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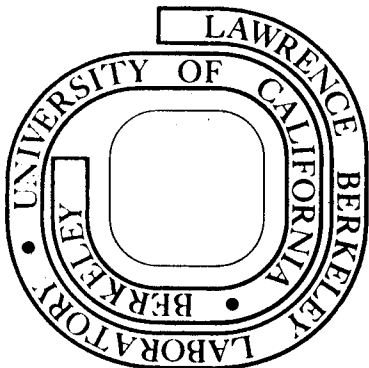
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# THE CHANGING ROLE OF METASTABLE AUSTENITE IN THE DESIGN OF ALLOYS

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## INTRODUCTION

A commonly employed procedure of alloy design consists of identifying and characterizing the fine-scale elements of structure (crystal structure, defect structure, and microstructure) and establishing the relationships between properties of interest and details of the structure. Earlier attempts to design alloys consisted mainly of trial-and-error procedures based on experience. Alloy design is now entering a scientific stage, but, to a considerable extent, is still a mixture of applied science and art, with the art gradually being replaced by science. The impact of science has accelerated rapidly during the past several decades. It is instructive to consider why this is so and to speculate about the future rate of progress in alloy design.

The structure-sensitive properties of alloys are determined by the chemical composition, the manufacturing process, and the microstructural elements of the solid as produced by controlled heat treatments. High-resolution instruments capable of analyzing composition on a microstructural scale and others capable of characterizing elements of microstructure with dimensions of a micron or less are now widely available. These instruments have greatly enhanced our knowledge of solid-state reactions and thereby have been responsible for ushering in a new era of alloy design. Developments along a different line are also contributing substantially to the progress of alloy design. For example, the development of a quantitative theory of fracture toughness has enabled metallurgists and mechanical engineers to formulate useful relationships between fracture toughness and the elements of microstructure. Applications of dislocation theory, thermodynamics, alloy chemistry, and micromechanics of deformation and fracture have been major factors in accelerating the advancement of alloy design. Dramatic changes have occurred during the last several decades in the metallurgists' conceptual approach to designing new structural alloys and improving old ones. This can be illustrated by examples taken from our own research efforts.

Illustrative of the rapid evolution of the alloy design of steels since World War II has been the ever-changing role of the microstructural constituent known to metallurgists as *metastable austenite*, which can exist at any temperature below the equilibrium  $\gamma \rightarrow \alpha$  transformation temperature. Being metastable, this austenite can decompose isothermally, given enough time at a constant intermediate temperature or, under certain conditions, it can be transformed to martensite by a stress- or strain-induced transformation. By investigating the differing roles that this microstructural constituent has played in several important classes of experimental steels, insight has been gained into controlling the morphology and defect structure of austenite in order to optimize combinations of strength and toughness. Three classes of alloys are used to illustrate the various roles that metastable austenite has played in alloy design and development. These three types have been classified as ausform, TRIP, and medium-alloy ultrahigh-strength (UH) steels. Information and figures for the section on ausform steels were taken largely from (2).

## DISCUSSION

### Ausform Steels

In the mid-1950s, before the extensive use of electron microscopy or fracture mechanics, one promising approach to alloy design was the use of thermo-

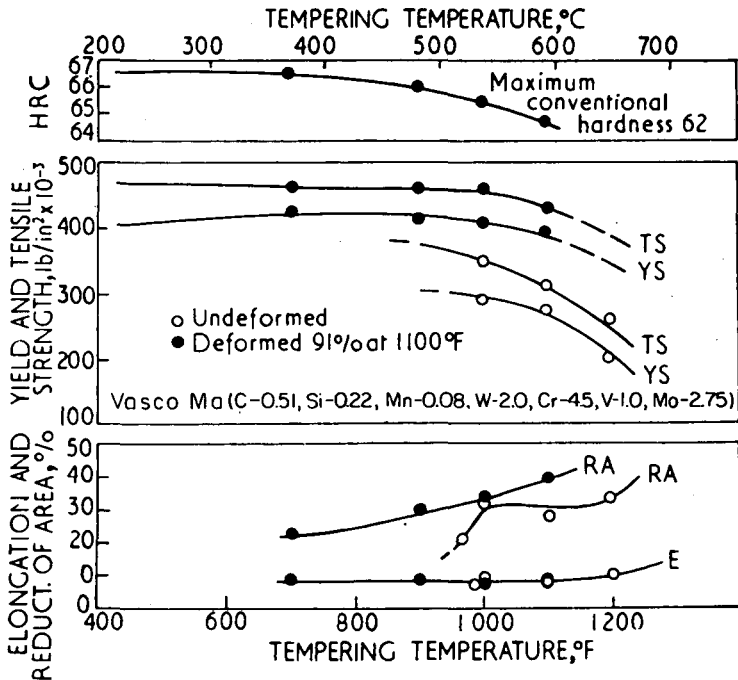


Figure 1 The mechanical properties of type H-11 steel in the ausform and conventionally heat-treated conditions as a function of tempering temperature.

mechanical treatments (TMT) to enhance mechanical properties. Although it had long been known that the strength of metals and alloys could be greatly increased by plastic deformation below the recrystallization temperature, the full potential of TMT had not been realized. One of the most productive of the TMT research efforts came to be known as the ausform process (1, 2), in which severe plastic deformation of the metastable austenite was superimposed on the heat-treating cycle of medium- to high-alloy steels in the temperature range below the recrystallization temperature and above the  $M_s$ , followed by quenching and tempering. The resulting martensite morphology (lath or plate size) and substructure were drastically altered by ausforming, as were the associated mechanical properties. The levels of strength, toughness, and fatigue strength that were attained have still not been exceeded. They are therefore of more than historical interest. Some of the extraordinary properties of steels processed in this manner are described below.

One of the surprising and provocative results was the virtual elimination in ausform steels of the secondary hardening peak, commonly found in medium- to high-alloy steels, as shown in Figure 1. The explanation for this behavior is presented later. The increase in yield strength produced by ausforming, above the yield strength provided by the standard heat treatment for these steels, was well over 100,000 psi. The tensile properties of VASCO MA (0.5C, 0.22Si, 0.08Mn, 2.0W, 4.5Cr, 1.0V, 2.75Mo) steel in both the conventionally treated and ausform conditions

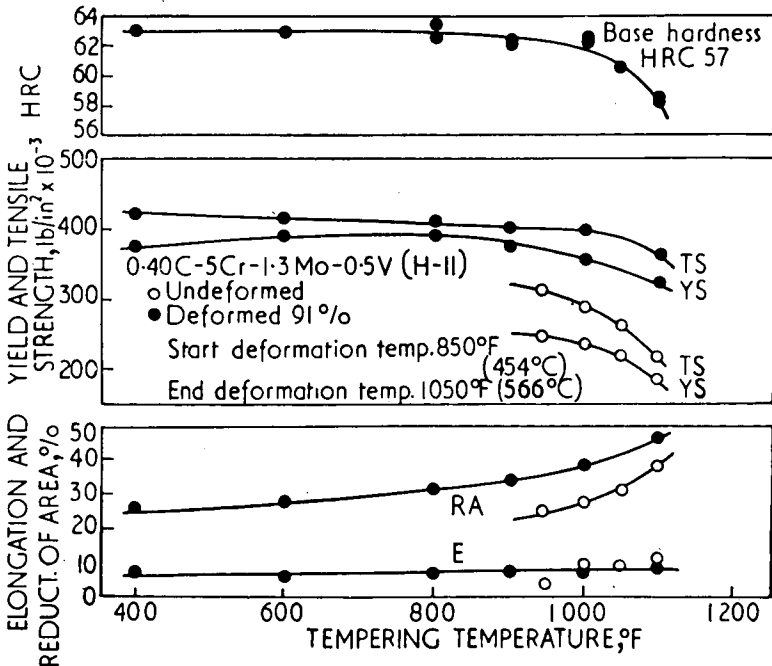


Figure 2 The mechanical properties of VASCO MA steel in the ausform and conventionally heat-treated conditions as a function of tempering temperature.

are shown in Figure 2. To our knowledge, the strength of this steel is the highest ever reported for a bulk metal specimen.

Lastly, the fatigue properties of steels in both the conventional and TMT-treated conditions are shown in Figures 3 and 4. The endurance limits at various survival levels were superior for the TMT steel, as shown in Figure 3. Similarly, the ratio of endurance limit to tensile strength remained unexpectedly high for the TMT steels at tensile strengths well above 200,000 psi.

During the early part of the last decade, extensive investigations were undertaken with high-resolution instruments to establish the structural and chemical factors responsible for the superior behavior of TMT alloys. Serious attempts were made to estimate the relative importance of the various strengthening mechanisms such as increased dislocation density, pinning of dislocations by solute atmospheres or precipitated particles, and the altered size and morphology of microstructural constituents. There was general agreement about the relative importance of each of these factors, except for one, that of dislocation-precipitate interactions. Although there was an abundance of indirect evidence suggesting that the solute atoms were not in random solid solution after TMT, opinions varied regarding proof of the existence of discrete precipitates (3-6). For example, the absence of secondary hardening peaks in the TMT steels could be interpreted as indicating that alloy carbides had formed during the ausform process. In marked contrast to the intensive investigations of the relation between structure and tensile properties, virtually no

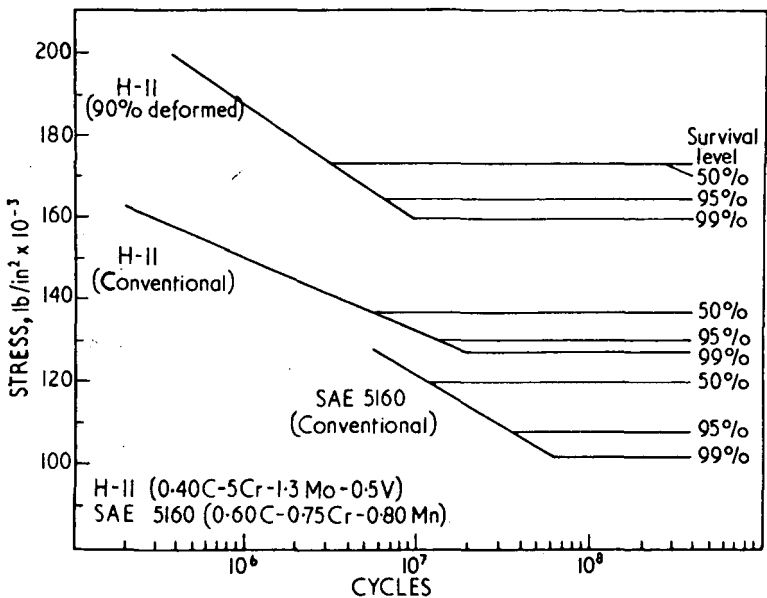


Figure 3 The endurance limits at various survival levels for conventionally treated H-11 and SAE 5160 steels and for ausformed H-11 steel.

investigations have been undertaken to provide an understanding of the superior fatigue properties.

In retrospect, the experiences of this early period of alloy design research were valuable, even though the approach was primarily qualitative. There were at least three major achievements during the early period. First, it became clear that optimum properties could be produced by controlling both the defect (dislocation) structures and the microstructures. These fine-scale structures could not be produced by the conventional variations of composition or heat treatment. It was reasoned that structural units of extremely small dimensions would be formed during TMT processing because of the short-range diffusion paths of solute atoms and the restricted dislocation mobility at the relatively low temperatures of ausforming. Second, the laboratory successes of the TMT studies provided the motivation for the development of practical processes, which are now, a decade and a half later, widely used in many applications (7, 8). Such processes have been applied to the low-alloy structural steels (the so-called HSLA steels), to the ultrafine grain size controlled recrystallization steels, to the processing of nickel- and cobalt-base superalloys, and to defense applications such as armor plate, advanced suspension systems, and high-performance bearings. Third, the mechanical properties obtained by TMT processes have established a quantitative upper limit of strength for bulk solids—a goal for alloy designers to achieve by the manipulation of the technologically more desirable variables of composition and heat treatment alone.

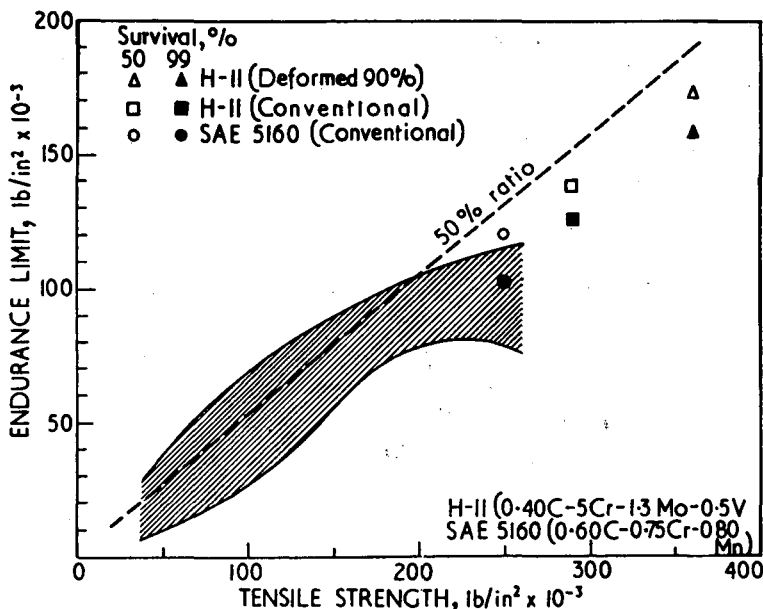


Figure 4 The endurance limit-tensile strength ratio for some ausformed and conventionally treated steels.

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The objective of using the ausform process was to produce severe plastic deformation of the metastable austenite prior to its athermal transformation to martensite. The chemical and structural changes induced by severe plastic deformation of the metastable austenite favorably altered the defect structure and microstructure, which, in turn, provided superior strength and toughness. In the next section, a class of alloys is discussed wherein the metastable austenite is transformed in service rather than during the heat-treating process. The transformation to martensite is induced by either stress or strain at a constant temperature.

### *TRIP Steels*

After about ten years of laboratory and commercial exploitation of the TMT processes, a quantitative form of analytical mechanics conceived and developed by mechanical engineers, known as linear elastic fracture mechanics, was widely used by metallurgists (9). The extremely important property of toughness of ultrahigh-strength steels (of moderate thickness) or of medium-strength steels (of relatively large thickness) could not be measured quantitatively prior to the advent of fracture mechanics, and metallurgists had no way of establishing meaningful relationships between microstructure and toughness. As a consequence, progress in the design of low- and medium-alloy steels with improved toughness was slow. Furthermore, ultrahigh-strength steels, as conventionally heat treated now, not only have marginal toughness but also exhibit low levels of uniform elongation. Ductility is desirable in these steels for ease of fabrication after heat treatment as well as for engineering safety in the event of structural overloading.

We considered the dual problem arising from low levels of toughness and ductility in ultrahigh-strength steels in the mid-1960s in the hope that ductile TMT alloys might be developed with superior toughness, as measured quantitatively by fracture mechanics. The approach was successful, and a new class of steels known as TRIP steels (transformation-induced plasticity) was developed (10). These steels exhibited levels of toughness and uniform elongation far superior to any obtainable with available commercial alloys. A brief description of the structure and associated properties of these steels and of how they led to the design of non-TMT steels having unusual properties is given in the following section.

Elastic and plastic deformation of structural alloys rarely produces a change of crystal structure. There is, however, a well-known type of diffusionless phase transformation, the martensitic transformation, which can be induced either by stress or by plastic strain. Because the mechanical properties of an alloy are often partly determined by its crystal structure, an alloy can be designed that transforms when overloaded in service or during testing. If such a characteristic is to be designed into an alloy, it must produce a favorable change in the properties of the alloy. This is the case for TRIP steels. The martensite transformation induced by deformation enhances both ductility and fracture toughness. Deformation-induced martensitic ribbons are distributed throughout the austenitic matrix and markedly alter the ductility, strain-hardening rate, tensile strength, and fracture toughness. When martensite forms during a tensile test, the strain-hardening rate increases and necking is delayed until high strains are reached. The uniform elongation and the

tensile strength are increased because of the high rate of strain hardening caused by the martensite laths, which act as "barriers" to plastic flow (11).

A stability index for high-strength metastable austenitic steels permits predictions to be made of the effect of composition and processing conditions on mechanical properties. In the following discussion, the Gerberich index (12) is used as a relative measure of austenite stability, with the objective of correlating the tensile properties of the steels with variations in a composition and processing. Gerberich et al (12) have reported that the volume fraction of martensite,  $V_\alpha$ , produced during a tensile test varies as

$$V_\alpha = m\epsilon^{1/2},$$

where  $m$  is a constant for a particular set of test conditions and  $\epsilon$  is the conventional strain. The value of  $m$  was obtained from the best linear relationship between  $V$  and  $\epsilon^{1/2}$ . Typical experimental data for a steel containing 8% Ni, 9% Cr, 2% Mn, and 0.325% C, deformed 70% at 450°C, are shown in Figure 5 for a test temperature of -78°C (13). Gerberich et al showed that the coefficient  $m$ , although approximate, was a useful index of austenite stability for TRIP steels having widely varying

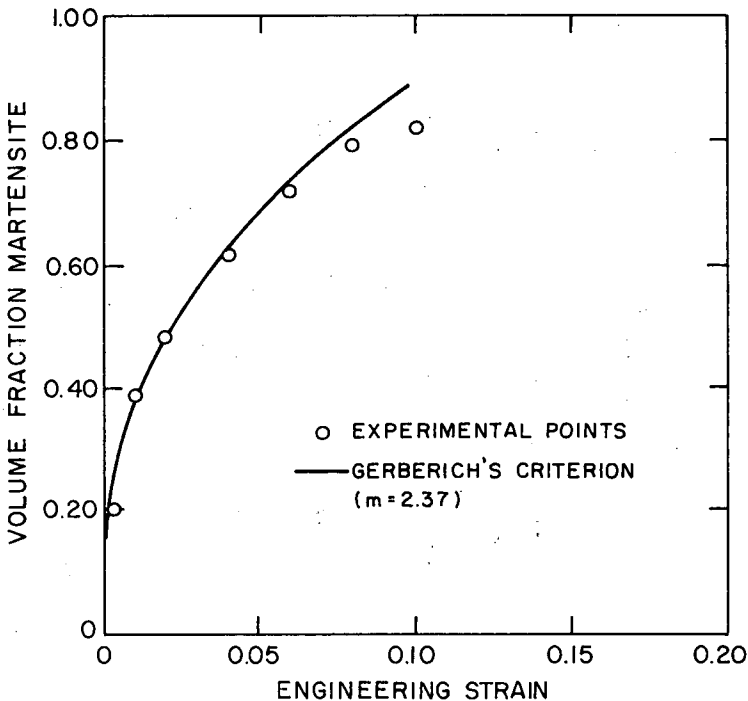


Figure 5 The relation between engineering strain and the volume fraction of martensite that is produced in a steel containing 8.0Ni, 9.0Cr, 2.0Mn, and 0.325C, deformed 70% at 450°C, when tested at a temperature of -78°C.

chemical compositions and processing histories. In these steels, the coefficient can be varied from zero (completely stable) to approximately 3.5 (highly unstable). The value of  $m$  is zero when the test temperature is at or above the  $M_d$  temperature—the temperature above which plastic strain will not induce a transformation (14).

The influence of the stability coefficient,  $m$ , on the elongation to fracture for a large group of TRIP alloys having widely varying compositions, processing histories, and test temperatures is shown in Figure 6. Similar correlations exist for the extent of the Lüders strain, the rate of strain hardening, and the tensile strength (12, 14). The stability of the metastable austenite can also be altered by varying the chemical composition; the stress-strain curves for three steels of different nickel contents, deformed 70% at 450°C and tested at -78°C, are shown in Figure 7. The differences between the curves are striking. The maximum elongation occurs when martensite is produced at an optimum rate with strain (12, 15, 16). Too little martensite forming per unit strain results in early necking and too much causes premature failure.

Several investigators have suggested that a stress- or strain-induced phase transformation might enhance the absorption of energy and thereby increase fracture toughness (17-22). The fracture toughness of TRIP steels has been studied from both the theoretical and experimental viewpoints. It is clear from these studies that toughness is dependent upon the austenite stability, the chemical composition of the

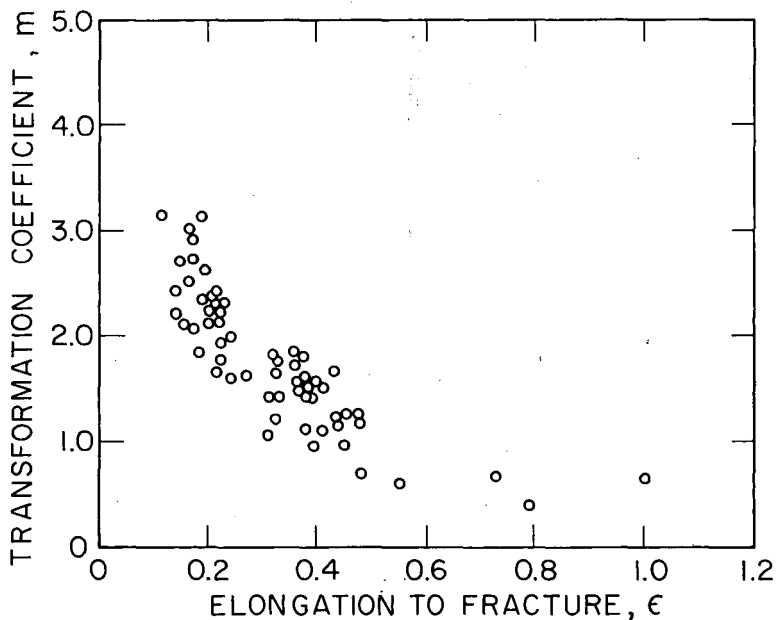


Figure 6 The correlation between the stability coefficient,  $m$ , and the elongation to fracture for a large group of TRIP steels of widely varying composition, processing histories, and testing temperature.

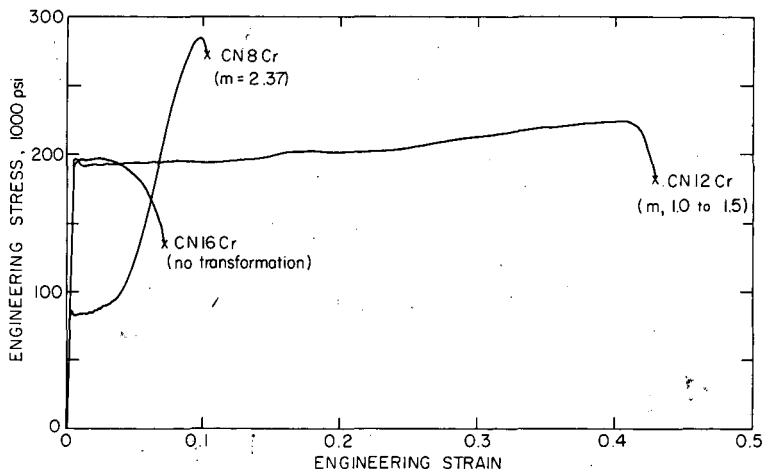


Figure 7 The engineering stress-stress curves for steels containing 8, 12, and 16% Ni, deformed 70% at 450°C and tested at -78°C. The values of the stability coefficient,  $m$ , are shown.

strain-induced martensite, and the strain rate. Gerberich et al (12) showed that, to a first approximation, the plane-stress fracture toughness  $K_{Ic}$  is proportional to  $m^{1/2}$ . At room temperature,  $K_{Ic}$  values of almost 500,000 psi-in<sup>1/2</sup> were reported for steels having yield strengths of 200,000 psi or higher; a summary of the data is shown in Figure 8. The fracture toughness is decreased with increasing concentrations of carbon and nitrogen in any alloy. Zackay & Parker (11) suggested that an important factor in the unusual fracture toughness of TRIP steels may be a change in the stress state existing near the tip of a crack in a steel undergoing a stress- or strain-induced transformation. When austenite transforms to martensite, there is a volume increase of about 3%, which effectively cancels a large part of the triaxial stress that exists near the root of a sharp crack or notch. The reduction in the triaxial component of stress has a marked effect on the behavior of thick specimens, where triaxiality is a major contributor to brittle behavior. As a consequence, the rate of decrease of fracture toughness with specimen thickness of TRIP steels is considerably less than that for quenched and tempered steels. As shown in Figure 9, the critical stress intensity factor ( $K$ ) of both the low-alloy quenched and tempered steel and the precipitation-hardening stainless steel, decreases with thickness more rapidly than for the TRIP steels (19).

There is now a general consensus among metallurgists that many of the excellent mechanical properties of ausform and TRIP steels are associated with the presence of metastable austenite either during (ausform) or after (TRIP) processing. Therefore, it appeared desirable to try to incorporate metastable austenite into the microstructure of medium-alloy ultrahigh-strength steels. This research effort, described in the following section, is a long-term project that is not yet complete.

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### Medium-Alloy Ultrahigh-Strength Steels

The medium-alloy ultrahigh-strength (UHS) steels, unlike the ausform and TRIP steels, are well established in the technology, and several million tons are produced annually for a wide variety of applications. Despite their versatility, economy, and excellent mechanical properties, these steels have several serious limitations. At yield strengths over 200,000 psi, the toughness in thin sections is low and in thick sections the toughness is inadequate for many structural applications. In addition, both the ductility and the ductile-brittle transition temperature (DBTT) are low. Low ductility is undesirable in the post-heat treatment fabrication of these steels, e.g. in fastener applications; ductility and toughness are outstanding in the TRIP steels.

An early promising discovery was the detection of relatively large amounts of

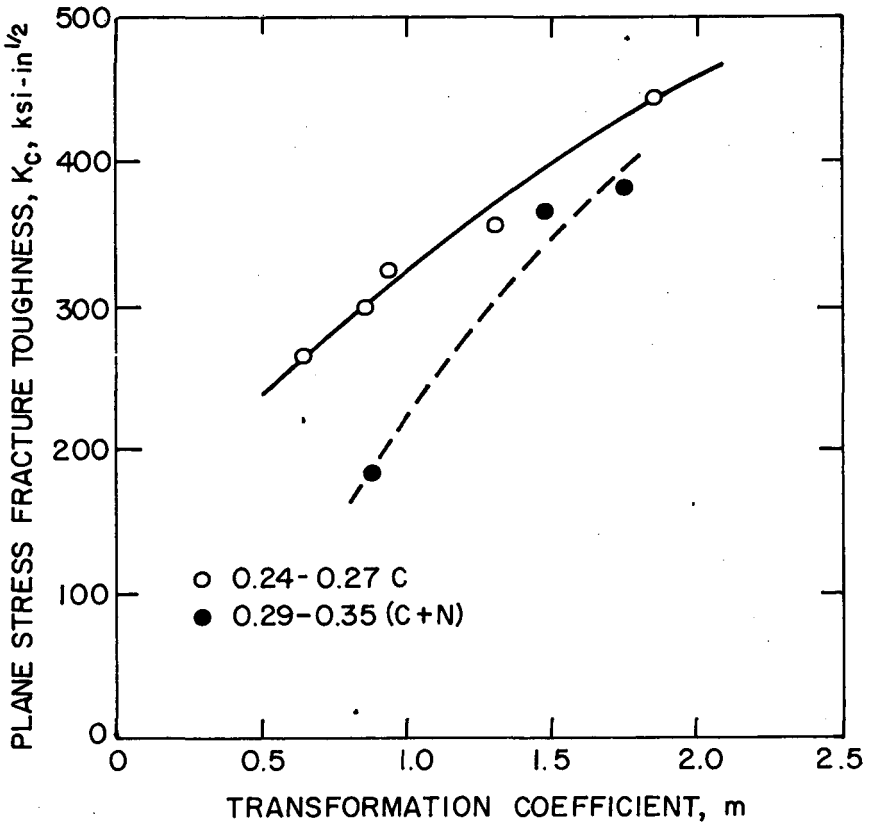


Figure 8 Influence of austenite stability ( $m$  value) on the plane-stress fracture toughness of high strength metastable austenite.

retained austenite in UHS steels after austenitizing at high temperatures. It was also unambiguously established that the presence of either brittle (carbides) or soft (ferrite) microstructural constituents degrade the fracture toughness of UHS steels and that the morphology and size of such microstructural constituents are important factors (11, 23-26). The role of the retained austenite in UHS steels is less clear. Webster (27, 28) and Antolovich et al (29), in studies of more highly alloyed

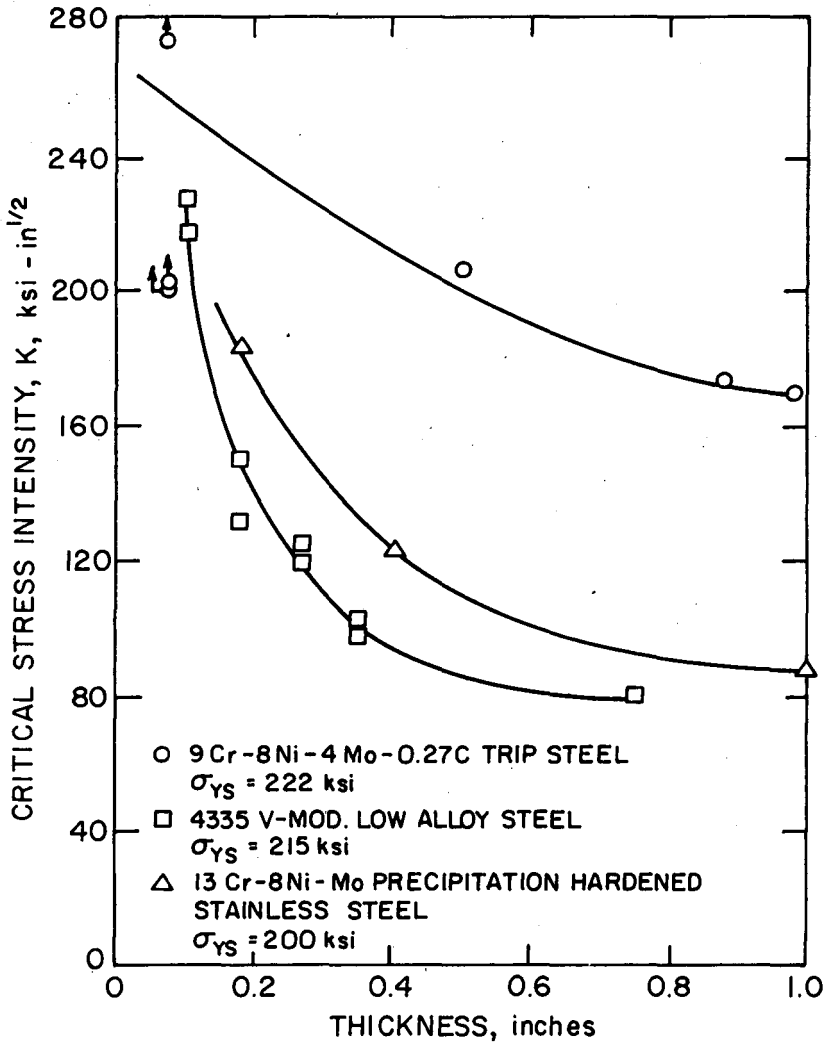


Figure 9 Influence of thickness on the critical stress intensity factor at room temperature for a TRIP steel and two commercial steels.

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steels, claimed that the presence of retained austenite had a beneficial effect on fracture toughness, but the influence of the stability of the retained austenite, i.e. whether it was desirable for the austenite to undergo a stress- or a strain-induced transformation in service, was not determined. Webster suggested that, in his particular alloys, crack blunting by the nontransformed austenite was the most likely mechanism for the enhancement of fracture toughness.

The morphology of the retained austenite was particularly interesting. Bright- and dark-field transmission electron micrographs of these steels revealed that the retained austenite was present as interlath films, as shown in Figures 10*a* and 10*b*. The thickness of these films was estimated to be of the order of several hundred angstroms, and cryogenic tests showed that the austenite remained untransformed at temperatures as low as  $-196^{\circ}\text{C}$ . Methods for controlling the volume fraction of austenite as well as its stability were investigated. It was found from a kinetic study of



Figure 10 Transmission electron micrographs of as-quenched AISI 4340 steel: (a) bright field and (b) dark field of an austenite spot for the high-austenitizing treatment.

the rates of isothermal decomposition of metastable austenite (30, 31) that the element silicon enhanced austenite retention. Silicon has long been known to affect the kinetics of tempering (32–35) as well as the mechanical properties of tempered martensite steels (36, 37). The reasons for this behavior are not known, but speculation has centered on the retardation of the nucleation of iron carbide by the silicon (33, 37) as well as its well-known influence on the thermodynamic activity of carbon (38).

The low temperature range of the T-T-T diagrams of AISI 4340 (containing 0.25Si), with and without 3.0% added silicon, is shown in Figures 11a and 11b. Clearly the silicon addition has a strong influence on the kinetics of bainite formation. The time for isothermal transformation of 50% of the austenite is approximately 20 min for the silicon-modified AISI 4340 steel, compared with a few hundred seconds for the standard AISI 4340 steel. In these studies, it was possible to vary the volume fraction of untransformed austenite over a wide range by changing the temperatures and times of isothermal transformation (30, 31, 39). In some recent but as yet



1 6 6 7 0 2 4 0 0 0 0



unpublished studies, it was found that the stability of the untransformed austenite, with respect to strain, could also be varied. This was accomplished by a tempering treatment close to the isothermal decomposition temperature of the untransformed austenite (350°C).

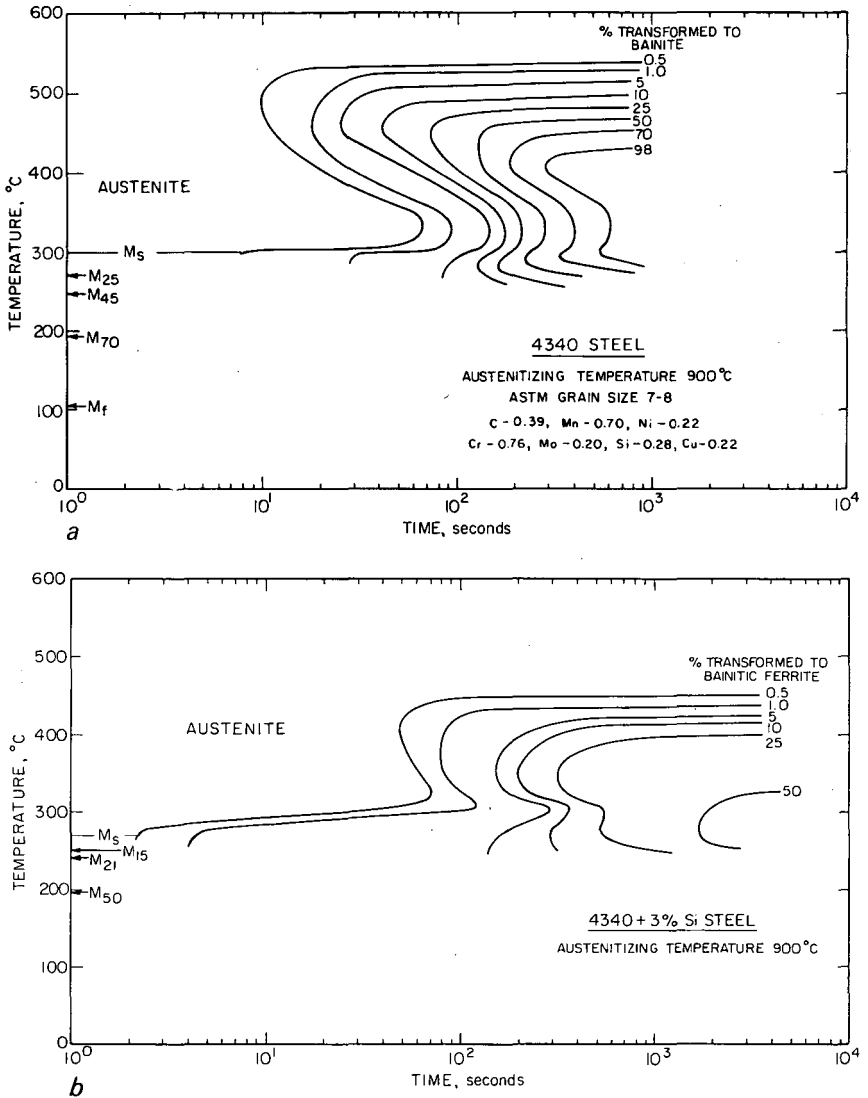


Figure 11 T-T-T diagrams of AISI 4340 steel: (a) with no extra Si addition, and (b) with 3.0% Si added.

**Table 1** The influence of retained austenite unstable to strain on the tensile properties of silicon containing steel<sup>a</sup>

Wt % Si added to AISI 4340 steel	Yield strength (psi)	Ultimate strength (psi)	Elongation (%)	Estimate of retained austenite (%) <sup>b</sup>
1	187,000	216,000	8	6
2	197,000	228,000	10	11
3	196,000	230,000	13	17

<sup>a</sup> Heat treatment: austenitized at 900°C (1 hr), isothermally held at 300°C (1 hr), cooled to room temperature and tempered at 350°C for 1 hr.

<sup>b</sup> Retained austenite measurements made with a saturation magnetization technique.

The combination of tensile and fracture properties that can be attained by variations of composition and heat treatment is now being determined, and some tentative conclusions can be drawn from these continuing tests. It appears that a major effect of relatively stable untransformed austenite is to lower the yield strength. The effect of this relatively stable austenite on the fracture toughness is therefore not clear. The enhanced toughness observed could be due to either a crack-blunting mechanism by the austenite as mentioned earlier or due to the lowered yield strength. Further research should resolve this question.

AISI 4340 steel modified with additions of 1, 2, and 3 wt % silicon were isothermally transformed at 300°C for 1 hr to obtain different amounts of untransformed austenite (40). They were then tempered at 350°C for 1 hr (after cooling to room temperature from the isothermal transformation temperature). Flat tensile specimens were used for determining the tensile properties and for measuring the amount of untransformed austenite; the latter was measured by a magnetic saturation technique described in detail elsewhere (41). Table 1 shows the results of this study. The values of elongation shown are low (by about a factor of 2) because thin (0.04 inch thick) flat tensile specimens were used. However, the effect of the increased percentage of retained austenite on the elongation is quite clear. For similar yield-strength levels, the more retained austenite present, the higher the elongation. It is clear from this preliminary data that interesting combinations of strength and ductility can be achieved by compositional and time-temperature variations.

## SUMMARY

The success of this current UHS steel design effort depends on 1. a working knowledge of the relationships between structure (defect structure and microstructure) and the mechanical properties of engineering interest and 2. a thorough comprehension of the solid-state chemistry (alloy theory, thermodynamics, and kinetics) of complex systems. To achieve the understanding described in statements 1 and 2, major advances in theory and sophisticated experimental techniques and instrumentation are required. In this regard, the UHS steel study reflects the rapid evolution,

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mentioned in the introduction, of the new applied science of alloy design. The ausform and TRIP steel efforts of earlier years were successful largely either because of skillful processing (ausform) or because of skillful processing coupled with the quantitative application of fracture mechanics (TRIP). Future advances in alloy design will therefore undoubtedly be made largely by the continued and rapid replacement of the empirical approach with the use of the basic principles of materials science.

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