The Embrittlement and Fracture of Steels: Part One

Abstract:
Most groups of alloys can exhibit failure by cracking in circumstances where the apparent applied stress is well below that at which failure would normally be expected. Steels are no exception to this, and probably exhibit a wider variety of failure mechanisms than any other category of material. While ultimate failure under excessive stress must occur and can be reasonably predicted by appropriate mechanical tests, premature failure is always dangerous, involving a considerable element of unpredictability.

Most groups of alloys can exhibit failure by cracking in circumstances where the apparent applied stress is well below that at which failure would normally be expected. Steels are no exception to this, and probably exhibit a wider variety of failure mechanisms than any other category of material. While ultimate failure under excessive stress must occur and can be reasonably predicted by appropriate mechanical tests, premature failure is always dangerous, involving a considerable element of unpredictability.

However, a detailed knowledge of structure and of the distribution of impurities in steels is gradually leading to a much better understanding of the origins and mechanisms of the various types of cracks encountered. Furthermore, the now well-established science of fracture mechanics allows the quantitative assessment of growth of cracks in various stress situations, to an extent that it is now frequently possible to predict the stress level to which steel structures can be confidently subjected without the risk of sudden failure.

Cleavage fracture in iron and steel

Cleavage fracture is familiar in many minerals and inorganic crystalline solids as a crack propagation frequently associated with very little plastic deformation and occurring in a crystallographic fashion along planes of low indices, i.e. high atomic density.

This behavior would appear to be an intrinsic characteristic of iron but it has been shown that iron, highly purified by zone refining and containing minimal concentrations of carbon, oxygen and nitrogen, is very ductile even at extremely low temperatures. For example, at 4.2 K reductions in area in tensile tests of up to 90 % have been observed with iron specimens of the highest available purity.

As the carbon and nitrogen content of the iron is increased, the transition from ductile to brittle cleavage behavior takes place at increasing temperatures, until in some steels this can occur at ambient and above-ambient temperatures. Clearly, the significant variables in such a transition are of great basic and practical importance.
Factors influencing the onset of cleavage fracture

The propagation of a cleavage crack in iron and steel requires much less energy than that associated with the growth of a ductile crack. There are several factors, some interrelated, which play an important part in the initiation of cleavage fracture:

- The temperature dependence of the yield stress
- The development of a sharp yield point
- Nucleation of cracks at twins
- Nucleation of cracks at carbide particles
- Grain size.

All body-centered cubic metals, including iron, show a marked temperature dependence of the yield stress, even when the interstitial impurity content is very low, i.e. the stress necessary to move dislocations, the Peierls-Nabarro stress, is strongly temperature dependent. This means that as the temperature is lowered the first dislocations to move will do so more rapidly as the velocity is proportional to the stress, and so the chances of forming a crack nucleus, e.g. by dislocation coalescence, will increase. The interstitial atoms, carbon and nitrogen, will cause the steel to exhibit a sharp yield point either by the catastrophic breakaway of dislocations from their interstitial atom atmospheres (Cottrell-Bilby theory), or by the rapid movement of freshly generated dislocations (Oilman-Johnson theory).

In either case, the conditions are suitable for the localized rapid movement of dislocations as a result of high stresses, which provides a favorable situation for the nucleation of cracks by dislocation coalescence.

The nucleation and the propagation of a cleavage crack must be distinguished clearly. Nucleation occurs when a critical value of the effective shear stress is reached, corresponding to a critical grouping, ideally a pile-up of dislocations which can create a crack nucleus, e.g. by fracturing a carbide particle.

In contrast, propagation of a crack depends on the magnitude of the local tensile stress, which must reach a critical level. Simple models of slip-nucleated fracture assume either interaction of dislocations or cracks formed in grain boundary carbides. However, recently it has been realized that both these structural features must be taken into account in deriving an expression for the critical fracture stress. This critical stress does not appear to be temperature dependent. At low temperatures the yield stress is higher, so the crack propagates when the plastic zone ahead of the crack is small, whereas at higher temperatures, the yield stress being smaller, a larger plastic zone is required to achieve the critical local tensile stress.

This tensile stress has been determined for a wide variety of mild steels. The scatter probably arises from differences in test temperature and carbide dimensions. This is conclusive evidence for the role of finer grain sizes in increasing the resistance to crack propagation. Regarding grain boundary carbide size, effective crack nuclei will occur in particles above a certain critical size so that, if the size distribution of carbide particles in particular steel is known, it should be possible to predict its critical fracture stress.

Therefore, in mild steels in which the structure is essentially ferrite grains containing carbide particles, the particle size distribution of carbides is the most important factor. In contrast, in bainitic and martensitic steels the austenite grains transform to lath structures where the lath
width is usually between 0.2 and 2 μm. The laths occur in bundles or packets with low angle boundaries between the laths. Larger misorientations occur across packet boundaries. In such structures, the packet width is the main micro structural feature controlling cleavage crack propagation.

**Practical aspects of brittle fracture**

At the onset of fracture, elastic energy stored in the stressed steel is only partly used for creation of the new surfaces and the associated plastic deformation and the remainder provides kinetic energy to the crack.

The phenomenon of brittle fracture became particularly prevalent with the introduction of welding as the major steel fabrication technique. Previously, brittle cracks often stopped at the joints of riveted plates but the steel structures resulting from welding provided continuous paths for crack propagation. Added to this, incorrect welding procedures can give rise to high stress concentrations and also to the formation of weld-zone cracks which may initiate brittle fracture.

While brittle failures of steels have been experienced since the latter half of the nineteenth century when steel began to be used widely for structural work, the most serious failures have occurred later, as the demand for integral large steel structures has greatly increased, e.g. in ships, pipelines, bridges and pressure vessels. Spectacular failures took place in many of the all-welded Liberty ships produced during the Second World War, when nearly 1500 incidents involving serious brittle failure were recognized and nineteen ships broke completely in two without warning.

Despite our increasing understanding of the phenomenon and the great improvements in steel making and in welding since then, serious brittle failures still occur. Brittle fractures of thick-walled steel pressure vessels are reminder that human error and lack of scientific control can be disastrous. Bearing in mind the temperature dependence of the failure behavior, and the widening use of steels at low temperatures, e.g. in Arctic pipelines, for storage of liquid gases etc., it is increasingly necessary to have steels with very low transition temperatures and high fracture toughness.

While there are many variables to consider in achieving this end, including the detailed steel-making practice, the composition including trace elements and the fabrication processes involved, the most important is probably **grain size refinement**.

The development of **high strength low alloy steels (HSLA)** or micro-alloyed steels, in the manufacture of which controlled rolling plays a vital part, has led to the production of structural steels with grain sizes combined with good strength levels and low transition temperatures. In these steels, to which small concentrations (<0.1%) of niobium, vanadium or titanium are added, the carbon level is usually less than 0.15 % and often below 0.10 %, so that the carbide phase occupies a small volume fraction. In any case, cementite, which forms relatively coarse particles or lamellas in pearlite, is partly replaced by much finer dispersions of alloy carbides, NbC etc.

Addition of certain other alloying elements to steel, notably **manganese and nickel**, results in a lowering of the transition temperature. For example, alloy steels with 9 % nickel and less than 0.1 % carbon have a sufficiently low transition temperature to be able to be used for large containers of liquid gases, where the temperature can be as low as 77 K. Below this temperature,
Austenitic steels have to be used.

Of the elements unavoidably present in steels, phosphorus, which is substantially soluble in iron, raises the transition temperature and thus must be kept to as low a concentration as possible. On the other hand, sulphur has a very low solubility, and is usually present as manganese sulphide with little effect on the transition temperature but with an important role in ductile fracture. Oxygen is an embrittling element even when present in very small concentrations. However, it is easily removed by deoxidation practice involving elements such as manganese, silicon and aluminum.

Finally, the fabrication process is often of crucial importance. In welding it is essential to have a steel with a low carbon equivalent, i.e. a factor incorporating the effects on hardenable ability of the common alloying elements. The main hazard in welding is the formation of martensite in the heat-affected zone (HAZ), near the weld, which can readily lead to micro cracks. This can be avoided, not only by control of hardenability but also by preheating the weld area to lead to slower cooling after welding or by post heat treatment of the weld region. However, in some high strength steels, slower cooling may result in the formation of upper bainite in the HAZ, which encourages cleavage fracture.

Attention must also be paid to the possibility of hydrogen absorption leading to embrittlement. The presence of hydrogen in steels often leads to disastrous brittle fracture, e.g. there have been many failures of high strength steels into which hydrogen was introduced during electroplating of protective surface layers. Concentrations of a few parts per million are often sufficient to cause failure. While much hydrogen escapes from steel in the molecular form during treatment, some can remain and precipitate at internal surfaces such as inclusion/matrix and carbide/matrix interfaces, where it forms voids or cracks. Cleavage crack growth then occurs slowly under internal hydrogen pressure, until the critical length for instability is reached, and failure occurs rapidly. Hydrogen embrittlement is not sensitive to composition, but to the strength level of the steel, the problem being most pronounced in high strength alloy steels.

**The Embrittlement and Fracture of Steels: Part Two**

**Abstract:**
There are several forms of embrittlement in steel like intergranular embrittlement, temper embrittlement, embrittlement caused by overheating and burning.

While cleavage fracture in steels is a common form of embrittlement, in many cases the embrittlement is intergranular (IG), i.e. it takes place along the grain boundaries, usually the former austenitic boundaries.

Temper embrittlement is quite common in slowly heavy solutions of steels tempered in the range from 400 to 560°C.

**Intergranular embrittlement**

While cleavage fracture in steels is a common form of embrittlement, in many cases the embrittlement is intergranular (IG), i.e. it takes place along the grain boundaries, usually the
former austenitic boundaries. This behavior is encountered in as-quenched steels, on tempering (temper embrittlement), after heating at very high austenitizing temperatures (overheating and burning), and in rock-candy fracture in cast steels.

These forms of embrittlement are exhibited at or around room temperature. There are, however, other phenomena involving failure along grain boundaries, which are essentially high temperature events, e.g., hot-shortness during the hot working of steels and high temperature creep failure.

It is clear that no mechanism will explain the various types of embrittlement, but the processes leading to intergranular fracture all lead to reduced cohesion along the grain boundaries. This can arise in different ways but the most relevant appear to be

- Segregation of solute atoms preferentially to grain boundaries
- Distribution of second phase particles at grain boundaries.

**Temper embrittlement**

Many alloy steels when tempered in the range 500°C-650°C following quenching to form martensite become progressively embrittled in an intergranular way. A similar phenomenon can also occur when the steels are continuously cooled through the critical range. It is revealed by the effect on the notched bar impact test, where the transition temperature is raised and the shelf energy lowered, the transgranular fracture mode being replaced by an Intergranular embrittlement (IG mode) below the transition temperature.

This phenomenon is now known to be associated with the segregation of certain elements to the grain boundaries, which reduce the intergranular cohesion of iron. Elements, which segregate, fall into three groups of the Periodic Classification. It has been shown that many of these elements reduce the surface energy of iron substantially and would, therefore, be expected, to lower the grain boundary energy and to reduce cohesion. Moreover, the actual segregation of atoms to the boundaries has been conclusively demonstrated by Auger electron spectroscopy on specimens fractured intergranularly within the vacuum system of the apparatus.

This technique has allowed the precise determination of the concentrations of segregating species at the boundaries, usually expressed in terms of fractions of a monolayer of atoms. These fractions vary between about 0.3 and 2.0 for steels containing the above elements, usually in bulk concentrations well below 0.1 wt%.

With the individual elements, the tendency to embrittle appears to increase both with Group and Period number, i.e. S, Se and Te in increasing order are the most surface-active elements in iron. However, it is doubtful whether they contribute greatly to temper embrittlement because they combine strongly with elements such as Mn and Cr, which effectively reduce their solubility in iron to very low levels.

While the elements in Groups IVB and VB are less surface active, they play a greater role in embrittlement because they interact with certain metallic elements, e.g. Ni and Mn, which are common alloying elements in steels. These interactions lead to co segregation of alloy element and impurity elements at the grain boundaries, and to resultant lowering of cohesion by the impurity element. Analysis of the composition of grain boundaries by Auger spectroscopy has
confirmed strong interactions between Ni-Sb, Ni-P, Ni-Sn and Mn-Sb. Therefore, the driving force for segregation to boundaries is a stronger interaction between the alloying element and the impurity element than between either of these and iron. If the interaction is too strong, segregation does not take place. Instead a scavenging effect is obtained, as exemplified by Ti-P and Mo-P interactions in Ni-Cr steels. In this connection it is well known that molybdenum additions to Ni-Cr steels can eliminate temper embrittlement. A third inter-alloy effect is also possible which is that one alloying element, e.g. Cr, promotes the segregation of Ni and P, also Ni and Sb.

In addition to solute atom segregation to boundaries, there are also microstructural factors, which influence the intensity of temper embrittlement. In most alloy steels in which this phenomenon is encountered the grain boundaries are also the sites for carbide precipitation, either cementite or alloy carbides. It is likely that these provide the sites for IG crack nuclei.

As in the nucleation of cleavage fracture, dislocations impinge on a grain boundary carbide particle and as it is not deformable the carbide will either crack or the ferrite/carbide interface will part. The latter separation is more likely if the interracial energy has been reduced by segregation of impurity atoms to it. This can occur by rejection of these impurity atoms during the growth of the carbide or by equilibrium segregation. Interfacial separation has been observed in iron containing coarse grain boundary iron carbide, the interfaces of which contained Sb, As, Sn or P. The effectiveness of this nucleating stage of IG crack formation will be influenced by the extent of grain boundary carbide and the concentration of surface active impurities in the steel, in particular at carbide/matrix interfaces.

The propagation of the grain boundary crack will depend not only on the cohesion of the boundary but also on the relative toughness of the grain interior. For example, if the grain interior has a microstructure, which gives high toughness, the IG crack nucleus is more likely to propagate along the boundary. Further, as the yield stress of a steel rises sharply with decreasing temperature IG failure will, like cleavage fracture, be encouraged by reducing the testing temperature. Increasing the austenite grain size, by use of high austenitizing temperatures, under the same conditions, should increase the embrittlement because the size of the dislocation arrays impinging on the grain boundary carbides will be larger and thus more effective in forming crack nuclei.

The optimum temperature range for temper embrittlement is between 500 and 575°C. However, in some steels embrittlement occurs in the range 250-400°C. This phenomenon is called 350°C embrittlement, and occurs at too low a temperature to attribute it to the diffusion of metalloids such as Sb to the austenite grain boundaries. It seems more likely that it could arise from smaller and more mobile atoms, e.g. P, which would be rejected during grain boundary growth of iron carbide, which takes place in this temperature range. However, the morphology of the grain boundary Fe2C, if predominantly sheet-like, could be a prime cause of low ductility in this temperature range.

Stress corrosion cracking (SCC) involves failure by cracking in the presence of both a stress and of a corrosive medium. It can occur in either a transgranular or an intergranular mode. The latter mode appears to be encouraged in some alloy steels by heat treatments, which produce temper embrittlement. For example, a temper embrittled Cr-Mo steel cracks along the grain boundaries when stressed in a boiling NaOH solution. Use of a heat treatment to remove the temper
embrittlement also removes the sensitivity to stress corrosion.

**Overheating and burning**

Many alloy steels when held in the range 1200-1400°C and subsequently heat treated by quenching and tempering, fail intergranularly along the original austenitic boundaries. There is strong evidence to suggest that this phenomenon is associated with the segregation of sulphur to the austenite grain boundaries at the high temperature, and indeed the phenomenon is not obtained when the sulphur content of a steel is less than 0.002%.

Sulphur has been shown to be one of the most surface-active elements in iron. Work by Goux and colleagues on pure iron-sulphur alloys has shown that an increase in sulphur content from 5 to 25 ppm raises the ductile/brittle transition temperature by over 200°C. Further, Auger spectroscopy on the intergranular fracture surfaces has given direct evidence of sulphur segregation.

However, this embrittling effect of sulphur as a result of equilibrium segregation is only seen in pure iron and not in steels where there are other impurity elements, and also where interaction of sulphur occurs with alloying elements, notably manganese and chromium. The presence of manganese substantially lowers the solubility of sulphur in both $\gamma$- and $\alpha$-iron, with the result that when sulphur segregates to high temperature austenite boundaries, manganese sulphide is either formed there or during subsequent cooling.

In either case, the manganese sulphide particles lying on the austenite boundaries are revealed by electron microscopy of the intergranular fracture surfaces where they are associated with small dimples. Thus, the grain boundary fracture process is nucleated by the sulphide particles, and the mode of fracture will clearly be determined by the size distribution, which will in turn be controlled by the rate of cooling from the austenite temperature, assuming that MnS forms during cooling. With very slow cooling rates, the intergranular fracture is replaced by cleavage or transgranular fibrous fracture as the grain boundary sulphide distribution is too coarse.

Oil quenching from the austenitizing temperature does not eliminate the phenomenon which is accentuated on tempering in the range 600-650°C. This arises from the redistribution of carbides, which will strengthen the grain interiors, and by precipitation at the grain boundaries, which may further reduce grain boundary ductility.

When very high austenitizing temperatures are used (1400-1450°C) extensive MnS precipitate is formed, often in impressive dendritic forms. In extreme cases, partial formation of liquid phase occurs (liquation) which, on subsequent heat treatment, greatly accentuates the intergranular embrittlement. In the absence of manganese, e.g. in wrought iron, liquid films of the iron-iron sulphide eutectic cause embrittlement during hot working processes down to 1000°C (hot shortness).

The fact that in normal steels burning occurs only at very high temperatures should not be allowed for detract from its significance. The phenomenon may well intrude in high temperature working processes such as forging if temperature control is not exact, but in any case it can certainly be significant in steels which are cast, and by definition pass through the burning and overheating temperature range. In many cases intergranular fracture is encountered in cast alloy steels where the as-cast grain structure is clearly involved. Examination of the fractures reveals extensive grain boundary sheets of manganese sulphide, often only 0.2-0.5 μm thick but covering
large areas.

Marked embrittlement can occur in the as-cast state or after subsequent heat treatment in the range 500-650°C, and is often referred to as cast brittleness or rock candy fracture. Precipitation of aluminum nitride may also play an important role in this type of fracture.

**The Embrittlement Phenomena in Hardened & Tempered Steel**

*By Daniel H. Herring*

While the end-use application of a component dictates its heat treatment, as heat treaters we know that we must achieve a delicate balance between the properties of strength and ductility. Nowhere is this fine line more evident than in the tempering process where precise control of time and temperature are critical to help produce a part with optimized microstructure and mechanical properties.

Essentially, tempering is the modification of this newly formed microstructure toward equilibrium. Almost all steels that are subjected to any type of hardening process are tempered. A temper is a subcritical heat treatment that alters the microstructure and properties. In general, tempering lowers strength and hardness while improving ductility and toughness of the as-quenched martensite. However, this is not always the case. Let’s learn more.

**What is Temper Embrittlement?**

In general, embrittlement is a reduction in the normal toughness of steel due to a microstructural change and chemical effects. Temper embrittlement is a phenomenon inherent in many steels, characterized by reduced impact toughness. It occurs in certain quenched and tempered steels and even in ductile irons with susceptible compositions. This form of embrittlement does not affect room-temperature tensile properties but causes significant reductions in impact toughness and fatigue performance. Although normally associated with tempered martensite, temper embrittlement can also occur if the matrix is tempered to the fully ferritic condition.
Types of Temper Embrittlement

When tempering steel, several types of embrittlement must be avoided. The first type, tempered martensite embrittlement (TME), is an irreversible phenomenon that occurs in the range of approximately 250–400°C (480°F–750°F) and is often referred to as “blue brittleness” or “350°C (500°F) embrittlement.” The second type, temper embrittlement (TE), is a reversible phenomenon occurring when steels are heated in or slow cooled through the temperature range of 375–575°C (705°F –1070°F).

Recently it has been reported that a transition from ductile to intergranular fracture in steel having greater than 0.5% C has been observed in martensitic steels tempered at low temperatures. Under tensile or bending stress, these higher-carbon steels are highly susceptible to intergranular fracture in both the as-quenched condition and after tempering at low temperatures generally considered to be safe from these embrittlement phenomena. In view of the fact that tempering is not required to render the microstructure susceptible to intergranular fracture, this type of embrittlement phenomenon is referred to as quench embrittlement. [2]

Why does it happen?

Tempered martensite embrittlement and temper embrittlement are examples of intergranular embrittlement. A common factor in such failures is the presence of elements that segregate to the grain boundaries. The chemical reaction rate or kinetics of segregation are such that they exhibit “C” curve behavior in the 350°C –550°C (660°F –1020°F) range. In other words, segregation does not occur uniformly. Both types of embrittlement are in part related to grain-boundary segregation of impurity elements (e.g. arsenic, antimony, phosphorus, and tin). Usually indicated by an upward shift in ductile-to-brittle transition temperature, both types of embrittlement develop during thermal processing after austenitizing and quenching to martensite.

Tempered martensite embrittlement is thought to result from the combined effects of cementite precipitation on prior-austenite grain boundaries or interlath boundaries and the segregation of impurities at prior-austenite grain boundaries.
Temper embrittlement that occurs in the range of 375–575°C (705–1070°F) is believed to be due to segregation of impurity elements (P, Sn, As, Sb) to prior austenite grain boundaries. This causes decohesion of the boundaries, resulting in the tendency for low-energy intergranular fracture under certain loading conditions.

**Which steels are affected?**

All steels are susceptible, so the real question becomes how susceptible and what factors affect that susceptibility. For example, while plain-carbon steels may contain some of the impurity elements that will cause the embrittlement phenomenon to occur, the segregation of these elements is often enhanced by or caused by the presence of other alloying elements in substantial quantities. As a result, alloy steels generally have more susceptibility than carbon steels.

It is important to understand that the degree of embrittlement is affected by the prior austenite grain size and hardness. So, if we are dealing with a fine-grained plain-carbon steel of low hardness, it may not experience embrittlement symptoms despite its phosphorous content whereas a more highly alloyed Cr-Ni steel used at higher hardness is more susceptible to impurity content.

Widely used alloying elements such as chromium, nickel and manganese tend to promote temper embrittlement with the highest embrittlement effect observed in Cr-Ni and Cr-Mo steels. Small additions of molybdenum in Cr-Ni steels (0.2-0.3% in solution) can diminish temper embrittlement being caused by phosphorus. Temper embrittlement can
be diminished by keeping silicon and phosphorus levels as low as possible, adding up to 0.15% molybdenum and avoiding the embrittlement heat-treating conditions.

Susceptibility also depends on impurity control, and here is where the steelmaking process is critical. For example, in plain carbon and Cr-Mo steels (those with no Ni) where phosphorus is the most important embrittlement element, the percentage can be controlled by the steelmaking process. In steels that contain significant amounts of nickel, antimony and tin are more potent embrittlement elements. Phosphorous has an effect, but not as large as it has in plain carbon and Cr-Mo steels. It should be noted, however, that antimony and tin in plain-carbon steels could cause other hot-working issues.

**How can we correct it?**

Tempered martensite embrittlement (TME) is irreversible and its effects are permanent. By contrast, the effects of temper embrittlement (TE) can be reversed. This is done by re-tempering above the critical temperature of 575°C (1070°F), then cooling rapidly, or by re-austenitizing and cooling rapidly. Impact toughness can be restored. If necessary, this process can be repeated.

**A Simple Example**

Alloy steel, which is susceptible to temper embrittlement, will exhibit a relationship such as shown below (Fig. 1). The lower-temperature energy trough, 250–400°C (480°F–750°F), is indicative of tempered martensite embrittlement while the trough at the higher temperature, 450-650°C (840–1200°F), represents temper embrittlement.

**Summing Up**

The susceptibility of a given steel to temper embrittlement depends on a number of factors including grain size, hardness, steel grade and the impurity control in the steelmaking process itself. Not all steels and not all steelmaking processes are equal.

Finally, as heat treaters we must avoid the temptation to temper to a given hardness value without understanding the consequences of our actions. Since we do not have a simple embrittlement test that can be used on the shop floor, we must understand the phenomenon and question specifications that put us into temper-embrittlement ranges.

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