related phenomena is discussed. Work on the origins of quench cracking and the formation of carbide platelets in prior austenite grain boundaries is also reported.

Introduction

The subject of intergranular fracture in iron and steel has been under investigation in our laboratory for several years. We have been concerned with the two most common forms: intergranular brittle fracture in low carbon ferrite at low temperatures, presumed to be due to oxygen segregation to grain boundaries, and the brittle fracture which occurs along prior austenite grain boundaries in alloy steels, of which the classical problem of temper brittleness is the prototype. This paper summarizes our recent results in both these areas.

Intergranular fracture of ferrite

The phenomenon of low temperature intergranular fracture in low carbon ferrite is by now well documented [1-3]. It has been surmised that the problem is caused by the presence of residual oxygen at ferrite grain boundaries and it appears to require a low ratio of segregated carbon to segregated oxygen at these boundaries. For example, in ferrite containing only 20 ppm oxygen and 50 ppm carbon it is possible to obtain a very large variation in intergranular strength by varying the amount of segregated carbon through the selection of the temperature from which the solution treated ferrite is quenched prior to low temperature testing [3]. Fig. 1 shows this variation and its correlation with the amount of intergranular fracture. The lack of ductility to the right of the peak is due to carbon insufficiency at grain boundaries, caused by the low amount of equilibrium segregation of carbon at high temperatures. The low ductility to the left of the peak is caused by ordinary carbide-initiated cleavage fracture. The ductility maximum occurs when sufficient carbon has segregated to scavenge the residual oxygen, but when formation of carbides larger than ~1μ thickness has not yet occurred.

An investigation has been carried out to determine whether this effect would be altered by the addition of other alloying elements which would interact with oxygen, such as aluminum and titanium [4]. Elimination of the embrittlement associated with high quenching temperatures by such additions would strongly support the oxygen-effect hypothesis and would be of technological relevance. It was also hoped to determine whether there was any additional grain boundary strengthening associated with the segregation of carbon, *per se*.

Results obtained by vacuum remelting of the original ferrite (Fig. 1) with the addition of 0·04 wt. % aluminum (see Table 1) and otherwise similar heat treatments, are shown in Fig. 2. It is apparent that the aluminum addition has indeed eliminated the high-quenching-temperature embrittlement and its attendent intergranular fracture. It appears that most of the embrittlement had been due to oxygen, but it seems possible from the ductility curve that there is some additional benefit from an increase in intergranular cohesion due to carbon segregation. However, this effect, if present, is minor compared with the oxygen-related effect.

Similar experiments with ferrite containing an addition of 0·15 wt. % titanium were unsuccessful; these specimens, whose composition is shown in Table 1, where extremely brittle when quenched from 700°C. It is known from other work [5, 6] that the titanium removes all carbon and nitrogen from solution in this material, and it appears that we were not able to bring the remaining titanium together with the residual oxygen, even after equilibration treatments of 600 h at 725°C.

From these results it appears that aluminum additions to low carbon ferritic steels would be very useful in avoiding problems associated with low intergranular carbon/oxygen ratios. This can often occur in localized regions which are heated to temperatures between 600 and 900°C and rapidly cooled, as, for example, in the heat-affected zones of welds. Finally, it would seem that the use of elements like titanium or zirconium, which interact with carbon as well as oxygen, should be discouraged.

Intergranular fracture of hardened steels

There are a number of circumstances under which quenched and tempered alloy steels exhibit brittle fracture along prior austenite grain boundaries. The best known is reversible temper brittleness, which arises when steels of commercial purity are heated in or cooled slowly through the temperature range ~375-575°C, and which requires the presence of one or more of four embrittling elements: antimony, tin, phosphorous, or arsenic [7]. The embrittlement does not occur in impure iron-carbon alloys from which other alloying elements, such as manganese, nickel, chromium, etc., are missing,

and it can be removed by reheating an embrittled steel above 600°C for a few minutes and rapidly quenching. Similar forms of austenite grain boundary separation which are thought to be intimately related to this phenomenon are: 500°F (or 350°C) embrittlement, intergranular quench cracking, hydrogen embrittlement, stress corrosion cracking, and some forms of cracking in welds and heat-affected zones of weldments.

Proposed model

The underlying premise of our work has been the hypothesis that the cause of separation of prior austenite grain boundaries is the presence of segregated impurities, such as those mentioned above, with or without the involvement of carbide particles on these boundaries. The general model which has been advanced for these phenomena [8, 9] can be summarized in terms of the four main embrittling elements as follows: The embrittling elements are assumed to segregate in austenite at high temperatures, but to segregate in ferrite only at much lower temperatures. This is in keeping with the available Fe-X equilibrium diagrams [10] which show the embrittling elements X to be 'gamma-loop' elements; that is, they are much more soluble in ferrite than in austenite. Thus, the embrittling elements segregate during austenitizing and are retained in the former grain boundaries after quenching. Upon tempering above ~ 200-300°C, carbide platelets form in the prior austenite grain boundaries (as well as elsewhere in the martensitic structure) and these become larger and cover a larger fraction of the grain boundary area as the tempering temperature is raised. The embrittling elements remain segregated until temperatures >~600°C are reached, where desegregation into the ferritic matrix becomes marked.

This model is consistent with the manifestations of temper brittleness and '500°F' embrittlement. In the latter the enrichment of the carbide-matrix interface by the embrittling elements being rejected by the thickening carbide probably plays an important role [11]. It is significant that '500°F' embrittlement has been definitely linked to the presence of the same embrittling elements which act to produce temper brittleness [12]. The reasons why the prior austenite grain boundaries are the preferred fracture paths are that they are the locus of the highest embrittling element concentration and they represent a *continuous* internal surface on which carbide precipitation has occurred. In the absence of embrittling elements this carbide precipitation is of little consequence, but if the cohesive strength of the carbide-ferrite interface is lowered by impurity segregation, then an especially fragile situation develops. This is because the interface between a hard, brittle particle and a plastic matrix is much easier to separate (during shear in the matrix) than is the interface between two plastic grains. In the latter case accommodation by plastic flow is a possibility; in the former case it is not.

Experimental evidence

The experimental evidence which supports this model is continually growing. Arkharov *et al.* [13] found that the intergranular fracture surface of an embrittled phosphorous-containing Ni-Cr steel was enriched in phosphorous over the bulk concentration. In their experiments layers of the fracture surface were etched away and the etchent was chemically analyzed. This same technique was used by Restaino and McMahon [8] to show that in antimony-containing Ni-Cr steel, the fracture surface contained excess antimony only in the temper brittle condition and not in the unembrittled or de-embrittled conditions. It was also shown that if antimony is allowed to segregate to carbide-ferrite interfaces in a high carbon ferrite, the interfaces can be made to split open in tension at low temperatures, whereas reheating to a higher (de-segregating) temperature and quenching restores the normal high tenacity of these interfaces [8]. This effect has recently been reproduced in another lot of Fe-C-Sb ferrite, and has also been shown to occur for two other heats containing arsenic and tin respectively. (See Fig. 3). The initial attempt to examine the effect of phosphorous failed, apparently because too much phosphorous was added, as shown in Table 2. The 0·8% phosphorous was sufficient to form what appeared to be a layer of phosphide around the carbides, and no interface splitting was found. The experiment will be repeated with a leaner alloy. It is expected that the splitting effect will be found, since experiments by Keh [14] on a Cr-Mn-P steel have indicated that fracture is initiated at carbide-ferrite interfaces, as we have predicted.

The experiments on the ferrite-carbide aggregates are important because they allow the embrittlement to be studied on a coarse scale. This will enable the temperature ranges and kinetics of segregation and desegregation to be determined for Fe-C alloys, and later on for similar alloys to which other alloying elements have been added.

The effects of the alloying elements is the one great puzzle remaining. They are obviously not needed to produce interface splitting, but they are apparently necessary to produce the effects associated with prior austenite grain boundaries. While it is known that particular alloying elements, singly and in combination, present very different enhancing effects in the presence of the different embrittling elements [15] the mechanisms by which they act is completely unexplored.

Cracking in as-quenched steels

One aspect of the model outlined above which has only been partly tested is the assertion that segregation of impurities occurs in austenite prior to quenching. Ideally one would like to obtain a completely intergranular fracture of as-quenched martensite and then apply the dissolution technique to obtain a chemical analysis of the grain boundary regions. We have succeeded

in obtaining such a fracture in our Ni-Cr-Sb steel by use of a slow bend test, and preparations are being made for the analysis. However, the very fact that such fractures have been obtained by us and by others [16] strongly suggests that segregation of an embrittling element has occurred.

It is very common to find quenching cracks which run along prior austenite grain boundaries in alloy steels with ~0·4% C which have been grain coarsened at high austenitizing temperatures and very rapidly quenched. (See Fig. 4.) In fact, we have been able to produce such cracks in an Fe-0·4% C alloy of fairly high purity. However, in a 'steel' made by carburizing a piece of ultra-high purity zone refined (Battelle) iron such cracking is not observed. This is convincing support for the hypothesis that this type of quench cracking is an impurity effect.

Our conclusions at this point are that these cracks are the result of impurity segregation, but that the required impurity levels are very low. (This can be seen by the results in the moderately high purity Fe-C alloy mentioned above, and also by the fact that a specially prepared heat of high purity Cr-Ni steel, which showed no susceptibility to temper brittleness, still quench-cracked when coarsened and rapidly quenched.) It is also interesting to note that this form of prior austenite grain boundary separation occurs in plain Fe-C 'steels', while temper brittleness does not. Clearly, *some* impurity segregation can take place in the absence of alloying elements.

Formation of carbides in prior austenite grain boundaries

It appears that the presence of carbide platelets in prior austenite grain boundaries plays an important role in the development of full temper embrittlement, although they are not the primary cause. Low *et al.* [15] have shown, for example, that removal of carbides from a Ni-Cr-Sb 'steel' (actually, a ferrite) causes the degree of embrittlement due to step cooling to drop by about two-thirds.

Because they are important, one naturally questions the reason for the presence of the coarse carbides in the grain boundaries, since they originate as a very fine dispersate in the martensite. Based on observations of intergranular facets in a Ni-Cr-Sb steel, it has been suggested that the formation of the platelets is catalyzed by the presence of segregated antimony in the austenite grain boundaries [17]. This was assumed to be due to the ability of the antimony to lower the carbide-ferrite interfacial energy. However, work by Capus [18] and by ourselves has shown that the grain boundary carbides also form in specially prepared vacuum-melted high purity alloy steels which are not susceptible to temper brittleness.

To find out whether the carbide formation had anything to do with the alloying elements, we have studied the tempering response of pure alloys of Fe-0·2% C and Fe-0·4% C and have found that the carbide formation occurs here also, and to a much greater degree than in the alloy steels [19]. They can easily be observed at optical magnifications for tempering temperatures greater than ~500 °C. Examples of both an alloyed steel and a pure Fe-C alloy are shown in Fig. 5. It appears that the carbide formation is a matter of enhanced coarsening in high angle grain boundaries, which provide paths of rapid carbon diffusion. The carbides in the prior austenite grain boundaries are no larger than in other high angle boundaries which remain from the former martenistic structure. It is obvious that the presence of the alloying elements actually acts to inhibit coarsening, including that which occurs along the prior austenite grain boundaries. It also seems clear that the grain boundary carbides are a consequence of the structural nature of the steel and it does not appear likely that they can be eliminated.

Acknowledgments

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Table 1
Composition of low carbon ferrites

	As-received	*Remelted with aluminum*	*Ti-modified*
C	0·0056	0·0056	0·0017
O	0·0023		0·0011
N	0·0008	0·0008	0·0011
Al	–	0·04	–
Ti	–	–	0·15

Table 2
Composition of high carbon ferrites

	% C	*% Embrittling element*
Fe-Sb	0·033	0·05 Sb
Fe-Sn	0·033	0·06 Sn
Fe-As	0·05	0·26 As

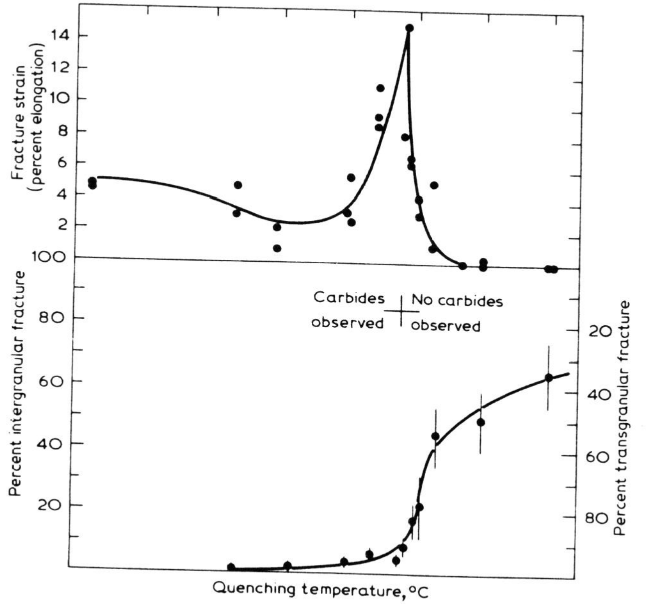


Fig. 1. Variation of ductility and mode of fracture with quenching temperature for iron with 20 ppm oxygen.

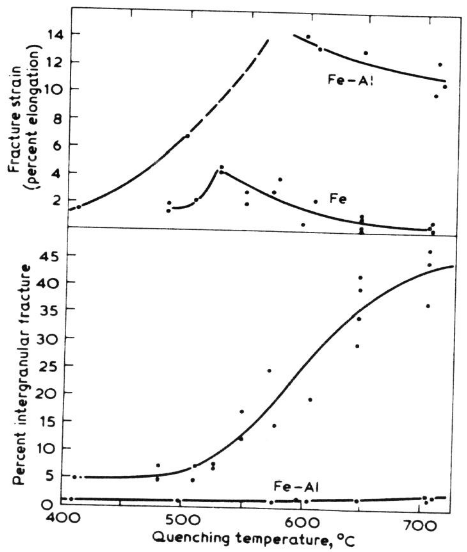


Fig. 2. Variation of ductility and mode of fracture with quenching temperature for iron-aluminum specimens.

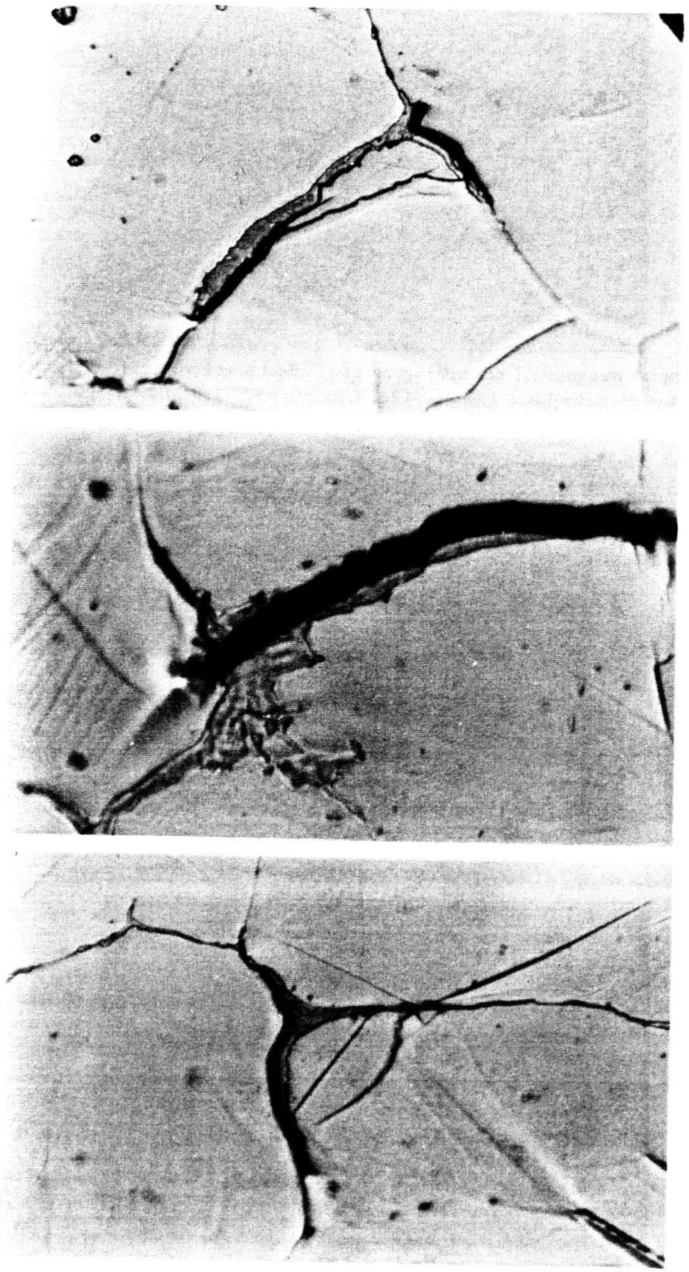


Fig. 3. Carbide-ferrite interface cracks in Fe-Sb, Fe-Sn, and Fe-As. Tested at 77°K. 800×.

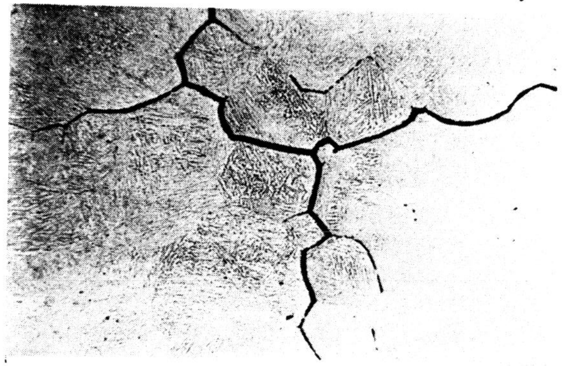
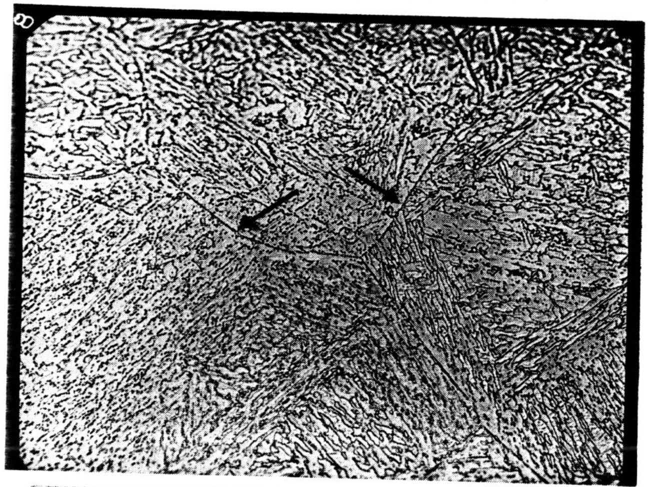
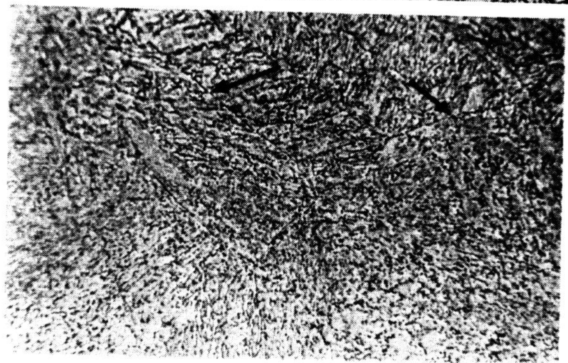


Fig. 4. Typical example of quenching cracks. 3340 steel austenitized for 4 hr. at 1250°C water quenched and tempered for 1 hr. at 650°C. 100×.



(a)



(b)

Fig. 5. Intergranular carbides in Fe-C and alloy steels; indicated by arrows,
(a) Vacuum melted iron – 0·4% C. Austenitized 1 hr at 1100°C, ice-brine quenched. Tempered at 600°C. 500×.
(b) High purity 3340 steel. Austenitized 4 hr. at 1250°C, water quenched. Tempered at 650°C for 4 hr 500×.