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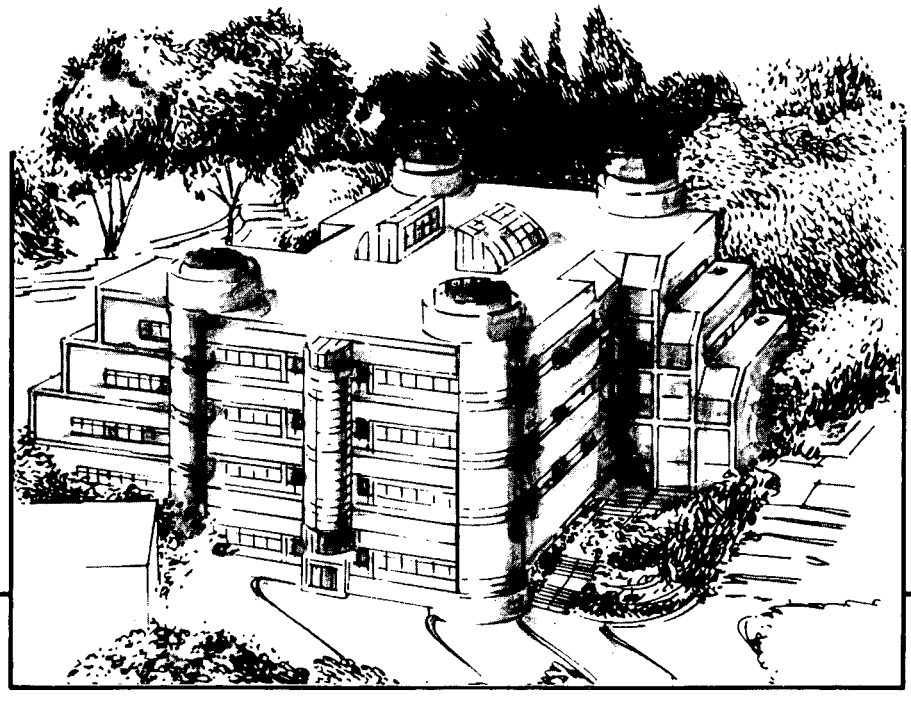

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The Influence of Deformation-induced Martensite on the Cryogenic Behavior of 300-series Stainless Steels

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The Influence of Deformation-induced Martensite on the Cryogenic Behavior of 300-series Stainless Steels

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The 300-series stainless steels that are commonly specified for the structures of high field superconducting magnets are metastable austenitic alloys that undergo martensitic transformations when deformed at low temperature. The martensitic transformation is promoted by plastic deformation and by exposure to high magnetic fields. The transformation significantly influences the mechanical properties of the alloy. The mechanisms of this influence are reviewed, with emphasis on fatigue crack growth effects and magnetomechanical phenomena that have only recently been recognized.

INTRODUCTION

The materials that are most commonly used for the structures of high field superconducting magnets are nitrogen-strengthened Fe-Cr-Ni stainless steels, such as AISI 304LN and 316LN (typical compositions are given in Table I). Nitrogen-strengthened 300-series steels offer high strength, good tensile ductility and high fracture toughness at cryogenic temperatures, and have the additional advantage that they are paramagnetic.

Table 1. Chemical compositions of 300-series steels [wt%]

	Cr	Ni	Mn	Mo	C	N	P	S	Si	Fe
304L	18.9	8.29	1.84	0.43	0.019	0.087	0.024	0.015	0.033	Bal.
304	18.6	8.11	1.52	0.3	0.039	0.089	0.023	0.005	0.26	Bal.
304LN	18.54	9.55	1.77	-	0.021	0.139	0.014	0.009	0.78	Bal.
316LN	17.15	12.88	1.45	2.45	0.023	0.166	0.030	0.005	0.32	Bal.
310S	24.66	19.11	1.84	0.41	0.025	0.062	0.024	0.012	0.52	Bal.

Both the paramagnetism and the good low-temperature ductility of the high-strength 300-series stainless steels are largely due to the fact that these alloys retain the high-temperature, austenitic (FCC) crystal structure even when cooled to temperatures near 4K. However, their cryogenic behavior is complicated by the fact that they are thermodynamically metastable with respect to transformation into the ferritic (BCC) structure. While 304 and 316 alloys that contain sufficient solute additions of carbon or nitrogen are stable on cooling to cryogenic temperatures, they undergo a partial martensitic transformation when they are plastically deformed. In most cases the martensitic transformation contributes to ductility and toughness, and is, in that sense, beneficial. However, the martensitic transformation is difficult to predict and control. To use these steels reliably in high-field magnet structures it is necessary to understand and account for the consequences of deformation-induced martensitic transformations.

In the present paper we briefly describe the dominant martensitic transformation in 300-series stainless steels and discuss its mechanical consequences. We shall focus on the influence of martensitic transformations on fatigue crack growth, and on the consequences of martensitic transformations in high magnetic fields. These aspects of the behavior of 300-series steels are particularly relevant to their use in highly stressed structures of large superconducting magnets, but have only recently come under study.

THE MARTENSITIC TRANSFORMATION

Several different martensitic transformations have been observed in 300-series stainless steels[1]. The most important of these carries the high-temperature γ-phase (face-centered cubic austenite) to a body-centered tetragonal (BCT) product that is called α', and is a slight distortion of the equilibrium α-phase (body-centered cubic ferrite). Other possible transformations take the parent γ to a hexagonal, ε-phase, which may appear in any one of several crystallographic modifications. The transformation to ε is critical to the behavior of many Fe-Mn alloys, but is not ordinarily significant to the behavior of high-strength 300-series steels.

The elementary crystallography of the γ-α' transformation is illustrated in Fig. 1, which shows how a body-centered tetragonal cell can be drawn in the FCC structure. The BCT cell is transformed to BCC if it is compressed along its long axis as shown in the figure at right. To preserve volume, the cell must be simultaneously expanded along each of the axes in its basal plane. The overall deformation is called the Bain strain. Since the BCC structure is more open than FCC, the transformation usually involves a slight increase in atomic volume as well as the shape change, or shear, of the Bain strain. Moreover, when the parent γ phase contains an appreciable concentration of interstitial solutes, such as C or N, the transformation product is slightly tetragonal (BCT), since the solutes distort the asymmetric interstitial sites in the BCC cell.

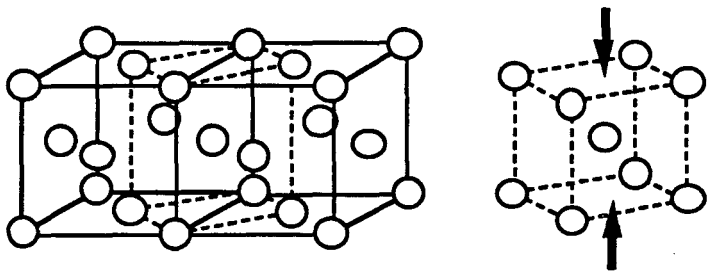


Fig. 1. The BCT cell within an FCC structure that transforms to BCC when given the tetragonal distortion shown at right.

When the γ-α transformation happens at high temperature, as it does in conventional ferritic steels, the transformation proceeds through the classical nucleation and growth of relaxed islands of α. However, the interfacial tension between γ and α is high, and at low temperature there is insufficient thermal energy to activate classical nucleation. The thermodynamic driving force for the transformation increases as the temperature drops, and eventually becomes large enough to drive a *martensitic* transformation, in which the FCC lattice spontaneously shears to accomplish the Bain strain and form the α' phase in the body of γ. The temperature at which this happens is called the *martensite start temperature*, M_S. The martensite transformation does not spontaneously go to completion at $T = M_S$. The formation of a martensite particle distorts the surrounding matrix, and the elastic distortion makes it difficult to continue the transformation. It is for this reason that a classic martensitic transformation occurs over a range of temperatures, being completed only after the temperature is decreased to the *martensite finish temperature*, M_f, which may be several hundred degrees below M_S. Between these limits the alloy is a mixture of γ and α' with a complex microstructure.

The martensitic transformation is influenced by three thermodynamic variables in addition to the temperature. The first is chemical composition. Substitutional solutes such as Ni and Mn stabilize γ and lower M_S, as do the common interstitial solutes, C and N. Structural steels such as 304LN and 316LN are compositionally stabilized to the extent that M_S is below absolute zero.

The second variable is mechanical stress. Since the formation of martensite involves a mechanical deformation, which ordinarily includes a volume expansion as well as a shear deformation, an applied tensile stress promotes the formation of martensite, and particularly promotes the formation of that crystallographic variant of martensite that is most elongated in the direction of the stress. When the parent phase is almost unstable, the martensite transformation can be triggered by the applied stress alone, and is said to be stress-induced. However, much higher stresses are generated within the body of the material by plastic deformation, which produces stress concentrations at dislocation tangles and microstructural discontinuities. The martensite that is generated by these stresses is said to be strain-induced,

and first appears at a reasonably well-defined temperature, M_d, that is substantially above M_s. When a sample is deformed below M_d the fraction of martensite increases with the plastic strain, and ordinarily increases as the temperature is decreased below M_d. An example is shown in Fig. 2, which illustrates the behavior of 304L and 304LN at room temperature and at 77K.

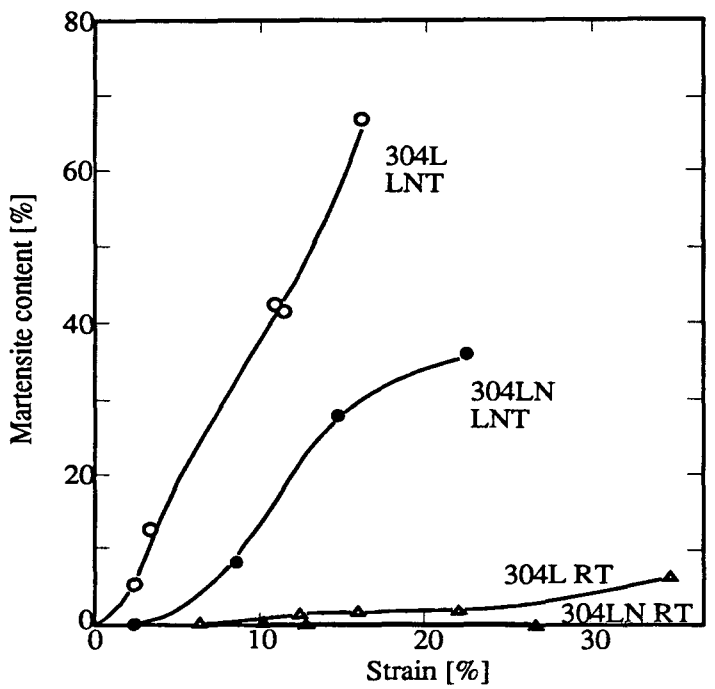


Figure 2. Increase of α' martensite with strain for 304L and 304LN at room temperature and at 77K [8].

The third variable is the magnetic field. Since α' is ferromagnetic while γ is not, a magnetic field promotes the transformation. The thermodynamic effect of a magnetic field is relatively small [2,3]; the predicted increase in M_s is only about 2K/Tesla. However, the kinetics of the transformation are affected as well. The application of a magnetic field significantly increases the extent of martensitic transformation in samples tested below M_s [4-6]. This phenomenon is easily explained if there is an activation step in the transformation with an activation energy proportional to the thermodynamic driving force. Then the fraction of martensite, f_α, should depend on the applied field, H, according to the relation [3].

$$f_\alpha(H,T) = f_\alpha(0,T)\exp\left[\frac{K_2MH}{kT}\right] \qquad (1)$$

where $f_\alpha(0,T)$ is the fraction of martensite in the absence of a field, K_2 is a constant, and M is the magnetic moment of α. The predicted exponential dependence of the initial

transformation rate has been observed [4], and may cause the sudden intrusion of martensite when a magnetic field is applied just below M_s or M_d.

THE DUCTILITY AND TOUGHNESS OF METASTABLE AUSTENITE

The steels of interest in this paper, such as 304LN and 316LN, have M_s below 0K, but M_d values such that martensite does appear during deformation at cryogenic temperature. The martensitic transformation influences alloy ductility and toughness. Depending on the details of the transformation, its mechanical consequences may be beneficial or harmful.

Tensile properties.

Deformation-induced martensite influences tensile behavior in three ways. First, because of the volumetric and shear strains it carries, the martensite transformation is a plastic deformation mechanism that contributes to the total plastic strain. If the martensite is stress-induced or intrudes at low strain, it lowers the proof stress of the alloy and causes a low strain-hardening rate at small strains (Fig. 3a). Second, the transformation produces a complex microstructure in which a relatively soft γ-phase is decorated by platelets of much harder fresh martensite. Both the introduction of the harder martensite phase and the local disturbance of the microstructure increase the strain-hardening rate. Since the tensile elongation is determined by a balance between the stress and the strain hardening rate, the transformation may enhance or curtail tensile elongation. If the martensite fraction increases rapidly with strain the material work-hardens quickly and the ductility is low (Fig. 3a). If the martensite fraction increases more slowly with strain, as it does in a relatively stable alloy, the transformation enhances the work hardening rate at high strains and the material exhibits exceptional ductility (Fig. 3b). (This latter behavior is the basis for the "TRIP" steels whose high elongations generated some excitement in the late 1960's.) Third, the fresh martensite introduced by the transformation is a brittle phase, particularly at cryogenic temperature. As a consequence, metastable austenitic steels have little or no post-necking elongation and produce fracture surfaces that are flat and brittle in appearance, even when the alloy has very high tensile elongation.

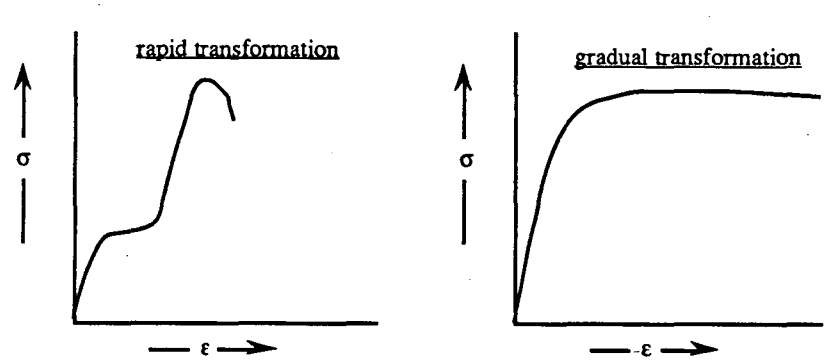


Figure 3. Characteristic stress-strain curves for (a) rapid martensitic transformation; (b) gradual transformation.

Fracture toughness.

Similar factors affect the fracture toughness of metastable austenitic steels. The transformation strain relieves the stress concentration at the tip of a crack or flaw. Its dilational component directly relieves the triaxial tension at a crack tip in plane strain. These effects raise the fracture toughness. (They are responsible, for example, for the relatively high fracture resistance of "transformation-toughened" ceramics.) The increased work hardening rate may also improve fracture toughness by increasing ductility and, hence, resistance to ductile fracture. The introduction of a dispersion of martensite at the crack tip also enhances resistance to crack growth by forcing a more tortuous fracture path. These benefits are counterbalanced, however, by the brittleness of the fresh martensite, which cleaves easily under tensile stress. As a consequence, unstable alloys that transform extensively at the crack tip have lower toughness than stable alloys of comparable strength, while metastable materials that undergo partial transformation at the crack tip have relatively high fracture toughness.

Fig. 4 shows the relative values of the ductility and toughness of 300-series stainless steels as the temperature is decreased from room temperature to 4K. These alloys tend to show a weak maximum in properties near 77K. The primary benefits of the martensitic transformation is obtained above 77K where the alloys are relatively stable. Below 77K the extent of transformation is relatively constant. The increase in mechanical strength decreases ductility and toughness.

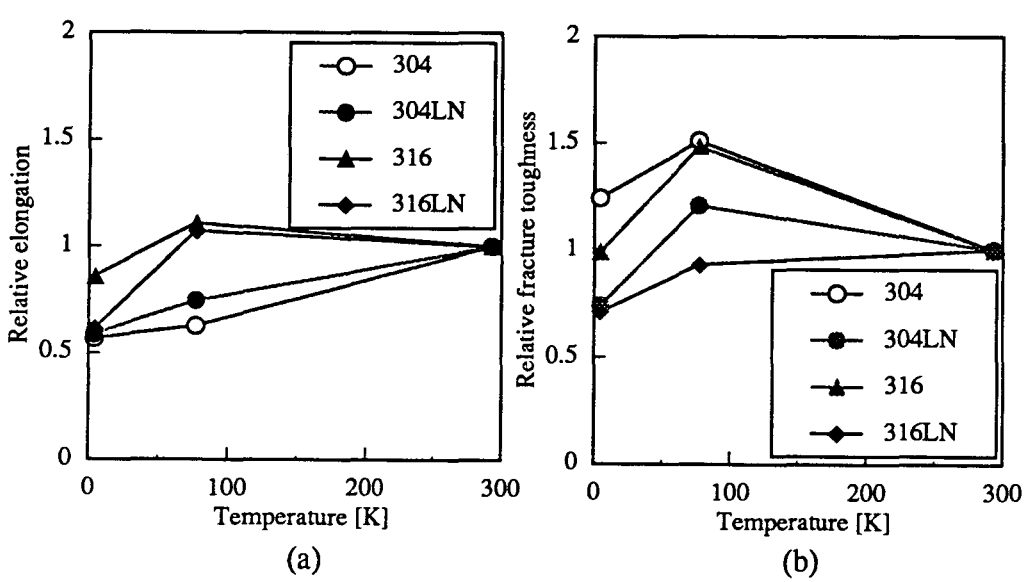


Figure 4. Relative (a) ductility and (b) toughness of 300-series steels between room temperature and 4K.

FATIGUE CRACK GROWTH IN METASTABLE AUSTENITE

When cryogenic structures are subject to cyclic stress their reliability is often limited by fatigue crack growth. It has been known for many years that materials that undergo strain-induced martensitic transformations have unusual fatigue crack growth properties [7]. The transformation ordinarily lowers the rate of fatigue crack growth. However, the effect has been difficult to predict with the accuracy that is needed to take advantage of it in design.

The fatigue resistance of a structural alloy is best measured by plotting the crack growth rate per stress cycle (da/dn) against the cyclic stress intensity, ΔK, which is a measure of the actual cyclic stress at the tip of a growing crack:

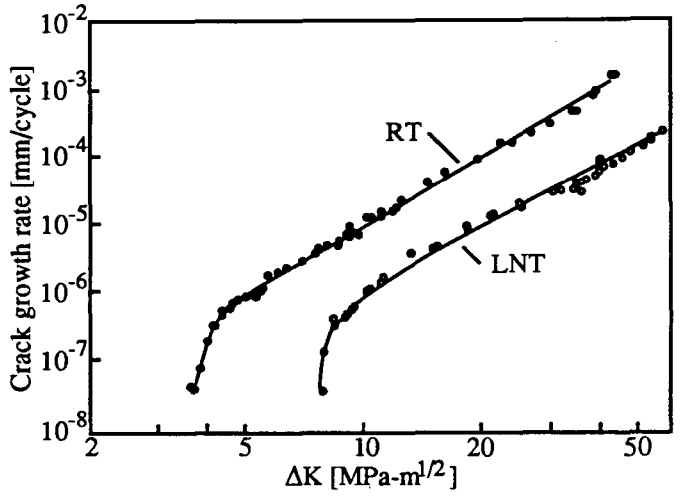
$$\Delta K = Q(\Delta\sigma)\sqrt{a} \tag{2}$$

where Q is a geometric factor, $\Delta\sigma = \sigma_{max} - \sigma_{min}$ is the applied cyclic stress, and a is the crack length. Example curves are shown in Fig. 5. These curves have three important features. First, there is a value of the cyclic stress intensity, which is called the threshold value, ΔK, below which a typical crack will not grow. ΔK_{th} defines the "safe" value of $\Delta\sigma$ for a given crack length, a. If ΔK is held below ΔK_{th}, the fatigue life is arbitrarily long. Second, there is a broad range of values of ΔK above ΔK_{th} for which the crack growth obeys a simple power law, called the Paris Law,

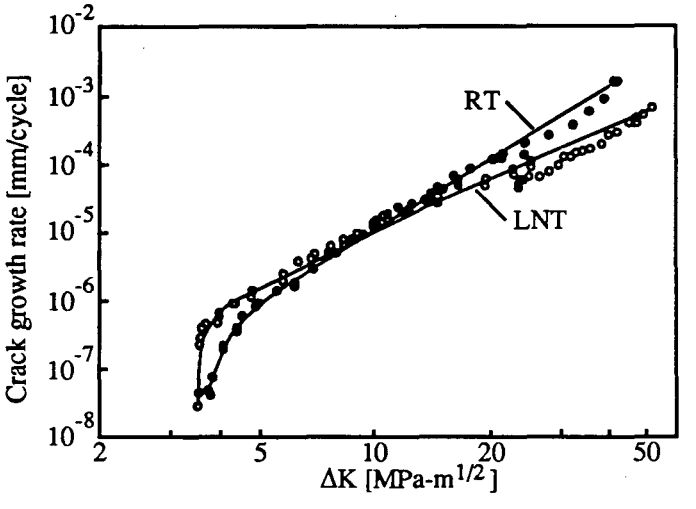
$$\frac{da}{dn} = A(\Delta K)^m \tag{3}$$

which provides a tractable constitutive relation to determine the fatigue life of a structure that is subject to cyclic stresses that are large enough to drive a crack. The third region of behavior is entered when K_{max} becomes comparable to the fracture toughness, K_{Ic}. The crack growth rate accelerates rapidly until the sample fails. However, if the toughness is reasonably high and the initial flaw size reasonably small, it can be shown that the fatigue life (cycles to failure) is almost insensitive to the value of K_{Ic}; the fatigue life is almost completely determined by the Paris Law if ΔK_{th} is exceeded.

Fig. 5a shows typical fatigue crack growth curves for 304L at room temperature, where it is almost stable, and at 77K, where it undergoes an extensive deformation-induced transformation. Fig. 5b contrasts the temperature dependence of fatigue crack growth in 304LN, which transforms only slightly at 77K. This and other data shows that temperature has very little effect on the rate of fatigue crack growth in these alloys, but that the martensitic transformation sharply decreases the fatigue crack growth rate in the linear (Paris) region, and also significantly raises the threshold stress intensity (ΔK_{th}) that is required to drive the fatigue crack. Both of these effects are highly beneficial. However, the magnitude of the effect is not only sensitive to the stability of the alloy, but also depends



(a)



(b)

Figure 5. Fatigue crack growth curves for (a) 304L and (b) 304LN at room temperature and 77K [8].

strongly on the load ratio $R = K_{min}/K_{max} = \sigma_{min}/\sigma_{max}$ at which crack growth occurs. Fig. 6 illustrates this phenomenon for the case of 304L at 77K. If R is greater than about 0.5 almost all of the benefit of the transformation has disappeared.

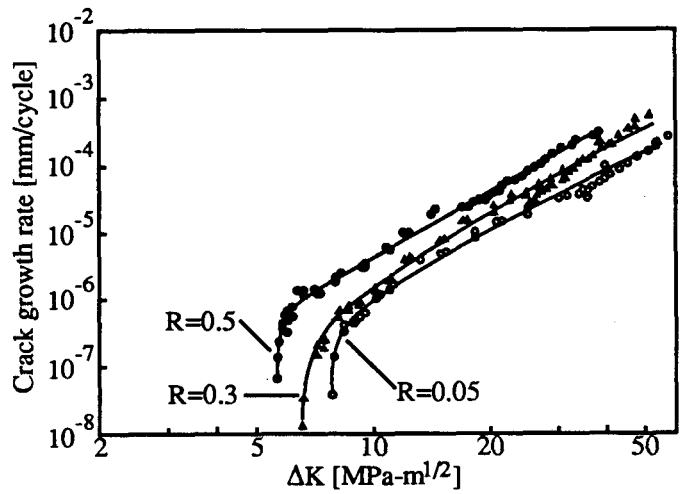


Figure 6. Change in fatigue crack growth rate with the load ratio, R, for 304L at 77K [8].

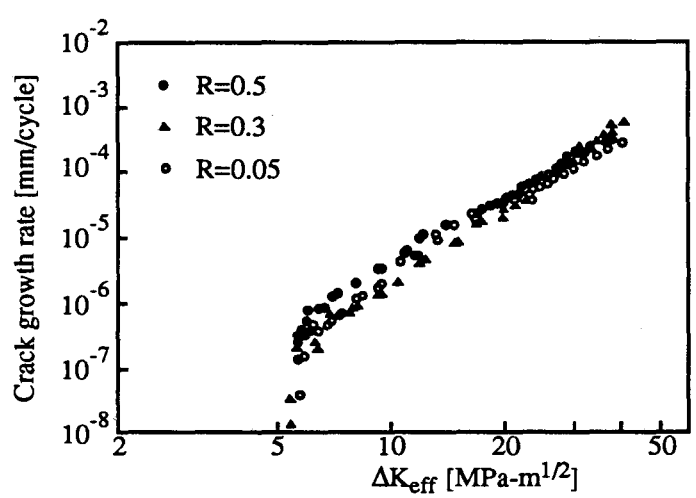


Figure 7. Fatigue crack growth rate of 304L at 77K as a function of ΔK_{eff} [8].

Fortunately, there is a relatively simple quantitative theory that accounts for most of the effect of the martensitic transformation [8]. It is based on the fact that the most important factor that limits fatigue crack growth at a given value of ΔK is crack closure. If the crack closes on itself at some value of the stress intensity, $K_{cl} > K_{min}$, then the crack tip does not experience the full stress cycle, ΔK. It only experiences the effective cycle, $\Delta K_{eff} = K_{max} - K_{cl} < \Delta K$, and grows more slowly. The crack closure that is normally encountered in fatigue crack growth is a relatively macroscopic effect. Growing fatigue cracks are irregular in shape, and asperities on the crack surface impinge to close the crack before the lips at the crack tip seal. This macroscopic closure is ordinarily responsible for the rapid decrease in

the crack growth rate near the threshold; however, its effect is only important when ΔK is near ΔK_{th} [9].

An important new crack closure mechanism is active in metastable austenitic steels [8,10]. The transformation at the crack tip causes a volume expansion. Given the shape of the transformation zone, which tends to follow a contour of constant shear in austenitic steels, the volume expansion compresses the crack tip and causes closure at a stress intensity, K_{trans}, that exceeds K_{min} over most of the crack growth range when R is small. This microclosure at the crack tip is responsible for the low crack growth rates of metastable austenitic steels in the Paris range. Its importance decreases as the load ratio increases, which is why the transformation offers little or no benefit when $R > 0.5$. The macroscopic closure condition, K_{cl}, is measurable, and the microclosure condition, K_{trans}, can be calculated to a reasonable approximation from measurements of the transformation zone size at the crack tip. If the cyclic stress intensity, ΔK, is replaced by

$$\Delta K_{eff} = K_{max} - \max\{K_{min}, K_{cl}, K_{trans}\} \tag{4}$$

the result is a constitutive relation that provides a good prediction of the crack growth rate in metastable austenitic steels (Fig. 7).

THE INFLUENCE OF HIGH MAGNETIC FIELDS

Since a magnetic field promotes the martensitic transformation, it should affect those mechanical properties that depend on the extent of the transformation, including tensile behavior, fracture toughness and fatigue crack growth. The available data shows these effects.

Tensile properties.

The influence of a high magnetic field on the tensile behavior of 304L is illustrated in Fig. 8, which compares the tensile stress-strain curve at 77K in the absence of a field to that in a field of 18T [11]. The effects include a slight decrease in the proof stress, a significant increase in work hardening at moderate strain, an increase in the ultimate tensile stress, and a decrease in the total elongation. These are the expected effects of an increase in the rate of transformation, as described above. Similar effects are observed at 4K, though they are obscured by the serrated form of the stress-strain curve at that temperature. Similar effects are also observed in the more stable alloy, 304LN, though they are less pronounced. Fig. 9 shows the influence of the magnetic field on the maximum flow stress of 304L and 304LN. The fractional increase in flow stress is almost linear in the applied field, and is almost independent of temperature at 77K and below. The magnetic field effect essentially disappears in 304L at fields below about 6T, and is negligible in 304LN at fields below about 10T.

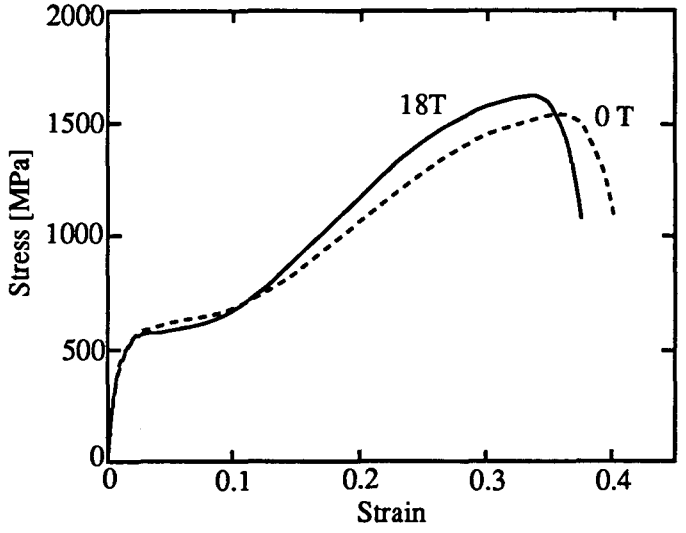


Figure 8. Stress-strain curve of 304L in fields of 0T and 18T at 77K [11].

Fracture toughness.

The influence of a magnetic field on fracture toughness is more complicated, and appears to depend on the stability of the alloy. Again, most of the pertinent data concerns 304-type alloys, and is confined to 8T fields. The results of tests by Fukushima, Murase and coworkers at Toshiba [12-14] and by the authors at LBL [15-17] produce results that are in good agreement with one another, and are generally described by Fig. 10. Unstable alloys, such as 304L, lose toughness in an 8T field, while more stable alloys, such as 304, gain toughness when the field is applied. Surprisingly, alloys that are only slightly unstable, such as 316LN [14,18] and 304N [13] also have lower toughness in an 8T field.

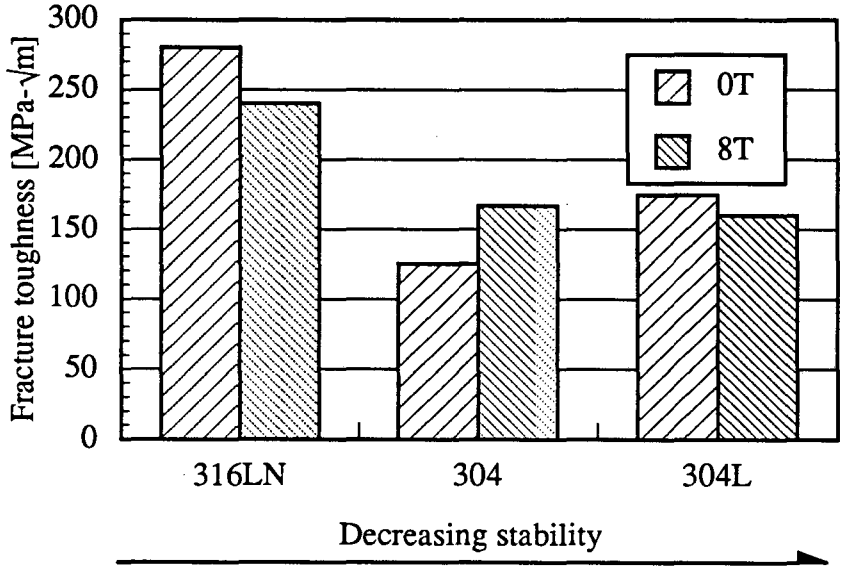


Figure 10. The influence of an 8T field on K_{Ic} for 300-series steels.

Fundamental research has shown that the magnetic field effect on fracture toughness is subtle [16]. While the martensite transformation at the crack tip is measurably more extensive in an 8T field, the increase in toughness in 304 is much greater than can be explained on the basis of existing theories of transformation toughening, and the decrease in toughness in alloys such as 304L and 316LN is counter to those theories. Fractographic studies [17] suggest that the increase in the toughness of 304 is largely due to a change in the microstructural pattern of the transformation. The martensite produced in 304 in an 8T field is both more densely distributed and more finely grained than that produced in the absence of the field, which produces a more tortuous crack path. The decrease in toughness in 304L is apparently due to the extensive transformation in the crack tip field, which produces a region that is essentially filled with brittle martensite. The toughness decrement in 316LN remains to be explained.

Fatigue.

The only investigation of fatigue crack growth in a high magnetic field that is known to us measured the crack growth rate of 304LN and 304L in an 8T field at 77K [19]. The measurements were confined to relatively high ΔK values in the Paris region. The results showed a slightly lower crack growth rate in the presence of the field. Since the field promotes the martensitic transformation, the results are consistent with the studies of fatigue crack growth in metastable austenitic steels in the absence of the field.

Cryogenic creep.

A final interesting effect of a high magnetic field is the cryogenic creep of metastable austenitic steels in a pulsed field [3]. In this experiment samples of 304L and 304LN were bolt-loaded to stresses slightly beyond the yield stress, and then subjected to multiple 16T pulses at 77K. The tensioned bolts experienced progressive strain as the magnet was pulsed. Post-test analysis suggested that the accelerated creep is due to two effects: progressive martensitic transformation, and plastic strain of the matrix to relieve the transformation strain.

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