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STEELS: FOR LOW TEMPERATURE APPLICATIONS

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STEELS: FOR LOW TEMPERATURE APPLICATIONS

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At sufficiently low temperature most structural steels become very brittle and, therefore, unsuitable for use in safety-critical structures. Since modern technology employs many devices that operate at very low (cryogenic) temperatures, it has become important to identify or develop structural alloys that can be safely used in this regime. A number of these devices, such as high field superconducting magnets, require exceptional combinations of strength and fracture toughness at temperatures as low as 4K (liquid helium). Other devices, such as those used for the transport and storage of liquefied natural gas, require exceptional structural reliability at temperatures near that of liquid nitrogen (77K), and must achieve this reliability at moderate cost.

The alloy steels that are used at cryogenic temperatures are tailored to combine high structural strength with good fracture toughness. For particular applications, they may also be required to meet other criteria, such as good fatigue resistance, weldability, low thermal expansion or low magnetic permeability. The steels that have been most often proposed for use in cryogenic structures can be conveniently divided into three categories: (1) Ferritic steels that contain 5-9Ni and are heat treated to have good combinations of strength and toughness at 77K. These are attractive because of their relatively low cost. (2) 300-series austenitic stainless steels, including particularly the low-carbon, high-nitrogen modifications, 304LN and 316LN, which combine high strength and toughness at 4K with good weldability. These alloys are metastable austenitic steels that transform under strain at 4K. (3) High-strength, stable austenitic alloys that have specifically developed for structural use at 4K. These include Fe-Ni-Cr-N alloys (e.g., JN1: 15Ni-25Cr-4Mn-0.4N-0.3Si-0.01C) and Fe-Mn-Cr-N alloys (e.g.,
JK1: 22Mn-13Cr-5Ni-0.2N-0.02C-0.5Si), recently developed in Japan and in the former Soviet Union, and Inconel 908, a nickel-based superalloy (48Ni-4.5Cr-3Nb-1.5Ti-1Al-0.02C) whose thermal expansion coefficient has been controlled for compatibility with Nb3Sn superconducting wire. Typical compositions and properties of these alloys are tabulated in several sources, including the references given at the end of this article. The present article concentrates on the metallurgical principles that underlie their behavior at cryogenic temperatures.

To understand the metallurgical considerations that govern cryogenic steels it is useful to focus on the basic mechanical properties that govern reliability: the yield strength, σ_y, (or ultimate tensile strength, σ_u) and the plane strain fracture toughness, K_{IC}. Both strength and toughness are critical properties since failure may occur through either ductile rupture or fracture. The combination is important since strength and toughness have an inverse relation to one another; an increase in strength at given temperature almost invariably leads to a decrease in fracture toughness. While there is no reliable quantitative theory of the strength-toughness relation of structural alloys, research on the mechanisms of yield and fracture has produced a qualitative understanding of the low temperature strength-toughness combination that is useful for materials selection, quality control and new alloy design. The following discussion summarizes current thinking, and is organized in terms of the mechanisms that may dominate the temperature dependence of the strength-toughness relation: the fracture mode, the tensile properties, and deformation-induced phase transformations.

The Fracture Mode

At the micromechanical level the fracture of a material is either ductile, in which case the material is torn apart after considerable local plastic deformation, or brittle, in which case the crack propagates with very little plastic deformation. In most cases there is a first-order correspondence between the level of toughness and the fracture mode; a change from a ductile to a brittle fracture mode causes a substantial drop in the fracture toughness. It follows that the first concern in addressing the strength-toughness characteristic is the control of the fracture mode.

The most familiar fracture mode change occurs at the ductile-brittle transition in ferritic steels and other BCC alloys. When the temperature falls below the "ductile-brittle transition temperature", T_B, the mode of crack propagation changes to brittle fracture
either by transgranular cleavage of individual grains or by intergranular separation along
grain boundaries. A ductile-brittle transition is also observed in many FCC alloys. In
this case the brittle, low-temperature fracture mode is usually intergranular.

To understand the metallurgical mechanisms that are used to suppress the ductile­
brittle transition, it is useful to refer to the "Yoffee diagram" shown in Fig. 1, which is a
qualitative representation of the relative likelihood of plastic deformation and fracture at
the tip of a pre-existing crack in a structural material. As the applied stress is increased
toward failure the stress at the crack tip reaches one of two levels first: the effective yield
stress at the crack tip, $\sigma_Y$, at which significant plastic deformation occurs, or the brittle
fracture stress, $\sigma_B$, at which the crack propagates in a brittle mode by the most favorable
mechanism. Extensive plastic deformation at the crack tip limits the local stress and
inhibits brittle fracture. Hence the fracture mode is ductile and the toughness high if $\sigma_Y <
\sigma_B$. In this picture, the ductile-brittle transition temperature, $T_B$, is that at which $\sigma_Y$ rises
above $\sigma_B$. The fracture mode below $T_B$ is that which provides the smallest fracture
stress, $\sigma_B$. In BCC material this may be either transgranular cleavage or intergranular
separation. In FCC material the brittle mode is almost always intergranular, if brittle
fracture is observed at all; the transgranular cleavage stress is very high.

The Yoffee diagram also suggests useful metallurgical mechanisms that can be
used to lower or eliminate the ductile-brittle transition. One obvious method is to lower
the alloy strength. The low-temperature strength increment can be specifically decreased
by removing interstitial solutes or by "gettering" them into relatively innocuous precipitates or second phases. For example, ferritic steels that are intended for cryogenic
service are often given intercritical heat treatments that gather carbon into isolated
pockets of retained austenite phase or are alloyed with Ti to getter carbon into precipitates.

The second obvious method is to raise the brittle fracture stress. The appropriate
method for doing this depends on the source of the brittle fracture mode. If the fracture is
intergranular its source is either a grain boundary contaminant, such as the metalloid
impurities S and P in steel, or an inherent weakness of the grain boundary, as is appar­
tently found in Fe-Mn alloys and in many intermetallic compounds. In the case of chemi­
cal embrittlement the alloy may be purified of deleterious surfactants, alloyed to getter
these into relatively innocuous precipitates, or heat treated to avoid the intermediate tem­
perature regime at which these impurities segregate most strongly to the grain boundaries.
When the grain boundaries are inherently weak the metallurgical solution is the addition of beneficial grain boundary surfactants that serve to glue them together. The most prominent of the beneficial surfactants is boron, which is extremely effective in suppressing intergranular fracture in Fe-Mn steels and in Ni$_3$Al intermetallics. Carbon and silicon are also effective surfactants in Fe-Mn steels when they are present in low concentration.

The austenitic steels that are commonly specified for cryogenic service are purified of metalloid impurities and, in the case of the Fe-Mn grades, lightly alloyed with beneficial grain boundary surfactants (C and Si). They are then solution strengthened with interstitial nitrogen. If the alloy has significant concentrations of Cr and Mn, the nitrogen solubility is high, and nitrogen concentrations of 0.2-0.4 wt.% can be added without embrittling grain boundaries. As a consequence, these alloys are not subject to brittle fracture, even when hardened to very high strength at 4K.

When the brittle fracture mode is transgranular, as it is in typical ferritic cryogenic steels, the ductile-brittle transition can be suppressed by decreasing the effective grain size of the alloy, which toughens the alloy by decreasing the mean free path of an element of cleavage fracture. This technique is widely used in the processing and welding of ferritic cryogenic steels. Fe-(5-9)Ni steels form a dislocated lath martensite structure on cooling. The laths are organized into "packets" of laths that have a close crystallographic alignment, and cleave as a unit below $T_B$. Two methods have been successfully used to refine the grain size by breaking up these packets. The most common is to give the alloy an "intercritical temper" at a temperature within the two-phase ($\alpha$ (BCC)+$\gamma$ (FCC)) region of the phase diagram. The intent of this temper is to introduce islands of thermally stable austenite ($\gamma$) along the lath boundaries of the parent martensite, disrupting the packet. In 9Ni steel a single temper at a relatively low temperature within the two phase region is sufficient to accomplish this. However, in the lower alloy grades (5-6Ni steels) a two-step tempering treatment is required. The first is done at a relatively high temperature within the two-phase region, and decomposes the alloy into a dense intermixture of laths with relatively high and relatively low Ni contents. The alloy is then tempered at a lower temperature to create a dense distribution of stable austenite within the high-Ni regions. Because of the similarity in the phase transformation behavior of Fe-Ni and Fe-Mn steels, similar treatments can be used to toughen Fe-Mn steels for cryogenic service, though these remain laboratory alloys.
A second method of refining the effective grain size is to cycle the alloy through the \((\alpha \rightarrow \gamma)\) transition. If the reversion is done sufficiently rapidly, the packet alignment of martensite is disrupted, and the microstructure is refined. This approach is used to permit the welding of ferritic cryogenic steels with ferritic filler wire. The successive passes of a multi-pass weldment can be used to heat-treat one another so that the weldment has a fine packet size and a low \(T_B\).

There is a third common method for decreasing the ductile-brittle transition that is less obvious from the Yoffee diagram: processing the material so as to promote delamination, perpendicular to the fracture plane, that divides the fracture into independent segments that are in nearly plane stress. This technique is ideally equivalent to replacing the plane-strain specimen with a laminate of thin sheets that fracture independently in a nearly plane stress condition. In terms of the Yoffee diagram the effect is to decrease the Yoffee yield strength, \(\sigma_Y\), at a constant value of the tensile yield strength, \(\sigma_t\). Processing treatments that achieve delamination have been successfully applied to suppress the ductile-brittle transition in high-strength, low alloy steels, particularly those destined for tankage and pipelines. Delamination may also play an important role in suppressing low-temperature intergranular fracture in some Al-Li alloys. However, delamination treatments have the disadvantage that they often decrease the fracture toughness in the ductile mode (the "shelf" toughness.) The metallurgical treatments that induce delamination change the microstructure, weaken it in the short transverse direction, and may liberate a low-energy tearing mode of fracture that is not possible in the monolithic plate.

III. Ductile Fracture

The fracture mode that is conducive to a favorable combination of strength and toughness is the ductile mode in which significant plastic deformation precedes fracture. The ductile fracture mechanism that is most important in cryogenic steel plate is microvoid coalescence. Voids nucleate at inclusions, large precipitates or microstructural flaws, and grow until they join one another.

There is no accurate quantitative theory that predicts the fracture toughness of steels that break by microvoid coalescence. However, there are a number of semi-quantitative models. For a given distribution of inclusions most of these lead to relations of the general form
where \( E \) is Young's modulus, \( \sigma_y \) is the tensile yield strength, and \( \varepsilon_f \) is the strain to failure, whose precise definition (and power) varies slightly from one model to another. This equation makes it appear that \( K_{IC} \) should increase with \( \sigma_y \) at given \( T \). In fact, it decreases. The reason lies in the dependence of the failure strain on the yield strength; \( \varepsilon_f \) decreases strongly and monotonically with \( \sigma_y \) at constant temperature.

The interplay between strength, elongation and work hardening in determining the ductile fracture toughness is illustrated by a simple model in which \( \varepsilon_f \) is assumed proportional to the uniform elongation, or necking strain, \( \varepsilon_c \). The strain at which a specimen becomes unstable with respect to necking is determined by the Consider criterion:

\[
\frac{d\sigma}{d\varepsilon} = \sigma
\]

where \( \sigma \) is the true stress and \( d\sigma/d\varepsilon \) is the true rate of work hardening. The flow stress, \( \sigma \), ordinarily increases with the strain while the work hardening rate, \( d\sigma/d\varepsilon \), decreases. The necking strain, \( \varepsilon_c \), is determined by the point at which the two cross, as illustrated in Fig. 2. Fig. 2(a) illustrates the effect of an increase in yield strength in a material that has a fixed strain hardening behavior. As \( \sigma_y \) increases, \( \varepsilon_c \) decreases substantially. Given this behavior, equation (1) suggests why the plane strain fracture toughness decreases as the yield strength is raised. Fig. 2(b) illustrates the effect of increasing the strain hardening rate at a given value of the yield strength; \( \varepsilon_c \) increases as the strain hardening curve is displaced upward (for simplicity, the figure ignores the change in the stress-strain curve due to the increased work hardening). These considerations suggest that \( \varepsilon_f \), and, hence, the plane strain fracture toughness, \( K_{IC} \), in the ductile mode, increase as the yield strength decreases or the work hardening rate increases.

In a typical FCC metal both the strength and the work hardening rate increase as the temperature decreases. The strength rises largely because of the increased effect of solution hardening species; the work hardening rate increases largely because of the difficulty of thermally activated cross-slip at low temperature. The net effect on the fracture toughness depends on the balance between the two; the toughness may rise or
fall. The austenitic steels that are designed for cryogenic service characteristically have very high work hardening coefficients at cryogenic temperature, giving them excellent ductility and very good strength-toughness characteristics.

The second parameter that may significantly influence the toughness of a ductile material is the inclusion content, which determines the density of nucleated microvoids that lead to failure. Ductile fracture theories suggest that a change in the inclusion count at constant values of the tensile properties causes the plane strain fracture toughness to rise according to the relation

\[ K_{IC} \propto \frac{\sigma^p_y}{\sqrt{N_v}} \]  

(3)

where \( N_v \) is the volume density of active inclusions and the exponent (p) is 1/2 or 1, depending on the model. Interestingly, the models predict that the inclusion count has a much stronger influence on the fracture toughness as the yield stress rises, which suggests that the effect should be most apparent at the lowest temperatures and in the highest-strength ductile steels. This prediction is in qualitative agreement with a number of recent observations on the behavior of ductile cryogenic steels. The high-strength austenitic steels that have exceptional combinations of strength and toughness are ultraclean alloys with very low inclusion counts.

IV. **Metastable Austenitic Steels**

The metastable austenitic steels that undergo martensitic transformation at low temperature are exceptional in that they may deform extensively because of the contribution of the martensitic transformation, but eventually fail in a brittle mode through cleavage of the fresh martensite. The best available theories of the "transformation toughening" effect suggest that it is primarily due to the relaxation of the stress at the crack tip by the strain associated with the martensite transformation. However, the transformation has at least three other effects that also influence the fracture toughness. It introduces a brittle martensite phase at the crack tip, which lowers the fracture toughness, it produces a complex microstructure at the crack tip, which forces a more tortuous crack path and raises the fracture toughness, and it changes the work hardening behavior, which may move \( K_{IC} \) in either direction. The net result may be either an increase or a decrease in \( K_{IC} \). A rough rule of thumb is that a moderate degree
of transformation, confined to the crack tip region, increases $K_{IC}$, while either a very slight or a very extensive transformation decreases it.

The extent of the deformation-induced martensite transformation increases as temperature decreases below the critical temperature, $M_d$, which leads to an increase in the fracture toughness as the temperature drops in most metastable austenitic steels. However, either of two effects can cause a maximum in the toughness of a metastable austenitic steel at some intermediate value of the temperature. First, the extent of transformation may become so great that a wide field of brittle martensite forms well ahead of the crack tip. Second, since the strain-induced martensitic transformation is often assisted by thermal activation, the extent of transformation at given strain may actually decrease when the temperature is lowered to 4K.

Since metastable austenitic steels are often specified for the structures of high field superconducting magnets, it is important to recognize that high magnetic fields promote the martensitic transformation and can, hence, affect mechanical properties. For example, when a relatively stable version of 304 stainless steel is tested at 4K in an 8-14T magnetic field, its fracture toughness increases. However, when a relatively unstable version of 304 (low-carbon 304L) is tested under similar conditions, its toughness drops. In this case the crack tip transformation is so extensive that the brittleness of the fresh martensite dominates the fracture toughness. Interestingly, high strength alloys that undergo only slight transformation at 4K, such as 316LN, also have decreased toughness in moderate fields (8T). In this case the small amount of martensite produced at the crack tip appears to act like a distribution of brittle inclusions, and lowers toughness. Higher fields (14T) produce a more extensive transformation of 316LN, and cause an increase in the fracture toughness.

Finally, a martensitic transformation ordinarily has a beneficial effect on the rate of fatigue crack growth. Crack growth is slowed by the relaxation of the stress field at the crack tip. Hence metastable austenitic stainless steels have relatively low fatigue crack growth rates at cryogenic temperature.

References

Handbook on Materials for Superconducting Machinery, MCIC-HB-04, Metals and Ceramics Information Center, Battelle Columbus Laboratories, Columbus, OH, Nov. 1975.


Fig. 1: (a) The decrease in toughness at the ductile-brittle transition. (b) The Yoffee diagram: a qualitative representation of the source of the ductile-brittle transition.
Fig. 2: The Considere criterion. (a) Elongation decreases as strength increases. (b) Elongation increases with the strain hardening rate.