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**Materials & Chemical
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IN HIGH-MANGANESE AUSTENITIC STEELS****M.J. Strum
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**CONTROL OF CRYOGENIC INTERGRANULAR FRACTURE IN
HIGH-MANGANESE AUSTENITIC STEELS**

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Ph.D. Thesis

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ABSTRACT

The sources of cryogenic intergranular embrittlement in high-Mn austenitic steels and the conditions necessary for its control are examined. It is shown that the high-Mn alloys are inherently susceptible to intergranular embrittlement due to both their low grain boundary cohesion and heterogeneous deformation characteristics. The embrittling influence of Mn in Fe-based alloys is predicted from its segregation behavior using existing models for solute influences on grain boundary cohesion. The heterogeneous deformation associated with the development of planar deformation bands and deformation-twinning are considered to promote stress concentrations at the grain boundaries.

Extrinsic sources of embrittlement which could account for the transition behavior are not observed. An Auger electron spectroscopy (AES) study shows no indication of impurity-segregation-induced embrittlement. No grain boundary precipitation is observed, and austenite stabilization does not ensure ductile fracture.

The influence of chemistry modifications on the ductile-to-brittle transition behavior were also examined through additions of N, Cr, and C to binary Fe-31Mn. Nitrogen additions increase the 77K yield strength at a rate of 2200 MPa per weight percent N, and increase the austenite stability, but also increase the susceptibility of ternary alloys to intergranular fracture. Quaternary Cr additions are effective in increasing the N solubility, and lower the transition temperature. Carbon additions result in complete suppression of intergranular fracture at 77K. Qualitatively significant changes in the deformation heterogeneity with chemistry modifications are not observed. The temper-toughening of Fe-Mn-Cr-N alloys is associated with the grain boundary segregation of boron and the redistribution of N. Both boron and carbon are expected to inhibit intergranular fracture through increases in grain boundary cohesion.

I. INTRODUCTION

Current needs for high-strength cryogenic structural materials have stimulated the development of new high-Mn austenitic alloys. Manganese additions to iron-based alloys stabilize the face-centered-cubic austenite phase and can be substituted for Ni which is more expensive and strategically important than Mn. New austenitic stainless steels in which Mn is partially substituted for Ni also show promise for improved cryogenic mechanical properties. The cryogenic mechanical properties of binary Fe-Mn alloys, however, are limited by a transition to intergranular fracture at low temperatures. Neither the mechanism of the intergranular embrittlement or the influence of individual alloying element additions on the ductile-to-brittle transition behavior have been clarified. It is postulated in this work that the high-Mn alloys are inherently susceptible to cryogenic intergranular fracture. The ductile-to-brittle transition temperature of austenitic high-Mn steels can be controlled by chemistry and processing modifications which are related to changes in grain boundary cohesion and deformation characteristics.

In Fe-Mn binary alloys, a transition to an intergranular fracture mode occurs with decreasing test temperature in both ferrite and austenite dominated microstructures [1]. Ferritic 12 to 17 percent Mn alloys and austenitic binary alloys with 30 percent or more Mn fracture intergranularly in Charpy impact tests at 77K. At intermediate Mn contents such as Fe-25Mn, the mechanical behavior is dominated by the presence of large quantities of hexagonal epsilon-martensite and no transition to intergranular fracture occurs. The avoidance of intergranular fracture in these alloys, however, is due to an alternative low-energy transgranular fracture mode associated with the high epsilon martensite contents [1]. To control against cryogenic intergranular fracture and improve the associated cryogenic mechanical properties of binary Fe-Mn alloys, further alloying additions are necessary.

It is the objective of this investigation to determine the cause and conditions necessary for the control of cryogenic intergranular fracture in Fe-Mn alloys. Chemistry modifications of binary Fe-Mn alloys demonstrate the potential of Ni-free, Fe-Mn-based systems as cryogenic structural materials. The metallurgical role of individual alloying elements present in many Fe-high Mn alloys will also be elucidated. In relating the cryogenic mechanical properties to changes in chemistry and processing, the metallurgical links between them are examined.

The approach taken in this investigation is to examine the influence of chemistry modifications to fully-austenitic Fe-Mn alloys. A base composition of Fe-30Mn was chosen which exhibits borderline behavior with respect to both austenite stability and fracture mode at 77K. The effects of alloying additions on each are thus expected to become evident. Ternary additions of N or Cr, and quaternary N plus Cr alloys are examined first. The effect of N additions are complex, with major influences on strength, austenite stability, and deformation behavior. While Cr is expected to play a minor role in solid-solution strengthening, it has been reported to be beneficial in controlling the fracture

mode [2]. Carbon additions to quaternary Fe-Mn-Cr-N alloys also significantly increase the resistance to cryogenic intergranular fracture.

The influence of alloy modifications on the metallurgical determinants of intergranular fracture are examined through mechanical property, microstructural, and micro-chemical characterization. The mechanical properties and transgranular-to-intergranular transition behavior are characterized for each alloy through notched-bar impact and uniaxial tensile tests between room temperature and 77K. As potential determinants of the fracture mode, both the grain boundary chemistry and the deformation behavior are examined. Grain boundary chemistries are measured by Auger electron spectroscopy using samples broken in-situ at low temperature and under ultra-high vacuum. The macroscopic deformation behavior is characterized by the flow strengths and strain-hardening coefficients of the alloys, while the microscopic deformation behavior is characterized through examination of the austenite stability, deformation mode, and slip dispersal. The influence of alloy processing variables are also considered; especially the cryogenic mechanical property dependence of changes in grain size and thermal history.

II. BACKGROUND

A. Alloy Design of High-Mn Alloys.

The earliest commercial austenitic high-Mn steels were developed by Hadfield. Using upwards of 1.0 percent C to stabilize the 10 to 14 percent Mn alloys, Hadfield steels outperformed traditional materials in service environments combining abrasion with heavy impact [3]. In the mid 1950's, the strategic importance of Ni prompted the development of low-Ni or Ni-free austenitic stainless steels, resulting in the AISI 200-series stainless steels. More recently, modification of these alloys to improve their strength and cryogenic mechanical properties have been explored. In addition to the substitution of Mn for Ni for socio-economic reasons, recently developed austenitic high-Mn alloys have shown potential superiority as non-magnetic and cryogenic structural materials relative to conventional 300-series austenitic stainless steels.

One area of improvement in high-Mn alloys was the development of high-strength austenitic stainless steels. The primary source of the increased strength was the addition of N, the solubility of which increases with Mn content [4,5]. The room temperature yield strength of Nitronic 40 [4,6], nominally 21Cr-6Ni-9Mn and containing 0.3N, is approximately twice that of comparable austenitic stainless steels such as types 304, 316 and 347. These new steels were also exceptionally stable against transformation to α' martensite [6], and showed promise for cryogenic applications.

New applications and requirements for cryogenic structural materials, such as in Japan's high-speed magnetic levitation railway system, and magnetic-fusion reactors stimulated further materials development. The designs for large superconducting magnets in magnetic-fusion reactors required new, weldable structural alloys with improved strength and toughness levels at 4K for the magnet cases. Target mechanical proper-

ties eventually rose to yield strengths over 1200 MPa and fracture toughness (K_{1C}) levels over 200 MPa $\sqrt{m}$ at 4K [7,8]. Two types of high-Mn alloys underwent further development; Fe-Mn austenitic steels, and high-Mn stainless steels. Both types of high-Mn alloys depend upon stable austenitic microstructures to maintain cryogenic toughness.

As mentioned earlier, Mn functions as an austenite stabilizer in Fe-based alloys. Within the binary Fe-Mn system a variety of phases evolve with increasing Mn contents, from ferrite to alpha-martensite (α'), epsilon martensite (ϵ), and austenite (γ); becoming fully γ above approximately 30 percent Mn [9]. The mechanical behavior of these binary alloys are principally determined by their constituent phase fractions, and their stability with respect to deformation-induced martensite transformations [1]. The best combinations of cryogenic strength and toughness are obtained in fully α' or fully γ alloys. A minimum in the 77K Charpy impact energy or tensile ductility as a function of Mn content occurs near 25Mn which corresponds to a peak in ϵ content. The presence of ϵ has been directly associated with this transgranular embrittlement. A maximum in the 77K impact energy occurs close to 30Mn. The decrease in toughness at higher Mn contents is associated with the predominance of intergranular fracture [1,10].

The addition of up to 10 percent Cr to Fe-Mn alloys appears to have only a small influence on the phase composition of as-cooled alloys [11]. Many of these alloys are metastable, however, and results of 8 percent Cr additions to metastable 16 and 20Mn alloys suggest that Cr favors the formation of deformation-induced α' [12]. In stainless alloys containing upwards of 13 percent Cr, the delta-ferrite phase may be retained in the as-cooled structure [11]. High Mn contents further stabilize the delta-ferrite phase. In addition to increasing the magnetic permeability, the presence of delta-ferrite decreases the cryogenic toughness of high-Mn stainless steels [13]. To avoid the presence of delta-ferrite in stainless alloys, limitations on Mn and Cr contents, as well as minor Ni additions may be required [13].

The cryogenic mechanical properties of Fe-Mn austenitic alloys are often limited by brittle fracture. To optimize the cryogenic mechanical properties in AISI 200-grade high-Mn austenitic steels, large matrices of chemical compositions have been tested including variations in Mn, Cr, Ni, C, and N. High-Mn stainless steels with excellent cryogenic properties have resulted, such as those developed by the Kobe Steel Company [13,14]. Beyond the influence of these chemistry modifications on phase stability, however, little is known concerning their effects on the metallurgical factors controlling the mechanical properties.

The interstitial contents in these alloys are important determinants of both their strength and γ stability. Carbon contents as high as 0.6 percent are used in Fe-Mn austenitic steels to raise the low-temperature yield strengths [15,16]. It was later determined that N additions are much more effective than C in raising the cryogenic strength, and also result in alloys less subject to precipitation problems [17]. While the strength level is adjustable through variations in the interstitial content, the resulting yield strength and toughness levels in high-Mn austenitic alloys are, in general, inversely related. The strength/toughness relations of these alloys can be adjusted somewhat by

thermo-mechanical-controlled-processing (TMCP) which modifies the grain size, cooling rate, and residual deformation in the material [14,18,19]. The toughness can also be increased independently of the yield strength through improved alloy cleanliness. Limitation of sulfur levels are exceptionally important and inclusion shape control such as through Ca additions dramatically improve the cryogenic toughness of ductile high-Mn stainless steels [20].

While the compositional dependence of the cryogenic mechanical properties in high-Mn alloys is becoming increasingly well documented, the connections to basic metallurgical phenomena remain poorly understood. A recent fundamental investigation of the microstructural dependence of Fe-Mn binary alloys shows that the cryogenic mechanical properties are principally dependent on the component phase fractions and their stability, with the most promising properties in fully-austenitic alloys [1]. The metallurgical source of the transition to intergranular fracture in binary Fe-Mn austenite at cryogenic temperatures, however, is not understood. Therefore the influence of individual alloying additions on the ductile-to-brittle transition in austenitic Fe-Mn alloys, and the corresponding changes in grain boundary chemistries and deformation behavior were investigated.

B. Intergranular Embrittlement

Intergranular separation is a potentially catastrophic fracture mode, which can occur after negligible macroscopic strains. Brittle intergranular separation is governed by the localized stress across the grain boundary, unlike strain-controlled ductile fracture modes. There is, therefore, a competition between fracture modes; the ductile process will proceed unless stress conditions across the grain boundaries exceed the cohesive strength.

The resistance of an alloy to intergranular fracture is a complex function of chemistry, microstructure, thermal history and service (or test) conditions. Incorporated in these factors are determinants of both a critical grain boundary fracture stress and the magnitude of stress concentrations developed at a grain boundary or a crack tip during deformation. The level of stress concentration is limited by the local resistance to plastic relaxation. The grain boundary fracture stress, or cohesion is most often described in terms of grain boundary chemistry, although structural effects may also be significant. The onset of brittle intergranular fracture is dependent on both the grain boundary cohesion and grain boundary stress conditions. The mechanics of intergranular fracture and the influence of grain boundary cohesion on intergranular embrittlement are discussed separately in the next two sections.

1. Mechanics of intergranular fracture. Intergranular fracture may occur under many different conditions. The micro-mechanisms of intergranular fracture can be separated into two general categories; fibrous, and brittle fracture. Fibrous intergranular fracture is characterized by the localization of a ductile fracture process to the region near the grain boundaries. This is observed, for example, in materials with weak precipitate-free-zones near grain boundaries [21,22], and also in high-

temperature creep cavitation [23]. Low-energy fibrous fracture may also result from the reprecipitation of inclusions at grain boundaries subsequent to dissolution during overheating [109]. Brittle intergranular fracture, however, will be the focus of further attention. Brittle intergranular fracture may result from grain boundary microcrack formation and growth such as between grain boundary precipitates or films [24], or as a result of weakened grain boundary cohesion. The conditions for crack initiation will be discussed, followed by an introduction of the important metallurgical factors influencing grain boundary stress concentrations.

The theoretical grain boundary fracture stress, like the transgranular cleavage stress, is expected to be many times larger than the macroscopic fracture stress [25,26]. To reach the brittle fracture stress, it is universally agreed that prior plastic glide, producing localized stress concentrations are required. There are two basic conditions which must be fulfilled before a crack is initiated. The first condition is that a critical fracture stress must develop, i.e.

$$\sigma_c > \sigma_m$$

where σ_c is the maximum tensile component of the stress concentration, and σ_m is the cohesive strength of the material. A related condition for fracture which considers the fact that a stress concentration can also be relieved by shear must also be fulfilled;

$$(\sigma_c/\tau_c) > (\sigma_m/\tau_m)$$

where τ_c is the shear component of the stress concentration and τ_m is the local shear resistance of the material [26]. Thus it is evident that the onset of intergranular fracture is also dependent on the local resistance to plastic relaxation at grain boundary stress concentrations.

The various models proposed for grain boundary microcrack formation, like those for cleavage, are based on the development of large stress concentrations at the heads of blocked deformation bands [27]. These stress concentrations may be produced by the blockage of either slip or twinning bands at obstacles such as grain boundaries or second phase particles. Thus, in addition to grain boundary decohesion, cracks may initiate at the particle/matrix interface or within the particles themselves. Cracking of carbides is commonly observed in ferritic steels, and cleavage fracture stresses are dependent on the volume fraction and size distribution of carbides [28,29].

While carbides or other hard second-phase particles at grain boundaries allow large stress concentrations to develop without relaxation by plastic flow, the resistance of grain boundaries to plastic accommodation of stress concentrations varies widely. Several dislocation models for the initiation of cracks at grain boundaries have been proposed [27,30]. Microcracks may form, for example, at grain boundaries to relieve the stress field at dislocation ledges formed by heterogeneous shear of the grain boundaries [30]. The maximum tensile stress across the boundary is limited by the local resistance of the grain boundary to shear accommodation. It should be noted here that bond-breaking at the

grain boundaries and plastic relaxation are competitive processes and both may occur before one begins to dominate [31-34]. The magnitude of grain boundary stress concentrations, and the shear resistance of the material are both expected to be strongly dependent on the microstructure and service variables.

The development of large stress concentrations at grain boundaries requires heterogeneous deformation. Both the deformation mode and the slip dispersal are important parameters influencing the degree of heterogeneity. In austenitic alloys with low stacking-fault energies (SFE), dislocation cross-slip is inhibited and slip becomes planar in nature [35], concentrating the deformation. Dislocation barriers are also expected to remain effective to higher stress levels in low-SFE materials [35]. In addition, deformation twinning may also occur in low SFE materials, especially at low temperatures and high strain rates [35-37]. The tip of a deformation twin can be envisioned as the head of a dislocation pile-up, and is thus considered as a potential crack initiation site [38,39].

Intergranular embrittlement has also been observed in alloys containing a homogeneous distribution of ordered coherent precipitates. Under conditions of particle shearing in these alloys, a coarse, heterogeneous distribution of slip develops, resulting in high grain boundary stress concentrations [22,40]. Coarse slip distributions are also favored by short-range order, a limited number of operating slip systems, and large grain sizes [40].

It is also important to consider the resistance of grain boundary stress concentrations to plastic relaxation. The importance of grain boundary structure itself has only recently begun to be addressed [41-44]. The fracture stress of a grain boundary is, for example, dependent on misorientation angle, increasing for low-angle and coincidence boundaries [44]. Grain boundary structure influences the ease of slip accommodation and potential grain boundary hardening due to secondary dislocation accumulation near the interface [42,45-47]. The resistance to plastic relaxation at a stress concentration also increases with increasing shear strengths and work hardening rates. These factors are directly related to the chemistry and microstructure of the material. Service conditions, such as low temperatures and high strain rates raise the shear strengths and limit thermally-activated, non-conservative dislocation motion which assists in relieving stress concentrations.

While the previous discussion has concentrated on conditions for the initiation of grain boundary cracks, many of same considerations are relevant towards crack propagation. The simplest criteria for crack propagation, given by Griffith, requires that a critical tensile stress intensity exceed the work to fracture. The total work of fracture is the sum of the ideal work of decohesion and a larger plastic term. As the grain boundary cohesive strength increases, the increase in the amount of plastic work required to reach the cohesive strength increases by a large multiple of the increase in the ideal work of fracture [31,34]. Thus the total work to fracture is strongly dependent on the grain boundary cohesive strength. This places additional emphasis on the importance of the grain boundary cohesive strength, and its dependence on grain boundary chemistry.

2. Grain boundary cohesion. The grain boundary cohesion is sensitive to the chemistry and thermal history of the material. Grain boundary embrittlement due to decreased cohesion is often associated with the segregation of impurity elements to the grain boundaries. The conditions resulting in segregation-induced intergranular embrittlement have become increasingly well understood through advances in the identification of: potent impurity species, the bulk and enrichment levels which become significant, and the basic mechanisms which operate [23]. The characteristics of segregation-induced intergranular embrittlement in well-known systems and methods to inhibit the embrittlement are outlined below. Theories for the chemistry dependence of grain boundary cohesion are also discussed.

Observations of the susceptibility of grain boundaries to serious weakening by impurity elements date back at least as far as those of Roberts-Austen in the 19th century [26,48]. While the incidence of segregation-induced intergranular embrittlement has been observed in many alloys, the best documented case is probably that of temper embrittlement in steel. When tempered alloy steels are aged between 375°C and 560°C or slowly cooled after tempering, a decrease in notch toughness and an increase in the ductile-to-brittle transition temperature occurs. A concomitant transition in the brittle fracture mode from cleavage to intergranular separation occurs due to the segregation of impurities to the grain boundaries during the embrittling treatments. Embrittling species have been identified through surface analytical techniques such as Auger electron spectroscopy which allow direct observations of the influence of bulk chemistries and thermal treatments on grain boundary chemistries.

A number of elements function as embrittling species in the temper embrittlement of steels. The most prevalent of these are Sb, Sn, and P, in order of decreasing potency [49]. Other elements identified as embrittling species include S, As, Si, Ge, Bi, Sc, Te, H and N. Alloying elements in alloy steels have been classified as either: (i) promoting segregation by cosegregating with impurities, such as do Mn and Ni; (ii) enhancing impurity segregation without segregating itself, as does Cr; or (iii) inhibiting segregation through chemical fixation, as reported for Mo and Ti [49]. Certain elements have also been reported to increase grain boundary cohesion, such as C in alloy steels [50,51], and B in both ferritic [52,53] and austenitic materials [54-56]. The tendency for impurity elements to segregate to interfaces, such as grain boundaries, is due to a corresponding reduction in energy. The interfacial free energy, which is related to unsatisfied bonding in the relatively disordered structure of the interface, is reduced by the accumulation of foreign atoms. There is also a decrease in elastic strain energy associated with the transfer of a solute atom from the matrix to an interfacial site. Grain boundary enrichment ratio's (grain boundary concentration/bulk concentration) are experimentally found to be inversely proportional to the solute solubilities for dilute solutions of a large number of solutes [23,57].

In equilibrium segregation there is a unique solute content at the interface for a given temperature which is approached at a rate governed by diffusion. Non-equilibrium forms of solute segregation due to a flux of vacancy-solute complexes such as in quench or stress-induced segrega-

tion, or due to solute rejection from growing precipitates can also occur. The equilibrium solute distribution will be approached again, however, at a rate governed by diffusion.

The Langmuir-McLean relation describes the effect of the free energy of segregation, ΔG , the bulk solute content, X_c ($X_c \ll 1$), and the temperature (T) on the equilibrium grain boundary solute content, X_b as follows:

$$-\Delta G/RT = \ln[X_b / ((1-X_b)X_c)]$$

where R is the ideal gas constant. This relation is consistent with observations that the level of grain boundary segregation increases as the bulk solute content increases and the temperature decreases. The description of equilibrium segregation in multicomponent systems must also include interactions between alloying elements and impurities, as in a model by Guttman [23,58,59]. In general, the larger the reduction in impurity solubility by an alloying addition, the more the addition enhances impurity segregation.

From the large number of investigations into the causes of temper embrittlement, much has also been learned concerning methods for its control. In addition to reducing the residual levels of potent embrittling species, many alternative metallurgical approaches have surfaced [23,60]. Alloy design methods to inhibit segregation-induced embrittlement include: (i) controlling the kinetics of segregation, (ii) reducing the segregated impurity concentration by increasing the interfacial area (grain refinement), (iii) competitive segregation, (iv) remedial segregation, and (v) chemical fixation or precipitation. These methods should be applicable to a wide variety of systems with segregation-weakened grain boundaries.

In addition to knowledge of embrittling species and their segregation behavior, it is of basic scientific interest to know why certain elements lower the grain boundary cohesion. The early theory of grain boundary fracture grew from Griffith and Polanyi's identification of the work to form two new fracture surfaces as the ideal work of fracture. For intergranular fracture, the ideal work of fracture, γ is:

$$\gamma = 2\gamma_s - \gamma_b$$

where γ_s and γ_b are the surface energies of the freshly produced fracture surfaces and the grain boundary, respectively. The work of fracture in metals, however, is dominated by plastic work for which Orowan suggested the addition of another term, γ_p to the above relation such that:

$$\gamma^* = (2\gamma_s - \gamma_b) + \gamma_p$$

While the plastic term is dominant, it is not an independent material parameter [31]. As discussed earlier, the magnitude of the plastic work prior to fracture is influenced by the grain boundary cohesive strength. Therefore a segregation-induced reduction in γ can result in a large reduction in γ^* . Three theoretical models for solute effects on grain boundary cohesion are discussed below: thermo-chemical, pair-bonding,

and electronic models. All three focus on calculation of changes in the ideal strength of the grain boundaries.

The thermo-chemical approach has already been briefly outlined above. The fracture work necessary to create two new surfaces depends on the balance of the resulting changes in grain boundary and surface energies. An embrittling segregant must lower the quantity $2\gamma_s$ by an amount larger than the corresponding decrease in γ_b . Equilibrium segregation will always reduce the interfacial energies. Therefore embrittling elements segregate more strongly to surfaces than grain boundaries.

This theory has so far assumed that γ_s and γ_b are equilibrium values of the surface and grain boundary interfacial energies. While the equilibrium value of γ_s may be appropriate for slow crack growth at high temperatures, little solute diffusion can occur during fast fracture at low temperatures. Thus equilibrium surface segregation is not always established. A correction in the thermo-chemical theory to incorporate the non-equilibrium surface energy of the fracture surface is given by Hirth and Rice [61].

Another problem with the thermo-chemical approach is the lack of appropriate thermodynamic data on interfacial energies and the difficulty of making interfacial energy measurements. Grain boundary energy measurements are typically made at high temperatures; segregation occurs at intermediate temperatures; brittle intergranular fracture occurs at low temperatures. Although available data support the theory, the difficulty of obtaining accurate interfacial energies limit the usefulness of the thermo-chemical model as a predictive tool.

An alternative approach is the quasi-chemical, pair-bonding model given by Seah [62]. This model makes use of more readily available thermodynamic data, allowing predictive calculation of solute effects on grain boundary cohesion for a large number of solute and matrix element combinations. In the pair-bonding approximation, the ideal energy of fracture is calculated from the energy required to break the bonds across the grain boundary. These energies are calculated from the sublimation enthalpies and give a measure of the influence of grain boundary chemistry on the cohesive energy.

The numerical approach uses nearest-neighbor bond terms, and assumes the grain boundaries separate without solute redistribution. The bond energies ϵ_{AA} and ϵ_{BB} are determined as:

$$\epsilon_{AA} = -2H_A^{\text{sub}}/NZ$$

where H_A^{sub} is the molar sublimation enthalpy of component A, Z is the coordination number, and N is Avogadro's number. The reduction in fracture energy, $\Delta\gamma$ for an ideal solution due to the fractional monolayer coverage of solute, X_b at the grain boundary is:

$$\Delta\gamma = (Z_g/Z)X_b[H_A^{\text{sub}*} - H_B^{\text{sub}*}]$$

where $H^{\text{sub}*}$ is the sublimation enthalpy per unit area, and Z_g is the coordination of atoms on one side of the interface to those in the

adjacent layer on the other side. For regular solutions a small additional term is added or subtracted from the $H^{\text{sub}*}$ terms, with attractive interactions between solute and matrix increasing cohesion and vice-versa.

According to this model, the fracture energy will decrease with the addition of solutes whose sublimation enthalpies are lower than that of the matrix, and also with the volume fraction of such solutes at the interface. The theory predicts the embrittlement of Fe by Sb, S, Sn, P, As, Ga, Ge, Mn, and Si in order of decreasing potency, and increased cohesion by N, B, and C in order of increasing remedial influence. The results of Seah's pair-bonding model give an estimate of solute effects on grain boundary cohesion for some seventy solutes.

The chemical bonding aspects of grain boundary embrittlement have recently been explored in greater depth through electronic models [63-67]. Quantum mechanical calculations support the view that embrittling species weaken the chemical bonds. Briant and Messmer [64-66] use a molecular orbital cluster method, simulating the local structure at grain boundaries as polyhedra. By placing impurity atoms at the center of a tetrahedron of host atoms they calculated the influence of these impurities on the molecular orbitals. Their results show that potent embrittling elements such as S draw charge from neighboring metal atoms, weakening the metal-metal bonds [64]. It is proposed that the weakening of these metal-metal bonds leads to embrittlement.

Such calculations also predict increasing embrittlement with increasing differences in electronegativity between the impurity and the metal atoms. Thus, as P is more electronegative with respect to Cr and Mn than Fe, alloying with Cr or Mn is expected to increase the embrittling potency of P. This is in agreement with experimental observations in alloy steels.

In terms of embrittling potency, Briant and Messmer's results [64] predict $S > Sb > P > C > B$. While from their calculations C was found to have little observable effect, B is predicted to enhance cohesion.

From the criteria given for intergranular fracture, it is clear that both the grain boundary cohesion and the deformation behavior can be controlling factors. A competition exists at a dislocation pile-up or crack-tip between bond-breaking and plastic relaxation. In many instances the segregation of embrittling species and the corresponding reductions in grain boundary cohesion result in brittle intergranular fracture. The deformation heterogeneity and resultant stress levels across the boundary are also important, and are expected to be both chemistry and processing dependent.

III. EXPERIMENTAL PROCEDURE

A. Materials Processing

The alloys prepared for this study were melted in 20 lb. (9.1 kg) heats in a vacuum induction furnace. Melting was performed in magnesia crucibles under an argon atmosphere. The initial charge consisted of mixtures of high-purity Fe, Mn, and Cr electrolytic chips. Nitrogen or carbon were added using a nitrided electrolytic manganese containing 6 wt. percent N or graphite, respectively. The charges were cast into 3 inch (76 mm) diameter Cu molds and furnace-cooled.

The as-cast ingots were homogenized at 1473K for 24 hrs in an argon atmosphere and air-cooled. A high-temperature oxidation-resistant stainless steel wrapping was used to protect the ingots during homogenization. After reheating to 1373K, the ingots were hot-rolled in 6-8 passes to 20 mm plates. The bottom halves of the ingots were cold-rolled to 35-40 percent thickness reductions, and recrystallized/annealed at 1273K for 1 hr. in protective stainless steel bags followed by water cooling. The resulting 11.5 mm plates were sectioned into Charpy impact test specimens. The 35-40 percent cold-roll and recrystallization treatment was repeated an additional two cycles to produce 3.8 mm plates which were sectioned for flat tensile specimens.

Where subsequent heat treatments were necessary, individual specimen blanks were encapsulated in quartz tubes which were evacuated and partially back-filled with argon gas to equalize pressures at the furnace treatment temperature. Quench treatments were performed by breaking the quartz tube within the quench medium while air-cooled samples were cooled within the quartz tubes.

Compositional analyses of the alloys used in this study are reported in Table 1. All of the experimental alloys are modifications of Fe-30 percent Mn, with N, Cr, C or Si additives. Alloy designations given are generally based on the number or type of elemental components (ie. ternary (T), quaternary (Q), carbon-containing (C), etc.). The Fe, Mn, and Cr contents were determined by energy dispersive X-ray analysis. Levels of C, S, P, and Si were determined by wet chemistry, and N and O contents by Leco inert-gas-fusion.

The yield ratios of N additions were approximately 80 percent but were limited by terminal solubilities of 0.12 and 0.22 weight percent N in Cr-free and 5 percent Cr alloys, respectively. The yield ratios for Mn varied, in general, between 95 and 98 percent. While the impurity levels of P remain below 50 ppm, S levels range from 90 to 160 ppm and oxygen from 20 to 400 ppm. These relatively high impurity levels result from the high S (280 ppm) and O (1800 ppm) contents of electromanganese melting stock.

B. Mechanical Testing

1. Charpy impact tests. The Charpy V-notch impact specimens were machined to ASTM standard (type A) dimensions as specified in Fig. 1, and

tested in accordance with ASTM E23-72 standard methods. Specimens were sectioned along the rolling direction and notches were machined with the notch base perpendicular to the surface of the plates. Tests were performed on a 302 J capacity, pendulum-type, simple-beam impact test machine. Impact values were determined for temperatures between 298K and 77K by immersion of the test specimens in controlled temperature baths using liquid-nitrogen-cooled isopentane. To preserve the quality of the fresh fracture surfaces the broken specimens were warmed in a water bath and blow-dried with warm air following an alcohol rinse.

2. Tensile tests. The uniaxial tensile properties were determined using pin-loaded flat tensile specimens tested in accordance with ASTM E8-69 standard methods. The gage regions of these specimens were 25.4 mm in length, 3.2 mm in width, and nominally 3.2 mm thick. The dimensional specifications are shown in Fig. 2. Tensile tests were performed on either an 11 kip (24,000 kg) capacity screw-driven, or 50 kip (110,000 kg) capacity servo-hydraulic load frame. Yield strengths were determined by the 0.2 percent offset strain method. The cross-head speed was 0.5 mm/min., corresponding to a strain rate of 0.02/min. The tensile flow curves are compared from tests using the servo-hydraulic machine. Early-stage flow behavior was determined in these tests using an extensometer placed within the uniform gage region. After digitizing the load vs. displacement recordings, the data were reduced by a computer program to produce true-stress verses true-strain tensile plots. The complete stress-strain curves were estimated from the load verses displacement recordings using linear corrections for both machine compliance and specimen strain outside of the gage region. No corrections were made for the localized necking prior to final failure. The strain-hardening coefficient $d(\log\sigma)/d(\log\epsilon)$, was calculated verses true strain using a least squares fit to a linerized power law expression (Holloman [35]):

$$(\ln\sigma_T = (b(\ln\epsilon_T))^m)$$

where: σ_T = true stress
 ϵ_T = true strain
 b, m = fitting parameters

This was differentiated to determine the strain-hardening coefficient for each strain value.

C. Microscopy

1. Scanning electron microscopy (SEM). Fractography of the Charpy impact and tensile specimens were performed by secondary electron imaging in the SEM. Interpretations of these fractographs were facilitated in certain instances by stereo-imaging, rotating the specimen approximately 10 degrees between exposures. A Robinson back-scattered electron detector was used to image the inclusion contents of each alloy on an arbitrary plane of polish. This method improves the contrast between the matrix and the lower-atomic-weight inclusions.

2. Optical microscopy. Specimens were prepared for optical microscopy by mounting in either thermoplastic or cold-setting resins, grinding through successive grades of SiC papers from 240 to 600 grit, and final

polishing with 6 μ m and 1 μ m diamond pastes on a lapping wheel. A suitable etch was obtained by vigorous swabbing of a mixed-acids reagent (10ml nitric acid and 20ml hydrofluoric acid in 40ml of glycerol). Grain sizes were determined using the mean-intercept-length method from measurements of the number of grain boundary intersections (P), along random test line lengths (L_T), at magnifications (M), from 50 to 100X. The mean-intercept-length grain size (L_3), is given by the equation below;

$$L_3 = L_T / (P(M))$$

These values of the grain diameters represent the mean distances between high-angle grain boundaries. The quite prevalent low-angle, annealing-twin boundary intersections were not counted.

The tensile deformation structure of incrementally strained, pre-polished flat tensile specimens were observed using polarized light in the optical microscope. While the as-deformed contrast due to slip steps on the specimen surface indicate the degree of slip dispersal, repolishing and etching reveals the degree of deformation-induced twinning or hcp epsilon martensite formation. The specimens were re-ground and polished prior to each strain increment.

3. Transmission electron microscopy (TEM). Deformed samples for TEM analysis were prepared by sectioning flat tensile specimens which were pre-strained 5 to 10 percent. The gage region was sectioned into 10 to 15 mil (0.25 to 0.38 mm) thick slices using a water-cooled 10 mil (0.25 mm) thick abrasive wheel. After chemically thinning to 4 to 5 mil (0.10 to 0.13 mm) thicknesses, the sections were spark-cut into 3 mm disk-shaped TEM specimens. The specimens were then mechanically thinned to between 1.5 and 2 mil (0.04 to 0.05 mm) on 240 to 600 grit SiC papers. Final thinning was performed by twin-jet electro-polishing using a solution of 75 gm CrO_3 , 400 ml acetic acid and 20 ml H_2O . The specimens were examined on a Phillips EM 301 operated at 100 kV.

D. X-Ray Analysis

An X-ray diffractometer was used to measure the phase composition of both as-annealed bulk specimens and specimens broken in tension at 77K. Although all as-annealed specimens consist of single-phase austenite (γ), hcp epsilon martensite (ϵ) formation may be deformation-induced. Quantitative analysis was performed using the direct comparison method described by Cullity [68]. The relative volume fractions of γ and ϵ phases are proportional to their integrated peak intensities and inversely proportional to their peak sensitivities. They are calculated for each peak from the following relations:

$$V_\gamma / V_\epsilon = (I_\gamma R_\epsilon) / (I_\epsilon R_\gamma)$$

$$V_\gamma + V_\epsilon = 1$$

where:

V = volume fraction of the indicated phase

I = integrated diffraction intensity for a particular peak

R = calculated sensitivity factor for a particular peak

and:

$$R = (1/v^2) |F^2|_p [(1+\cos^2 2\theta)/(\sin\theta \cos\theta)] e^{-2M}$$

where: v = volume of the unit cell
 F = structure factor
 p = multiplicity factor
 e^{-2M} = temperature factor

Volume fractions were estimated from the γ_{200} and ϵ_{101} diffraction peaks with R values calculated as 89 and 174, respectively.

Both the bulk and tensile-deformed X-ray samples were prepared similar to those for optical microscopy, with a 1 μ m final polish. All analyses were performed on as-polished surfaces due to the preferential etching of the ϵ phase in chemically-thinned specimens and the corresponding relative loss in intensity of the ϵ peaks. The phase compositions of the tensile specimens, which were tested to failure at 77K were determined from the uniformly reduced sections of the tensile gage regions.

While all bulk as-annealed samples were single-phase γ in the polished condition, rough grinding on 600 grit SiC paper produced large fractions of ϵ martensite in the near surface region. This grinding deformation treatment produced larger fractions of ϵ martensite than the specimens fractured in tension at 77K, and therefore was used as a sensitive measurement of γ stability with respect to ϵ formation. The phase fractions determined by the X-ray diffraction pattern analyses are primarily used as a qualitative tool to indicate the relative γ stability between the different experimental alloys.

E. Auger Electron Spectroscopy (AES)

Surface chemical analysis was performed using a PHI model 590 scanning Auger microscope (SAM) equipped with a scanning electron microscope, argon ion-sputtering gun, and in-situ cryogenic fracture stage. A schematic of the system is shown in Fig. 3. In-situ fracture specimens machined to the dimensions specified in Fig. 4 were cooled to a minimum temperature of 117K by conduction from liquid nitrogen flowing through the fracture stage. The notched specimens were fractured by impact under a vacuum of $5(10^{-10})$ to $1.5(10^{-9})$ torr. Selected areas of the fracture surface were chosen for analysis through examination by in-situ SEM. Grain boundary chemistries were compared to the bulk chemistries by choosing an average of 5 intergranular regions and 5 transgranular regions for spectral surveys. The survey locations were programmed for automatic data acquisition using a multiple-technique analytical computer system (MACS). Each region was scanned over the energy range from 0 to 1000 eV in 1 eV increments at a rate of 50 msec per point. After sequentially surveying each of the 10 regions, the surveys were automatically repeated. Total survey times of approximately 5 minutes per region produced sufficient signal for analysis. A primary electron energy of 5 kV and a peak-to-peak modulation of 3 eV were used. The

probe diameter for the surveys ranged from 1 to 2 μm , allowing chemical analysis of specific features on the fracture surfaces.

Grain boundary segregation is often measured by depth profile analysis using Ar^+ sputtering. Following AES analysis of the fresh fracture surface, selected samples were sputtered at 3 kV for 2 to 5 minutes at a maximum equivalent rate of 100 nm Ta_2O_5 per min. Due to the varied incident angles between the ion beam and the particular grain boundary surveyed, however, the actual sputter yields are unknown. A qualitative measure determined by monitoring the depletion of adsorbed oxygen and/or the presence of argon indicated which regions were successfully sputtered and which were not. Another factor to consider when sputtering is ion bombardment-induced compositional modification. The preferential sputtering of Mn with respect to Fe, the high interstitial mobility, and variations in adsorbed oxygen levels limit the usefulness of depth profile analysis in this alloy system.

The surface chemistries were determined using a semi-quantitative technique. Independent peaks corresponding to each element present were selected. These are the Fe peak at 703 eV, Mn at 542 eV, Cr at 529 eV, O at 503 eV, N at 379 eV, C at 272 eV, Ar at 215 eV, B at 179 eV, and S at 152 eV. For each element identified, the peak-to-peak amplitudes were measured on a plot of the derivative of the intensity with respect to energy during modulation (dN/dE) versus energy (E). The amplitudes were scaled by empirically determined sensitivity factors. The experimentally determined sensitivity factors are: 0.236 for Fe(703eV), 0.131 for Mn(542eV), 0.485 for Cr(529eV), and 0.297 for N(379eV). Handbook values of sensitivity factors [69] were used for elements whose transgranular surface concentrations could not be taken as representative of known bulk concentrations. The atomic concentration of each element is given by the equation below;

$$C_x = (I_x/S_x)/(\sum_i(I_i/S_i))$$

where;

C_x	= atomic concentration of element x
I_x	= peak to peak amplitude for a particular peak
S_x	= sensitivity factor for a particular peak

Although the Auger surveys were obtained from in-situ fractured specimens under ultra-high vacuum, contamination from the atmosphere remains a significant concern. Carbon and oxygen peaks are observed in all spectra and increase with time after fracture. While surveys were typically completed within 2 hours after fracture, 5 to 10 percent oxygen and 2 to 5 percent carbon contents were normally measured on the specimen surfaces. These levels are not reported in the surface chemistry results but were continuously monitored for comparison purposes. While AES is an extremely surface sensitive technique, the electron mean-free-path can far exceed the interplanar spacing, ranging from approximately 0.3 nm at 10 eV to 1.5 nm at 1000 eV. Therefore the measured surface concentrations represent averaged chemistries including surface and sub-surface atomic layers.

IV. EXPERIMENTAL RESULTS

The experiments performed in this investigation address two general concerns. First the potential of simple systems and the effects of individual alloying elements on the cryogenic mechanical properties of Fe-Mn alloys are unclear. Therefore the ductile-to-brittle transition behavior and its relationship to the fracture mode is documented for each of the experimental alloys. Also of concern is the determination of the metallurgical sources of the transition to intergranular fracture in Fe-Mn alloys and the conditions required for its control. Because of their individual importance in controlling the transition to intergranular fracture, both the grain boundary chemistries and the deformation behavior of these alloys are investigated. Further insight into the mechanisms controlling the fracture behavior of these alloys is provided through examination of their processing dependencies.

A. Mechanical Properties: Ductile-to-Brittle Transition Behavior.

1. Fe-Mn-N Alloys. Binary alloys based on Fe-30Mn were modified through N additions. Nitrogen additions are known to increase strength through interstitial solid-solution hardening, but the influence on the cryogenic mechanical behavior is expected to be complex. Nitrogen is known to increase the austenite stability with respect to α' martensite formation in 300-series stainless steels [70-72], but has also been reported to lower the stacking-fault-energy (SFE) [73], which is associated with α' martensite formation in binary Fe-Mn alloys. The ternary Fe-Mn-N experimental alloys contain 0.025, 0.05, and 0.12 wt. percent N. A maximum N level of 0.12 percent could be retained in Fe-30Mn alloys with our melting practice. However, no evidence of porosity was observed in any of the alloys.

The Charpy impact values for these alloys in the as-annealed condition are presented as a function of temperature in Fig. 5. While the Charpy impact energy for an Fe-31Mn binary alloy moderately decreases at 77K (-196°C) relative to room temperature, the decreases in Charpy impact values become increasingly sharp with increasing N contents. The Charpy impact energy of Fe-30Mn-0.12N (alloy T3) decreases to 25 J at 77K.

The rapid decreases in impact energy with decreasing test temperatures correspond to a change in fracture mode. A clear correlation exists between the sharp decreases in the Charpy impact energy and the onset of intergranular fracture, as observed by scanning electron microscopy (SEM) examination of the fracture surfaces of these specimens. For example, the room temperature fracture mode of alloy T3 is completely ductile, as shown in Fig. 6a. This is observed for all of the experimental alloys. As the temperature is decreased, fracture occurs by a mixed transgranular and intergranular mode. As the test temperature is decreased further, the percentage of intergranular fracture increases. At 77K the fracture mode of alloy T3 is predominantly intergranular, as shown in Fig. 6c.

The amount of intergranular fracture also increases with increasing N content in these ternary alloys. The percentage of intergranular

fracture at 77K increases continuously with increasing N content, becoming predominant at 0.12 percent N (see Fig. 7). Although the onset of intergranular fracture is associated with low impact energies, considerable plastic work may occur prior to grain boundary separation. Thus the Charpy impact energy of the binary or 0.025 N alloys remain near 125 J despite significant amounts of intergranular fracture at 77K. Nevertheless, the impact values decrease as the percentage of intergranular fracture increases.

Although all room temperature Charpy impact specimen fail by ductile void coalescence, the impact energies vary considerably between alloys (see Fig. 5). The energy absorbed during ductile fracture is known to be strongly dependent on the number and distribution of void nucleation sites. One source of void nucleation sites are the oxide inclusions. If the upper-shelf energy for these alloys is plotted versus residual oxygen content, as in Fig. 8, a good correlation is seen. The highest absorbed fracture energies at room temperature are associated with the lowest oxygen contents. The residual oxygen contents also scale with the number of inclusion particles, due to significant proportions of oxide inclusions.

The tensile properties of the Fe-30Mn matrix are also strongly affected by the solid-solution strengthening influence of N additions. The yield and tensile strengths at room temperature increase roughly linearly with increasing N contents as shown in Fig. 9 (the data for N contents greater than 0.12 percent are for quaternary Fe-Mn-Cr-N alloys). With the addition of up to 0.36 percent N, the yield and tensile strengths at room temperature both increase at a rate of approximately 80 ksi (560 MPa) per wt. percent N.

Nitrogen additions also increase the temperature dependence of the yield strengths. Between room temperature and 77K the yield strength of binary Fe-30Mn increases from 23 ksi (160 MPa) to 43 ksi (295 MPa), while the yield strength of alloy T3 increases from 32 ksi (220 MPa) to 75 ksi (520 MPa) over the same temperature range. With the addition of up to 0.22 percent N, the 77K yield strengths increase at a rate of approximately 320 ksi (2200 MPa) per wt. percent N. While the 77K yield strengths increase roughly linearly with increasing N contents, as shown in Fig. 10, the tensile strengths do not. In general, the amount of work-hardening prior to failure (the difference between yield and tensile strengths) decreases with increasing N content. The tensile elongation of high-N tensile specimens at 77K are limited by fracture prior to necking. The tensile elongations at room temperature and 77K are shown in Fig. 11.

The onset of intergranular fracture limits the low temperature tensile ductility of these alloys. Typical fracture surfaces of Fe-30Mn-0.05N tensile specimens tested at room temperature and 77K are shown in Fig. 12. While final fracture at room temperature results from the strain dependent coalescence of microvoids, intergranular separation interrupts this process, leading to early failure.

The usefulness of ternary Fe-Mn-N alloys as cryogenic structural materials are limited by their N solubility and transition to intergranular fracture at temperatures below 145K. The N solubility limits

the yield strengths and the Charpy impact values rapidly decrease with the increasing amounts of intergranular fracture at low temperatures.

2. Fe-Mn-Cr-N Alloys. It has been observed that Cr additions of at least 3 percent effectively inhibit intergranular fracture in similar high-Mn steels [2]. While increased austenite stabilities were assumed, the source of its beneficial effect has received little attention. The influence of Cr additions on the DBT and associated metallurgical characteristics were therefore investigated.

Three quaternary Fe-Mn-Cr-N alloys as well as a N-free ternary Fe-Mn-Cr alloy based on Fe-30Mn were melted. The N solubility in these alloys is a strong function of the Cr content. The actual N contents are compared with the melt additions of N in Table 2. A maximum of 0.12 percent N is retained in ternary Fe-30Mn alloys. However, a maximum of 0.22 percent N is retained with 5 percent Cr additions, and at least 0.36 percent N can be retained in 12 percent Cr alloys. The complete chemistries for these alloys are listed in Table 1.

The Charpy impact values for these Cr-containing alloys in the as-annealed condition are plotted as a function of test temperature in Fig. 13. The DBT has shifted to lower temperatures relative to the ternary Fe-Mn-N alloys despite the increase in N content. A ductile-to-brittle transition temperature (DBTT) can be arbitrarily defined for comparative purposes as the temperature at which the impact value has decreased to one-half of the room temperature value. These temperatures are plotted versus N content in Fig. 14. While the transition temperature increases with N content in the ternary alloys, a clear drop in the transition temperature occurs in the Cr-containing 0.16 percent N alloy. Further increases in N content again raise the transition temperature. The DBTT of the N-free Fe-30Mn and Fe-27Mn-4.5Cr alloys are below 77K.

The Charpy impact energy transitions in the Cr-containing alloys are again associated with the onset of intergranular fracture at low temperatures. Decreased impact energies at low temperatures result from increasing percentages of intergranular fracture. The impact energy of Fe-31Mn-5Cr-0.16N (alloy Q1) at 77K remains relatively high at 92 J but decreases to 23 J in Fe-31Mn-5Cr-0.22N (alloy Q2). A mixed intergranular and ductile-transgranular fracture mode occurs during impact testing of alloy Q1 at 77K while almost completely intergranular fracture occurs in alloy Q2 (see the SEM fractographs in Fig. 15).

Although no transition temperature could be ascribed to either of the N-free alloys, their 77K fracture modes are quite different. In binary Fe-30Mn a significant amount of intergranular fracture is observed, as shown in Fig. 6. In Fe-27Mn-4.5Cr, however, the fracture mode remains transgranular at 77K despite a Charpy impact value of only 70 J, as shown in the fractographs of room temperature and 77K Charpy impact specimens (see Fig. 16).

At the very high N contents in Fe-31Mn-12Cr-0.36N, the surface roughness of the fracture facets increases considerably (see Fig. 17). This is a deviation from the trend of increasingly smooth intergranular facets associated with the decreases in ductility at high N contents. These regions can be characterized by both stepped, planar surfaces and

the presence of river patterns on the facets typical of brittle transgranular fracture. Similar features have been observed on the low-temperature fracture surfaces of stable austenitic alloys with high-N and Cr contents by other investigators [74-76]. The transgranular facets were identified as $\{111\}_\gamma$ cleavage planes using etch-pit techniques [75]. The useful N content in these alloys can thus be limited by the onset of low-energy transgranular cleavage fracture at cryogenic temperatures, irrespective of the ability to resist intergranular separation.

The yield strengths of the Cr-containing alloys follow a N content dependence very similar to Cr-free alloys. The potency of the N additions overshadow any solid-solution strengthening due to the Cr addition itself. The yield strengths increase continuously with increasing N contents at both room temperature and 77K as shown in Figs. 9 and 10, respectively. More than a three-fold increase in the 77K yield strength occurs between that of binary Fe-30Mn (295 MPa) and Fe-31Mn-12Cr-0.36N (948 MPa).

The influence of N additions on the tensile strengths of quaternary alloys changes with test temperature. At room temperature the tensile strengths increase continuously with increasing N contents. At 77K the tensile strength of alloy Q1 is relatively high at 156 ksi (1075 MPa), but the tensile strengths decrease with further increases in N content. The elongation prior to failure at 77K decreases dramatically from over 60 percent in alloy Q1 to only 3.5 percent in alloy Q2 (see Fig. 11b). Fractography of these tensile specimens reveal predominantly intergranular fracture associated with the poor ductilities.

In general, the percentage of intergranular fracture at 77K decreases in tensile specimens relative to impact specimens of the same alloys. In alloy T3 for example, the 77K tensile elongation is approximately 45 percent and large regions of ductile transgranular fracture are present while intergranular fracture is predominant in impact specimens. Most notable is the completely ductile-transgranular fracture surfaces of quaternary alloy Q1 tensile specimens at 77K (see Fig. 18). These results indicate a significant strain rate sensitivity of the transition to intergranular fracture in these alloys.

While both strength and toughness levels are individually important engineering parameters, it is generally observed that they are inversely proportional. The usefulness of structural materials are therefore best described by their combinations of strength and toughness. The Charpy impact values are plotted versus corresponding yield strengths for individual binary, ternary and quaternary alloys in Fig. 19. Each data pair in the figure corresponds to a specific test temperature between room temperature and 77K. The strength/toughness combination of binary Fe-30Mn is improved through the addition of 0.12 percent N, and further improved by the addition of 5 percent Cr in a 0.16 percent N alloy. The ternary N addition increases both the strength and impact toughness at room temperature relative to binary Fe-30Mn. The high strength at 77K, however, is accompanied by low-energy impact behavior due to intergranular fracture. Clearly, control of the intergranular fracture mode is necessary to ensure high cryogenic toughness.

The strength/toughness relationship of Fe-31Mn-5Cr-0.16N is much improved relative to Cr-free alloys. The chromium additions significantly reduce the DBTT and the amount of intergranular fracture at 77K. Higher N contents in quaternary alloys increase the cryogenic yield strengths but result in catastrophic loss of impact toughness associated with predominantly intergranular fracture.

3. Fe-Mn-Cr-C(Si)-N Alloys. While Cr additions improve the cryogenic mechanical behavior, the transition to intergranular fracture in 77K Charpy impact specimens is not completely avoided. This is particularly disconcerting as Cr additions have been attributed with preventing intergranular fracture in similar alloys [2]. Therefore the importance of other factors such as the melting and thermo-mechanical processing techniques were considered. It is known, for example, that the experimental ingots contain relatively high concentrations of oxygen and sulphur (See Table 1). Also, elements such as carbon are normally present in commercially melted alloys at much higher levels than in these experimental alloys. The levels of such elements and other trace impurities are dependent on the particular melting stock, crucible material and melt variables used.

To determine the importance of differences in processing, two alloys with nominal chemistries similar to alloys known to possess fully-ductile behavior below 77K [2,18] were melted. An alloy with the composition Fe-33Mn-5Cr-0.6Si-0.14C-0.12N (alloy J) is similar to that investigated by Japan Steel Works. The other test composition is a Ni-containing, high-Mn stainless steel produced by Kobe Steel. The composition of this alloy (alloy K), is Fe-23Mn-13Cr-5Ni-0.3Si-0.05C-0.21N.

The Charpy impact values for these two alloys as a function of temperature are presented in Fig. 20. In alloy J, the impact resistance remains almost constant between room temperature and 77K. Failure occurs in an entirely ductile, transgranular mode at 77K (see Fig. 21a). In alloy K, the impact values decrease to approximately 100 J at 77K. The fracture mode, however, remains ductile with no indication of any intergranular separation (see Fig. 21b). The impact resistance of these fully-ductile alloys is known to become increasingly sensitive to oxygen and sulphur levels at low temperatures [20]. The actual impurity levels are relatively high in alloy K, as shown in Table 1.

While the impact toughness of alloy J remains roughly constant verses temperature, the yield strength increases to 100 ksi (689 MPa) at 77K. This strength level exceeds that of quaternary Fe-31Mn-5Cr-0.16N at 77K. The 111 ksi (765 MPa) yield strength of alloy K at 77K is also high relative to the other alloys. The 77K tensile properties for several alloys including alloys J and K are listed in Table 3.

The maintenance of a high-energy ductile failure mode in alloy J at 77K suggests the major importance of C or Si additions in preventing cryogenic intergranular fracture in Ni-free, high-Mn alloys. These elements may be present in commercial alloys, however, solely for economic reasons. Carbon, for example, is present at significant levels in commercial grades of ferro-manganese melting stock. Silicon is a useful addition for the deoxidation of steel and may also be present at residual levels.

To verify the importance of these minor additions on control of cryogenic intergranular fracture, two new alloys were melted. Both based on alloy Q1, alloy C contains a 0.12 percent carbon addition and alloy S contains a 0.5 percent Si addition. The complete chemistries of these alloys are given in Table 1.

The Charpy impact energies of alloys C and S verses temperature are presented in Fig. 22. It is clear that the cryogenic impact toughness of alloy C is superior to carbon-free alloy S. The impact values for alloy C decrease gradually with decreasing temperature to 140 J at 77K. In alloy S, there is a sharp loss in impact resistance below 150K and the 77K impact value drops to 72 J. The relatively low room-temperature impact energies are associated with high oxygen levels, and the resulting high concentration of oxide inclusions which assist the ductile fracture process.

SEM fractography of the 77K Charpy impact specimens of alloy C reveal a ductile transgranular fracture mode absent of intergranular separation (see Fig. 23a). Alloy S, however, fractures by a mixed transgranular and intergranular mode at 77K (see Fig. 23b). This difference in fracture behavior occurs despite nearly equal yield strengths at 77K (see Table 3). Thus carbon additions are effective in decreasing the susceptibility of these alloys to cryogenic intergranular fracture.

B. Processing Influence on Mechanical Properties.

Microstructural development is controlled not only by alloy chemistry but also by the processing history of the material. Therefore the influence of processing on microstructural features considered important to the transition behavior are examined. Of special interest are the effects of grain size and grain boundary chemistry redistributions. Correlation of the processing dependence of the transition behavior with microstructural changes also provide further insight into the metallurgical determinants of cryogenic intergranular fracture in these alloys.

1. As-annealed microstructures. Many microstructural characteristics, and the resultant mechanical properties are expected to be processing dependent. To evaluate chemistry effects in the as-annealed alloys, however, the processing should be kept constant in order to maintain consistent microstructures. This is difficult in practice. Melt-to-melt variations in the inclusion levels and final grain sizes still occur despite the relative insensitivity of the microstructure to their nominal chemistries, and attempts to keep the thermo-mechanical processing nearly constant.

The experimental alloys all possess fully-austenitic microstructures in the as-annealed condition. Optical micrographs of the etched structures of typical ternary, and quaternary alloys are presented in Fig. 24. These microstructures appear quite similar, consisting primarily of equiaxed austenite grains within which numerous annealing twins are present. Upon deformation, however, the structures of these alloys may evolve differently depending on the stability of the austenite.

The processing was kept uniform by maintaining 25 to 30 percent cold work prior to a repeatable recrystallization and annealing treatment of 1 hr at 1000°C followed by water cooling. These treatments resulted in mean-linear-intercept grain sizes between 40 and 80 μm . The as-annealed grain size for each experimental alloy is given in Table 4. Grain size variations between alloys are expected to result from such differences as work-hardening characteristics (which influence the strain energies due to cold-rolling) and inclusion contents (which influence the number of potential grain boundary pinning sites during annealing). Therefore, some variation in grain size is expected between alloys, even with identical thermo-mechanical processing. The significance of changes in grain size on the mechanical properties will be presented in a later section.

2. Inclusion contents. Inclusion contents can directly influence the fracture process. It is generally accepted that inclusion particles function as void nucleation sites. In the ductile regime, inclusion content limits the total plastic deformation required for failure. Inclusions may also function as microcrack nucleation sites during brittle fracture.

Energy-dispersive X-ray chemical analysis of inclusions has shown that the inclusions are primarily either MnS-type, or Mn-rich compounds of light elements such as oxides which are not directly detectable by X-ray emissions analysis. The level of inclusions in each of the experimental alloys is therefore expected to depend on the sulfur and oxygen contents of each heat. While the S contents are relatively constant, oxygen levels vary considerably from heat to heat. Final oxygen contents are dependent on a number of variables including the cleanliness of the melting stock and crucible, and the history of the charge with respect to temperature and oxygen partial pressures in the furnace atmosphere. Comparison of inclusion levels with alloy chemical compositions show that the inclusion levels scale with residual oxygen contents. The reciprocal square root of the number of inclusions per mm^2 of diameter greater than 0.5 μm is used as a measure of these inclusion spacings. Both the inclusion spacings and the room temperature Charpy impact energies decrease with increasing oxygen contents (see Fig. 8).

3. Influence of Cooling Rate. The chemistry distributions within an alloy are strongly influenced by the thermal history of the material. Processes such as the nucleation and growth of precipitates as well as equilibrium segregation are diffusion-controlled phenomena. As presented earlier, segregation-induced embrittlement is often responsible for the transition to brittle intergranular fracture at low temperatures. Therefore an attempt was made to inhibit the onset of brittle intergranular fracture by controlling the kinetics of potentially harmful grain boundary segregation.

Heat treatments were thus designed which minimize potential grain boundary segregation. One method investigated was to rapidly quench the material subsequent to formation of fresh grain boundaries by recrystallization. To simulate these conditions an alloy was cold-rolled to a 40 percent reduction in thickness, recrystallized at 950°C (1223K) for 6 min., and quenched in an ice-brine solution.

Another method investigated was to quench-in a homogenized structure by heat treating the material at a very high temperature, minimizing both bulk and interfacial segregation. An alloy was annealed at 1225°C (1498K) for 48 hrs. followed by a rapid quench in ice brine. As shown in Table 5, neither of these treatments improve the 77K impact values of alloy Q1. The cooling rate from the annealing temperature, however, largely influences the 77K impact energy. A temper-toughening phenomena is observed and the impact values increase at intermediate cooling rates.

This toughening phenomena is observed in 77K Charpy impact specimens as the post-anneal cooling rate is decreased. While a rapid quench in an iced-brine solution leads to increased cryogenic embrittlement relative to the water-cooled, as-annealed plate, air-cooling can dramatically improve the cryogenic impact toughness. This is especially evident in alloy Q1 (see Table 5). In Charpy impact tests at 77K, the water-cooled, as-annealed material absorbs 92 J. A rapid quench in ice-brine lowers the impact energy to 41 J, while air-cooling within the protective quartz capsule raises the 77K Charpy impact energy to 183 J.

This large increase in impact toughness is associated with the suppression of intergranular fracture. While rapidly cooling alloy Q1 increases the percentage of intergranular fracture, air-cooling results in an almost completely ductile-transgranular fracture mode at 77K. The influence of these treatments on the 77K fracture mode of alloy Q1 are compared by SEM fractography in Fig. 25. Thus with the proper processing history, intergranular fracture can be avoided at 77K in quaternary Fe-Mn-Cr-N alloys.

Since the air-cool treatment so dramatically improves the cryogenic toughness of alloy Q1, it is of interest to determine the effect of even slower cooling-treatments. Therefore the impact behavior of alloy Q1 after furnace-cooling from 1000°C (1273K) was measured. The result was a return to intergranular failure at 77K, as shown in Fig. 26, and the Charpy impact energy fell to 80 J. It is anticipated that nitride precipitation is responsible for the return to intergranular fracture in the furnace-cooled condition as observed in previous investigations on the sensitization of austenitic steels [24]. The critical temperature range responsible for these toughening or re-embrittling phenomena, however, cannot be determined from continuous-cooling treatments.

To obtain information on the temperature sensitivity and kinetics of these phenomena, quench-and-age treatments were performed. Following a rapid quench from the annealing temperature, the specimens were isothermally aged at intermediate temperatures. The temperature dependence of the remedial influences observed during slow cooling from the annealing temperature were measured by isothermally aging at temperatures from 750°C (1023K) to 450°C (723K). The results of 77K Charpy impact tests are presented in Table 6. The treatment of 450°C (723K) for 30 min. followed by water-quenching raised the 77K impact energy to 129 J from 95 J in the as-annealed and water-quenched condition. While this represents only a partial restoration in ductility, it indicates the remedial influence of relatively low-temperature treatments. Aging at 600°C (873K) for 30 min. increased the 77K ductility further. Decreasing the cooling rate from 600°C (873K) by air-cooling results in only a small

increase in Charpy energy. Longer aging times at 600°C (873K), as after 16 hrs result in a return to embrittlement. A similar embrittlement is observed after aging at 750°C (1023K) for only 30 min. Thus the optimal remedial aging treatments represent extremely short diffusion distances for most of the elements present in these alloys.

Lastly, the aging response of alloy Q1 at 500°C (773K) was measured. A series of Charpy impact specimens were water-quenched and isothermally aged for various times at 500°C (773K). The results of 77K Charpy impact tests are presented in Fig. 27. Behavior similar to that at 600°C (873K) was observed, with a relatively rapid increase in Charpy values at short aging times and a subsequent reduction after long aging times. The toughness of the as-air-cooled material, however, was not surpassed through any of the isothermal aging treatments.

The tensile properties of specimen isothermally aged at 500°C (773K) were also measured. No significant changes in yield strengths occur in these specimens. The yield strengths varied from 88 ksi (607 MPa) in the as-quenched condition to 89 ksi (614 MPa) after subsequent aging at 500°C (773K) for 1 hr, while the Charpy impact values increased from 41 J to 87 J. Therefore changes in yield strength cannot account for the observed cooling-rate dependence of the impact toughness.

The potential engineering importance of controlled cooling rates on the DBT warrant an extension to investigate its influence in other alloys. Therefore the 77K Charpy impact values were measured for several different experimental alloys, after ice-brine quench (BQ), water quench (WQ), and air-cool (AC) treatments. These results are presented in Table 7. With the exception of ternary Fe-30Mn-0.12N, the 77K Charpy impact energies all increase with decreasing cooling rates.

The dependence of ternary Fe-30Mn-0.12N (alloy T3) on cooling rate is unusual. The 77K impact toughness is effectively independent of cooling rate in the range between air-cooling and brine quenching. Unlike most other alloys, T3 fractures in a completely brittle manner at 77K. Therefore the influence of cooling rate was also measured at -125°C (148K), which is in the fracture-mode transition region for this alloy. Again, unlike the behavior of the other alloys, the Charpy impact energy of alloy T3 decreases from 99 J after a rapid water quench to 70 J after air-cooling.

The largest increases in Charpy impact energies with decreased cooling rates occur in alloys within a fracture mode transition region at the test temperature and correspond to reductions in the amounts of intergranular fracture. In the ductile carbon-containing alloys such as alloy C or J, the increase in impact energies between BQ and AC specimens is only 10 to 30 percent. The Charpy impact energies of quaternary alloys Q1 and Q2 which are within a fracture-mode transition region at the 77K test temperature, increase 350 and 500 percent, respectively. Although slow-cooling treatments increase the 77K toughness substantially, the high-N quaternary alloys Q2 and Q3 continue to fail in a predominantly intergranular manner.

4. Grain size. In as-annealed, single-phase austenitic alloys, grain size is perhaps the single most important processing-dependent parameter

determining alloy strength. Yield strengths are generally inversely proportional to the square root of the average grain diameter. While strength and toughness are typically inversely proportional, the effects of grain size on toughness can be complex under conditions involving a transition to a brittle fracture mode. Microstructural factors such as the unit brittle fracture length and slip-line lengths both increase with grain size, and the total grain boundary area, which can influence grain boundary impurity concentrations, decrease with increasing grain size. Although increased grain sizes lower the yield strength for all of the experimental alloys, the influence of grain size on cryogenic impact toughness is alloy-dependent.

The grain-size dependence of the yield strength for alloys T3 and Q1 are plotted in Fig. 28. As expected, the yield strengths decrease with increasing grain size. The decrease in yield strength with increasing grain size is larger, however, for the higher strength Cr-containing alloy than for the ternary alloy.

The influence of grain size on the transition behavior and cryogenic Charpy impact values are also of interest. Therefore alloy T3, which fails in a completely intergranular manner at 77K, was tested in a transition region at 148K. Charpy impact energies for alloy T3 as a function of grain size in both the water-quenched and air-cooled conditions are plotted in Fig. 29. The impact toughness decreases with increasing grain size in both conditions. The fracture mode remains primarily intergranular for the grain sizes measured.

The influence of grain size on the 77K Charpy impact values of alloy Q1 in the air-cooled condition is plotted in Fig. 30. The Charpy impact energies at 77K increase with grain size in this alloy. Grain refinement through cold-roll and recrystallization treatments to a 20 μ m grain size decrease the Charpy impact energies. The return of a mixed ductile and intergranular fracture mode appears in the 20 μ m grain size specimen (see Fig. 31). These results suggest competitive grain-size influences on intergranular fracture; bulk flow strength favors brittle fracture with grain refinement; the mechanics of brittle fracture favor brittle fracture with grain coarsening.

In summary, processing parameters affecting the grain size, thermal history, and inclusion contents are important in determining the mechanical properties and transition behavior of these alloys. Characterization of the processing dependence provides information on the parameters controlling intergranular fracture which are of both engineering and fundamental importance. The influence of processing modifications on the DBT cannot be explained solely on the basis of a yield strength dependence, however, and further microstructural characterization is required for a mechanistic understanding of cryogenic embrittlement in these alloys.

C. Deformation Behavior.

In describing the response of a material to deformation, both the macroscopic parameters such as flow strength, and the micro-mechanical parameters influencing stress concentrations are important. The term,

deformation behavior, will be used to generically refer to the materials response to deformation. Changes in deformation behavior with decreasing temperature result in a transition from a ductile-transgranular to a brittle-intergranular fracture mode. To characterize the influence of alloy chemistry and processing on the ductile-to-brittle transition behavior, the macroscopic work-hardening and micro-mechanical behavior, including the austenite stability, tensile flow curves, and deformation heterogeneity are examined.

1. Austenite stability. Phase stability strongly influences the mechanical behavior of binary Fe-Mn alloys. Both the yield strength and work-hardening rate (WHR) are primarily controlled by the initial phase compositions, and the deformation-induced martensite transformations [1]. Austenite stability increases with Mn content, and at 30 percent Mn the binary alloys become fully-austenitic in the as-cooled condition. Upon tensile deformation, however, the Fe-30Mn binary alloy partially transforms from austenite (γ) to the hcp epsilon-martensite phase (ϵ).

Utilizing X-ray diffractometry, the influence of alloying modifications on the phase stability of Fe-30Mn were determined. In the as-cooled condition the ternary Fe-Mn-N and quaternary Fe-Mn-Cr-N alloys remain fully-austenitic. No indication of ϵ martensite is observed on the diffractometer traces. These results are consistent with optical micrographs of the as-cooled alloys.

To determine the relative phase stabilities of these alloys during deformation, uniformly-reduced sections of tensile specimens fractured at 77K were examined by X-ray diffractometry. While 23 volume percent ϵ was measured in binary Fe-30Mn tensile specimens, the amount of ϵ formation continuously decreases with increasing N content, as shown in Fig. 32. Only small (4%) to indistinguishable ϵ contents were measured in Fe-30Mn-0.12N tensile specimen. Higher N content, Cr-containing alloys remain fully-austenitic.

A more sensitive measure of austenite stability than from fractured tensile specimen is possible through X-ray diffractometry of as-cooled plus surface ground specimens. While all bulk, as-cooled alloys are single-phase γ , large fractions of ϵ formation occur after surface grinding on 600 grit SiC paper. This room temperature grinding treatment results in a measured 90 percent ϵ in binary Fe-30Mn, relative to only 23 percent ϵ after approximately 70% tensile elongation at 77K. Similar to measurements from 77K tensile specimens, the ϵ volume fraction continuously decreases with increasing N content, as shown in Fig. 33. The γ stability with respect to ϵ formation is linearly dependent on N content while apparently independent of Cr content. The increased ϵ contents measured after grinding are most likely due to a combination of the large imposed strains and the plastic relaxation of transformation strains at the surface, resulting in ϵ formation in the near surface region which is probed through X-ray techniques.

The $\gamma \rightarrow \epsilon$ transformation, unlike α' martensite formation, results in a volume reduction. From the X-ray data, the volume reduction during the $\gamma \rightarrow \epsilon$ trans can be estimated as 2.5 percent. Nitrogen, on the other hand, is known to increase the austenite lattice parameter [77-79]. Unfortunately, chemistry influences on the ϵ and γ lattice parameters

could not be resolved; broadening of the x-ray peaks from the grinding deformation necessary for the $\gamma \rightarrow \alpha$ transformation exceeds the expected chemistry-dependent peak shifts.

2. Flow curves/work-hardening. The tensile flow curves are the principal means of measuring the resistance of an alloy to plastic flow. The strain dependence of the macroscopic flow stresses and work-hardening behavior are derived from the tensile flow curves. These parameters provide an important measure of the alloying influence on development of the stress conditions necessary for intergranular fracture. They also indicate the propensity for hardening at regions of strain localization, such as crack tips. Both the early stages of deformation and complete tensile flow curves are compared for each alloy.

The flow curves for the early stages of deformation at 77K are shown for several alloys in Figs. 34 and 35. It is clear that early stage flow stresses at a given strain increase dramatically with increasing N content. The flow stresses at 77K are relatively constant, however, for the mid-N content alloys such as alloys J and C with carbon, and alloys Q1 and S without carbon additions. In the range of 0 to 2 percent true strain the WHR's are very similar with the exception of alloy Q0, as indicated by the shapes of the true-stress, true-strain curves in Figs. 34 and 35.

The complete stress-strain curves at 77K were calculated from load verses cross-head displacement data. These curves are plotted for several alloys in Figs. 36-38. While the yield strengths at 77K increase with N additions, the flow stress of binary Fe-30Mn increases beyond that of the N-containing ternary alloys at large strains (see Fig. 36). For comparison, the flow curve for binary Fe-35Mn which remains nearly fully-austenitic [10] is also included. The flow strengths in the stable binary alloy remain below those of the N-containing Fe-30Mn alloys.

In Cr-containing alloys the flow strengths at a given strain increase with N contents (see Fig. 37). The N-free alloy Q0 strain hardens much more appreciably at 77K than the fully-austenitic N-containing alloys. The flow stress of alloy Q0 exceeds that of alloy Q1 at large strains.

While alloy Q1 exhibits localized plastic flow (necking) prior to failure, the high-N alloys Q2 and Q3 do not. These high-N alloys fail in a brittle manner after relatively small strains at flow stresses considerably below the tensile strengths of the lower-N quaternary alloy.

The flow curves of the modified quaternary alloys J, C, S, and K are quite similar (see Fig. 38). The higher-N alloy K, however, exhibits higher strength, and the Si-modified alloy S fails after relatively low total strain.

The work-hardening behavior of these alloys can be characterized by their strain-hardening coefficients (n), where $n = (d \log \sigma / d \log \epsilon)$. In non-ideal power-hardening materials this coefficient varies with strain. Therefore the n -values for each alloy are plotted as a function of true strain at 77K. In binary Fe-30Mn the n -value increases sharply to over 0.7 but rapidly decreases at true strains greater than 0.3 (see Fig.

39). With increasing N contents the n-values increase much less rapidly and the maximum n-values are reduced. In binary Fe-35Mn the n-values are relatively constant over a wide range of strains.

Unlike the other alloys, the n-values of alloy Q0 remain quite high at low strains (see Fig. 40). The strain-hardening capacity also peaks at relatively low total strains, as in binary Fe-30Mn. The strain-hardening behavior of alloy Q1 is quite similar to both ternary alloy T3 and the more complex alloys (see Fig. 41). The high-N quaternary alloys Q2 and Q3 fracture in the low strain-hardening region at relatively low strains.

3. Deformation heterogeneity. A coarse, non-uniform distribution of strain in an alloy is expected to result in stress concentrations which are conducive to the operation of brittle fracture processes. In high-Mn austenitic alloys, planar slip traces created by the concentration of slip into planar deformation bands can be observed on the pre-polished surfaces of tensile deformed specimens, as well as on decohered grain boundaries. The chemistry dependence of this deformation heterogeneity is investigated. Following fractographic observations of intergranular fracture surfaces, the deformation heterogeneity will be characterized through observations of slip dispersal, and by the microstructural evolution associated with alternative deformation modes.

Evidence of stress concentrations at grain boundaries due to deformation heterogeneity can be observed directly from the features on intergranular fracture surfaces. Deformation ledges form on many grain boundaries, as revealed through SEM fractography (see Fig. 42). It is unclear, however, whether the ledges are created prior to fracture or due to the relaxation of dislocation pile-ups after fracture. In either case, the ledges constitute potential microcrack nucleation sites. Although observed only rarely, secondary grain boundary cracks occur which consist of a series of cracked regions separated by narrow ligaments with spacings similar to the deformation bands, as if a series of microcracks had initiated at dislocation ledges and blunted (see Fig. 42a).

The slip dispersal is compared qualitatively for three alloys: binary Fe-30Mn, ternary alloy T3, and quaternary alloy Q1. Pre-polished tensile specimens were deformed in 2 percent strain increments, and the resulting surface contrast observed under polarized light in the optical microscope. The specimens were repolished prior to each strain increment, allowing observation of surface relief due to 2 percent strain increments at large total strains. The typical surface contrast of as-deformed tensile specimens due to strains between 0 and 2 percent, 2 and 4 percent, and 15 to 17 percent total strains are shown for the three alloys in Figs. 43, 44, and 45.

Qualitative features which can be recognized in these as-deformed specimens include the deformation band lengths and spacings, ledge heights, and degree of planarity. Quantitative measurements are difficult due to random grain orientations and the resulting variations in the degree of local deformation, apparent ledge heights, and spacings. The lack of three-dimensional analytic capability and relatively low resolution in the conventional optical metallograph is also limiting.

SEM techniques suffer due to insufficient specimen contrast, and although extraction replicas may allow TEM analysis, it was decided that significant changes in the deformation behavior would be qualitatively obvious.

It should be pointed out that some of the features in the as-deformed specimens are spurious and should not be confused with strain-induced contrast. Most of the large dark particles are inclusions, while the finely dispersed particles on some surfaces are corrosion products formed during specimen preparation and testing. Polishing marks may also be present, but can be distinguished from deformation bands as they extend several grain diameters.

The most obvious differences in the deformation structures occur between the binary and more complex alloys. After 2 and 4 percent strain the deformation bands in the binary alloy are relatively coarse (see Figs. 43,44). These bands are relatively widely spaced, planar in nature with large ledge heights, and generally extend from one grain boundary to another. The deformation bands in ternary alloy T3 and quaternary alloy Q1, however, are much finer with closer spacings and lower ledge heights. The bands in these alloys continue to be planar in nature and fully extend between grain boundaries. Exceptionally finely-spaced and uniformly-distributed slip bands are observed in alloy Q1.

At larger total strains, as for the 15 to 17 percent strained specimens in Fig. 45, the deformation band spacings in alloys T3 and Q1 coarsen, becoming similar to those in the binary alloy. However, while the deformation bands in the binary alloy remain planar, regions of wavy deformation become evident in alloy Q1 at this strain. At these larger total strains the lengths of the deformation bands are significantly reduced in some regions, especially in the binary alloy.

While the deformation modes cannot be differentiated in the as-deformed specimens, comparison with polished and etched structures allow further identification. In polished and etched specimens, no contrast is observed due to deformation by slip. Deformation modes which create internal interfaces, however, such as ϵ phase formation and deformation twinning will result in preferential etching contrast. Optical micrographs of the polished and etched structures for the same three alloys after 2, 4, and 15 percent true strains are presented in Figs. 46, 47, and 48, respectively.

In the binary Fe-30Mn alloy a large percentage of the deformation after 2 percent strain is due to non-slip deformation modes (see Fig. 46). Most of the deformation bands extend until blocked by grain boundaries or annealing twin boundaries. In alloys T3 and Q1, no deformation-induced etching contrast is observed after 2 percent strain, indicating slip as the sole deformation mode (see Figs. 46). The only etching contrast in these specimen is due to inclusions, grain boundaries, or annealing twins present in the as-annealed microstructure. Surface undulations observed in some micrographs are an artifact resulting from linear agitation of the etchant.

The density of etched deformation bands in the binary alloy increase after 4 percent total strain, as can be seen in Fig. 47. An

increased density of banding on secondary systems is also observed. While the bands typically extend to grain boundaries or annealing twins, some also arrest at band intersections. Sharp tips can be seen on many of the deformation bands, especially on those ending within a grain. No deformation-induced etching contrast is observed in either alloy T3, or Q1 after 4 percent strain.

After 15 percent strain, deformation-induced contrast is observed in the polished and etched microstructures of all three alloys (see Fig. 48). In the binary alloy copious amounts of deformation banding have led to the overlapping and coarsening of some bands, and a refinement of the band lengths due to blockage at band intersections. In alloys T3 and Q1, deformation bands also appear in the etched structures after 15 percent strain. The bands are non-uniformly distributed, with the density of deformation bands varying widely from grain to grain; highly localized concentrations appear at some grain boundaries. The levels of deformation bands in alloys T3 and Q1, however, are similar. Sharp tips are again visible at the leading edges of the deformation bands.

It is also of interest to further identify the character of these etched deformation bands. It is known from X-ray diffractometry that the only deformation-induced phase transformation occurring in these alloys is ϵ formation. The ϵ content in binary Fe-30Mn after 70 percent tensile elongation is only 23 percent, however, and no ϵ is observed in high-N alloys. Therefore, ϵ formation alone cannot account for the observed etching contrast of the deformed specimens. Another deformation product which results in creation of internal interfaces and orientation changes is deformation twinning. Like ϵ phase, deformation twins are expected to form by an overlapping stacking fault mechanism in austenitic alloys [80,81]. The presence of deformation twins have been previously identified in similar high-Mn austenitic alloys, especially at low deformation temperatures [82].

The deformation structure of quaternary alloy Q1 deformed 10 percent in tension at 77K was examined by transmission electron microscopy. The bright-field image in Fig. 49a, shows deformation bands impinging on a grain boundary. This micrograph supports the view that individual stacking faults extending across the grains overlap to form deformation bands of twinned austenite or hcp ϵ . In Fig. 45(b,c,d) several of these thin bands are identified as deformation twins. The deformation twins are illuminated in the dark-field image using a twin reflection (see sketch of the selected-area diffraction pattern). Like the faulted dislocations, the fcc deformation-twins form on the close-packed $\{111\}_{\gamma}$ planes. No evidence of ϵ martensite was seen in this alloy.

D. Grain Boundary Chemistry

It is well known that changes in grain boundary chemistry can significantly alter the resistance of a material to intergranular fracture. The grain boundary chemistries are determined by the bulk alloy and impurity contents, as well as by the thermal history of the material.

The grain boundary chemistries of the high-Mn specimens were ana-

lyzed by Auger electron spectroscopy (AES) after fracture under ultra-high vacuum at -150°C (123K). Equipped with SEM capabilities and a 1 to 3 μm beam size, selected areas on the fracture surfaces were analyzed. Differences in grain boundary and matrix chemistries were examined by both a direct comparison of transgranular and intergranular regions, and from a compositional profile obtained by removal of surface layers through inert gas ion-sputtering. The high sensitivity of AES to light elements also allows chemical analysis of light element compounds such as inclusions on the fracture surfaces. Results of chemical analyses of as-annealed fracture surfaces are followed by characterization of the influence of thermal history on the grain boundary chemistries.

1. **As-annealed fracture surfaces.** The grain boundaries of as-annealed specimens were analyzed by AES for chemistry changes which may be responsible for the susceptibility of these high-Mn alloys to intergranular fracture. The surfaces were carefully analyzed through spectral surveys of individual grain boundary regions for the presence of any impurity element segregation. The surfaces were similarly examined for alloying element segregation. Data from both a direct comparison of transgranular and intergranular regions on the as-fractured surfaces, and from ion-sputtering techniques are presented.

The as-fractured surfaces of several alloys have been analyzed for grain boundary impurity segregation. A typical AES survey of a grain boundary in ternary alloy T3 is shown in Fig. 50. No grain boundary impurity segregation is observed in any of the alloys. Impurity levels of 0.1 atomic percent S or P were readily detected.

Due to the relatively high level of inclusions in these alloys, an inclusion particle is often present within the surveyed region. Most of these inclusions have been identified as either Mn-rich sulfides or oxides. When a high sulfur concentration is present in an AES survey, it is always in conjunction with high Mn contents from the associated inclusion particles. Most grain boundaries surveyed are sulfur-free, while many of the transgranular regions surveyed contain large sulfur peaks. A sulfur map and corresponding SEM image from the SAM system is shown in Fig. 51. The sulfur content is localized to transgranular regions with exposed inclusions.

In addition to inclusion effects, extra or modified peaks can appear in the AES surveys due to in-situ surface modifications such as residual gas adsorption. The rate of surface adsorption from residual gases such as oxygen and carbon (from cracking of CO), are dependent on the vacuum condition. Even under the best experimental conditions available in this system, i.e., $5(10^{-10})$ torr, C and O peaks are always present in the Auger spectra. Under relatively poor vacuum conditions, or after long exposures, the oxygen peak in particular can become quite large.

The principal concern associated with the presence of oxygen is preferential adsorption which can alter the apparent alloy concentration at the surface. The influence of surface oxygen content on the apparent Mn level at the fracture surface is presented in Table 8. Increased levels of oxygen adsorption decrease the Mn/Fe peak ratio, decreasing the apparent Mn content. Therefore it is important to use comparative

methods to measure potential alloying element segregation, and also to monitor the level of oxygen adsorption.

Two different comparative methods were used to examine alloy segregation to the grain boundaries. In one method, the as-fractured intergranular surface chemistry is compared to that of the underlying region through removal of surface layers by Ar^+ sputtering. Alternate sputter and survey cycles can allow compositional profiling verses depth below the fracture surface. The sputter yields on fracture surfaces, however, are unknown due to the extreme sensitivity of sputter yield on surface orientation. In fact many grain orientations show no evidence of sputtering, as monitored by the presence of an Ar peak on successfully sputtered surfaces. Comparative analysis by this technique is also sensitive to varying levels of oxygen, which are reduced during sputtering. A better sputter technique is to compare AES spectra from the as-fractured surface with that of the deeply-sputtered bulk surface using complete surveys to monitor all peaks, and maintaining similar periods of surface exposure prior to the surveys.

The preferred method, however, is that of direct comparison. In this method the chemistries from AES surveys of intergranular regions and neighboring transgranular regions (representing bulk chemistries) on the as-fractured surfaces are directly compared. Transgranular regions were chosen to avoid inclusion effects, and only low-sulfur surveys are used in the comparisons. While both the direct and sputter comparisons may be valid in some systems, the results of Mn distributions differ between these methods.

A binary Fe-30Mn alloy was analyzed for Mn segregation using both direct and sputter comparison methods. The results are presented in Table 9. Comparing the transgranular and intergranular regions of the as-fractured surface, no segregation of Mn is observed. The oxygen and sulfur levels in these spectra were also nearly constant (5.9 at% O and 0.05 at% S in the transgranular spectra, and 6 at% O and no detectable S from transgranular regions). After a heavy sputtering dosage equivalent to the removal of 50 nm of TaO_2 , these same regions were resurveyed. In successfully sputtered regions, the Mn content decreased by approximately 30 percent in the intergranular region. This would normally indicate the previous enrichment of Mn at the grain boundaries. A transgranular region, however, shows a similar decrease in Mn content after sputtering. Therefore, a sputtering-induced compositional modification is indicated. Oxygen levels remain roughly constant at 7.8 and 7.0 at. percent for transgranular and intergranular regions, and no sulfur was detected at either location. The implications of these results will be discussed later, in reference to the chemical-bonding dependence of ion-bombardment-induced compositional modifications of surfaces.

2. Influence of thermal history. In addition to alloy chemistry modifications, the cooling rate also exerts a strong influence on the transition behavior. To investigate the influence of thermal history on the grain boundary chemistries, in-situ fracture specimens of alloy Q2 are examined by AES in the water-quenched, intermediate air-cooled, and isothermally-aged conditions. Although the ductility of this high-N alloy improves dramatically in the slowly-cooled condition, the fracture mode remains mixed transgranular and intergranular, allowing surface

analysis of both regions. As the carbon-containing alloys are resistant to intergranular fracture, alloy C is examined in a rapid-water-quench condition, as is ternary alloy T3. Finally, the grain boundary chemistry changes in alloy Q1 associated with a severe embrittlement phenomenon stemming from exposure to the furnace atmosphere is examined.

A strong influence of thermal history is observed in the transition behavior of alloys such as quaternary alloy, Q2. The 77K Charpy impact values of alloy Q2 increase from 9 J in the brine-quenched condition to 62 J after cooling from the annealing temperature in a 500°C (773K) furnace for 10 min followed by air-cooling. The changes in grain boundary chemistries associated with these thermal treatments were examined by AES. In addition, the influence of a longer-term aging treatment of 36 hrs. at 500°C (773K) was investigated as well.

The results of AES surveys from several individual transgranular and intergranular regions of these specimens are shown in Table 10. While no grain boundary segregation of Mn is observed, both N and Cr enrichments occur. Chromium is slightly enriched at the grain boundaries in all heat treatment conditions, especially after the longer-term aging treatment at 500°C (773K). Nitrogen enrichment is present at the grain boundaries after the rapid quench, but disappears in the air-cooled specimen. The grain boundary nitrogen enrichment returns, however, upon aging at 500°C (773K) for 36 hrs. The high Mn concentrations which were observed in the transgranular regions of the aged specimen are coupled with high sulfur contents, presumably from MnS inclusions.

The presence of harmful impurity segregants were not detected in any of the specimens. However, boron, which is known as a remedial segregant, is present at the grain boundaries of the slowly-cooled specimens. In the intermediate air-cooled condition, boron is present at all intergranular regions surveyed with an average concentration of over 1 at. percent. Boron was not detected in any of the transgranular regions. The identification of boron segregation by AES is based on the position of its peak at 179 eV, and its characteristic peak shape. Typical spectra from transgranular and intergranular regions of these specimen are shown in Fig. 52.

In the water-quenched condition, little to no boron is detected either on the grain boundaries or transgranular regions. After aging at 500°C (773K) for 36 hrs, a lower concentration of boron is detected on the grain boundaries than after the interrupted air-cool treatment, and a small but detectable level of boron is observed in some transgranular regions.

Carbon additions are associated with greatly improved cryogenic ductility in these alloys. In the rapid water-quenched condition, however, a few isolated grain boundaries are present and were surveyed by AES. Results of transgranular and intergranular chemical comparisons are presented in Table 11. No impurity segregation is observed, and both the Mn and Cr levels at the grain boundaries match those of transgranular regions. Nitrogen, however, is slightly enriched at the grain boundaries. The segregation behavior of carbon could not be determined. In-situ adsorption of carbon on the fracture surfaces is several times larger than the expected alloy contribution.

Ternary alloy T3 was also examined in the rapid water-quenched condition by AES. The results of transgranular and intergranular chemistry comparisons are shown in Table 11. Again, no impurity segregation, and no significant difference in Mn concentrations occur between transgranular and intergranular regions. A small increase in N content is observed at the grain boundaries relative to transgranular regions on this primarily intergranular fracture surface.

Another embrittling condition was investigated by AES. Specimens exposed to the furnace atmosphere during annealing treatments fail in a catastrophically brittle, intergranular fracture mode. A typical SEM fractograph of such an embrittled Charpy impact specimen (which absorbed only 3 J at 77K) is shown in Fig. 53a. The arrest of intergranular cracks initiated at the surfaces of exposed tensile specimen, as shown in Fig. 53b, confirm the embrittlement of material exposed to the furnace atmosphere.

A furnace-exposed AES specimen of alloy Q1 was prepared by annealing at 1000°C for 1 hr in a pin-pricked stainless steel bag followed by air-cooling. While this specimen failed primarily in a ductile manner, intergranular fracture predominated at the outer perimeter of the specimen. Intergranular surface chemistries measured verses distance from the edge of the specimen are shown in Table 12. The only element segregated to the grain boundaries is nitrogen, which increases to approximately 2.7 at. percent near the exposed surface. Although oxidation is also expected, grain boundary oxygen levels remain quite low and constant at 4 to 5 at. percent. In addition to implicating N as a potent embrittling agent at these concentrations, high-Mn alloys are shown to be highly sensitive to intergranular embrittlement after exposure to air at elevated temperatures.

V. DISCUSSION

While certain high-Mn austenitic steels have shown excellent potential as high-strength structural materials for use at 4K [7,13-15], binary Fe-Mn austenitic alloys are susceptible to intergranular fracture at cryogenic temperatures [1]. The purpose of this investigation has been to identify both the metallurgical sources, and conditions for control of cryogenic intergranular embrittlement in high-Mn austenitic steels. The influence of individual alloying element modifications on the DBT, and the potential of these simple alloy systems as cryogenic structural materials are also of interest. Mechanistic information on the sources of intergranular fracture is obtained through characterization of both the chemical and microstructural changes associated with variations in the transition behavior.

The chemistry dependence of the cryogenic mechanical properties and transition behavior are reviewed, followed by discussion of the importance of processing modifications. The microstructural sources of intergranular fracture in high-Mn alloys are also discussed. Potential mechanisms of intergranular embrittlement are reviewed, followed by a discussion of the native properties of Fe-Mn alloys, and the influence of chemistry modifications on the metallurgical determinants of intergranular fracture.

A. Alloy Design.

1. Chemistry modification. The best cryogenic mechanical properties in the binary Fe-Mn system occur in high-Mn, fully-austenitic alloys [1]. As the Mn content is lowered, large fractions of hcp ϵ intrusion result in low-energy transgranular fracture. Although fully-austenitic alloys are the most promising, they suffer from relatively low yield strengths, and a tendency towards intergranular fracture which increases with increasing Mn content. Therefore, further alloying element additions are necessary to obtain useful high-Mn cryogenic structural materials.

Nitrogen additions to austenitic Fe-Mn alloys are exceptionally effective in increasing the cryogenic yield strengths. The 77K yield strengths increase at a rate of 320 ksi (2200 MPa) per wt. percent N. While interstitial strengthening is limited by solubility constraints in ternary Fe-Mn-N alloys, Cr additions significantly increase the solubility of N in these alloys. Cryogenic embrittlement associated with the high resultant flow stresses at N contents of 0.22 wt. percent N or above becomes the limiting factor. While adequate yield strength is often a necessary requirement, more often the usefulness of a structural material is best judged by its combination of strength and toughness.

The influence of alloy chemistry modifications on the 77K yield strengths and Charpy impact energies of the as-annealed alloys are summarized in Fig. 54. While ternary N additions increase strengths, the impact resistances decrease. This is not an uncommon trend, but indicates the inability to obtain useful cryogenic structural materials in ternary Fe-Mn-N alloys. The quaternary addition of Cr is effective in improving the impact resistance even though the strength level is higher than in the ternary alloys. The yield strengths of Cr-containing

alloys continue to be proportional to N contents. The useful strengths in the quaternary Fe-Mn-Cr-N alloys, however, are limited by reembrittlement at high N contents (as in alloys Q2 and Q3). While the combinations of strength and notch-impact toughness in Cr-containing, N strengthened alloys are greatly improved relative to binary and ternary alloys, intergranular fracture is not completely suppressed at 77K. Further chemistry modification through carbon additions are required for completely ductile fracture in the as-annealed condition at 77K.

A trend shared among most alloys is the decrease in toughness with increases in strength or decreases in temperature. Thus, while N additions raise the cryogenic strengths, the DBTT is also raised relative to binary Fe-Mn alloys. The influence of Cr and C additions, however, are unusual. Additions of Cr lower the transition temperature, as in alloy Q1, despite an increased yield strength. This improvement in the transition temperature results in increased impact energies at 77K associated with a decrease in the amount of intergranular fracture. In carbon-containing alloy J, no decrease in impact resistance is measured between room temperature and 77K, and the fracture mode remains ductile in nature. Thus both Cr and C are beneficial alloying additions, improving the cryogenic mechanical properties of high-Mn austenitic steels through the suppression of intergranular fracture.

2. Processing dependence. The susceptibility of these alloys to intergranular fracture is also processing-dependent. The influence of processing on the mechanical properties is discussed here, and the mechanistic information on the cause and control of intergranular embrittlement is deferred to a later section. In addition to inclusion content and grain size, the thermal history influence on the mechanical properties is significant.

While the inclusion levels in these alloys are relatively high in comparison to commercial products, this is considered to promote a ductile rather than brittle fracture mode. As shown in Fig. 8, the Charpy impact energies absorbed in the ductile fracture process at room temperature decrease with increasing inclusion contents (which are also proportional to the total residual oxygen contents). Losses in low-temperature toughness due to high inclusion contents, as in the 77K impact resistance of alloy C relative to the cleaner alloy J, is not associated with any increase in the amount of intergranular fracture. Higher inclusion levels are observed to decrease the impact resistance through facilitation of the ductile fracture process of microvoid coalescence rather than by promoting intergranular fracture.

The cryogenic impact resistance is also strongly influenced by grain size. But the response of these alloys to variations in grain size are chemistry dependent. This dependence appears to be primarily governed by the dominant fracture mode of the alloy, although the grain size dependencies of the yield strengths are also significant. In ternary alloy T3, which is dominated by intergranular fracture in the transition region at 148K, the cryogenic impact resistance decreases with increasing grain size. This is similar to the behavior of ferritic steels [83]. In addition to the potentially high stress concentrations due to increased slip line lengths and dislocation pile-ups, increased grain sizes result in coarser intergranular fracture units. Although the

decrease in yield strength due to increased grain size in alloy T3 is relatively low, no indication of the ability to control intergranular fracture through grain refinement is seen in this alloy. The as-annealed impact specimen fail in a predominantly intergranular mode at 77K, and grain refinement is difficult in these single-phase austenitic alloys.

In ductile alloys such as air-cooled quaternary alloy Q1, the impact resistance at 77K increases with increased grain size. This behavior is similar to that observed in other ductile austenitic alloys. Decreased yield strengths, which are strongly grain size dependent in this alloy, are expected to promote high-energy ductile fracture. No evidence of intergranular fracture is observed on the grain coarsened 77K impact specimens and the impact values remain high at large grain sizes. Flow stress effects are also considered to be responsible for the transition to brittle fracture as the grain size is reduced to approximately 20 μm in this alloy. The increased yield strengths with grain refinement in this alloy appear to outweigh the benefits of reduced strain localization at the grain boundaries such as through decreased slip-line lengths.

Intergranular embrittlement through the grain boundary segregation of harmful impurity elements is also processing-dependent. Grain boundary segregation of impurities such as S, P, Sb, and Sn result in the well-documented temper embrittlement of low-alloy steels [49]. Equilibrium segregation is diffusion-controlled, and occurs during slow cooling or low-temperature tempering treatments. The experimental alloys, however, show no indication of impurity-segregation-induced intergranular embrittlement. No segregation of embrittling species to the grain boundaries are observed by AES analysis. Also, rapid-cooling treatments designed to inhibit segregation-induced embrittlement through control of the kinetics of segregation fail to decrease the susceptibility of these alloys to intergranular fracture.

On the contrary, a temper-toughening phenomena is observed. Reduced cooling rates from the annealing temperature suppress intergranular fracture and improve the impact energies at 77K. Although reductions in yield strengths may occur with slower cooling rates, this effect alone does not account for the observed increases in ductility. Changes in grain boundary chemistries, however are expected to produce significant effects. In addition to the elimination of nitrogen enrichment at the grain boundaries, segregation of residual boron occurs during the slow-cooling treatments.

B. Susceptibility of High-Mn Alloys to Intergranular Fracture.

1. Intergranular fracture mechanisms. There are many potential mechanisms for a transition from a transgranular to an intergranular fracture mode. As discussed in the background, the development of grain boundary stress concentrations and limitation of plastic relaxation, as well as the grain boundary cohesion, control the transition to intergranular fracture. Examination of the microstructural characteristics of the intergranular fracture process in these alloys, and comparison with potential fracture mechanisms indicate the inherent susceptibility of high-Mn alloys to intergranular fracture.

One class of intergranular fracture mechanisms result from the localization of ductile fracture events to the grain boundary regions. An example is the concentration of deformation within the low-strength precipitate-free-zones (PFZ's) of age-hardened alloys [21,22]. Another is through the coalescence of voids nucleated from precipitates which are localized to the grain boundaries as in overheated structures [109]. Although intergranular in appearance on the scale of the grain size, close examination of the intergranular facets reveals the ductile nature of the fracture mode. In these high-Mn alloys, however, no indication of ductile dimples are observed on the intergranular fracture surfaces. Typical intergranular facets are shown in Fig. 55. It is clear that intergranular separation occurs through a brittle rather than a ductile fracture process in these alloys.

The transition to brittle intergranular fracture in these alloys occurs as the test temperature is decreased from room temperature to 77K. With the increased resistance to plastic flow at low temperatures, new fracture mechanisms can become operational. One potential mechanism of intergranular embrittlement is through precipitation of a brittle grain boundary phase. Brittle grain boundary films, intermetallics, or discrete carbo-nitride precipitates all provide crack initiation sites and a brittle intergranular crack path. The only particles observed at the grain boundaries of the as-annealed high-Mn alloys, however, are inclusions. Although the inclusion content strongly influences the energy of ductile fracture, the transition behavior is not obviously correlated to the inclusion contents. The level of inclusions in alloys which remain fully ductile at 77K may match or exceed that in alloys which fracture in a brittle-intergranular mode.

Another common mechanism of brittle intergranular fracture at low temperatures is segregation-induced embrittlement. However, AES analysis shows no evidence of the segregation of embrittling species to the grain boundaries. The sulfur present on some of the grain boundaries is precipitated as MnS inclusions which are distributed throughout the bulk. Inhibition of segregation by limiting the diffusion kinetics through rapid cooling treatments fail to improve the transition behavior. It is therefore concluded that impurity segregation-induced embrittlement is not responsible for the transition behavior observed in these alloys.

While most cases of intergranular embrittlement involve sensitization of the alloy through an extrinsic mechanism, such as impurity segregation or precipitation effects, high-Mn austenitic alloys are inherently susceptible to cryogenic intergranular fracture.

2. Native properties. The intrinsic properties of high-Mn alloys are considered responsible for their transition to intergranular fracture at cryogenic temperatures. Potential sources of intergranular fracture intrinsic to high-Mn alloys are low grain boundary cohesion and deformation heterogeneity. First the importance of grain boundary cohesion and the detrimental influence of Mn additions are considered. Next the importance of an alloy's deformation characteristics and the deformation heterogeneity in high-Mn alloys are discussed.

The grain boundary cohesion defines an interfacial fracture stress

which strongly influences the energy of intergranular fracture. This cohesion is largely a function of the grain boundary chemistry and the resulting chemical bonding. Decreases in cohesion due to changes in grain boundary chemistry account for the often observed phenomenon of segregation-induced embrittlement. Theoretical models have been developed which explain the influence of grain boundary chemistry on the susceptibility of a material to intergranular fracture. Both the thermo-chemical and pair-potential models predict the embrittling influence of Mn additions in steels.

While each of these models predict the ideal work of fracture (γ^*), the actual work of fracture in metals is dominated by the energy expended in plastic deformation (γ_p). The importance of grain boundary chemistry and the associated ideal work of fracture on intergranular embrittlement, however, is well documented. These facts can be reconciled through recognition that although the work of fracture is dominated by plastic deformation, γ_p is not an independent material parameter [31,34]. It is dependent on γ^* , from which a critical fracture stress is defined. As the critical fracture stress decreases, the plastic work required to develop the conditions for crack initiation and propagation also decrease. Changes in the ideal work of fracture are therefore significant determinants of the susceptibility of an alloy to intergranular embrittlement.

The pair-potential model predicts the influence of solute additions on the energy of bond-breaking using a quasi-chemical measure of nearest-neighbor bond strengths [62]. This model correctly predicts embrittlement by the species known to promote intergranular fracture in well-documented systems such as low-alloy steels [49] (see Fig.56). The model also predicts that Mn additions to an Fe matrix decrease the grain boundary cohesion.

The degree of embrittlement predicted by this model is proportional to both the decrease in the sublimation enthalpy of the solute relative to the matrix, and the volume fraction of solute at the interface. Although Mn is a less potent embrittling addition to Fe than the commonly observed embrittling species such as S, P, Sb, or Sn, the decrease in fracture energy from the addition of 30 at. percent Mn to an Fe matrix is equivalent to interfacial concentrations of S, P, Sb, or Sn which are large relative to those found in heavily embrittled low-alloy steels. The detrimental influence of increasing Mn concentrations on the susceptibility to intergranular fracture has also been observed experimentally (see Fig. 57). The 77K Charpy impact energies of fully austenitic, binary Fe-Mn alloys decrease between 30 and 45 wt. percent Mn as the fracture mode becomes increasingly intergranular [1,10].

The thermo-chemical model can also be used to predict the influence of Mn on the resistance to intergranular fracture. The equilibrium segregation of an element to an interface is generally assumed to decrease the interfacial energy. If the solute segregation to the surface exceeds that to the grain boundaries (such that $2\Delta\gamma_s > \Delta\gamma_b$), the intergranular fracture energy will decrease, promoting embrittlement. In AES surface analysis of the experimental high-Mn alloys, no significant grain boundary segregation of Mn is observed in any of the alloy conditions examined. On the other hand, surface segregation of Mn occurs, as

indicated by ion-bombardment-induced compositional changes. An approximately 30 percent decrease in Mn content is measured by AES analysis of the near surface region after Ar^+ sputtering. Therefore in addition to the absence of grain boundary segregation there is a strong tendency for Mn to segregate to the surfaces. From the thermo-chemical model both of these factors should contribute to the promotion of intergranular fracture in high-Mn steels.

The ion-bombardment-induced compositional modification of surfaces has been observed in many alloy systems [84-87]. Preferential sputtering during ion bombardment was originally thought to correlate to differences in the masses of the constituent species. Mass correlations, however, fail to explain the experimental observations in a great many systems [84,87]. Mass effects in an alloy system such as Fe-Mn, consisting of elements neighboring in atomic number, are expected to be minimal. The ion-bombardment-induced compositional modifications in Fe-Mn are explained quite well, however, through chemical bonding considerations. Of the three most prominent bonding-related mechanisms considered by Kelly [84,87]: cascade sputtering (proportional to the surface binding energy), thermal sputtering, and the combination of surface segregation with sputtering, only the surface segregation model leads to the level of compositional changes observed in many experimental systems.

Surface segregation is enhanced during ion-bombardment due to creation of a layer of high defect density near the surface, increasing diffusion rates [88]. As in the pair-potential method of predicting interface decohesion, the free-energy of surface segregation can be estimated using values for the sublimation enthalpy. The species with lower sublimation enthalpy will segregate to the surface, decreasing the surface energy. Once segregated, this species is subject to preferential removal by sputtering. Thus Mn additions to an Fe-based alloy lower the grain boundary cohesion and result in alloys inherently more susceptible to intergranular embrittlement.

The deformation characteristics of an alloy are also important determinants of its susceptibility to intergranular fracture. It is well known that stress concentrations are necessary for the initiation of intergranular cracks. Crack growth is also influenced by the deformation characteristics governing the plastic relaxation of stresses at a crack tip. The low stacking-fault energy (SFE) of high-Mn steels and their resultant deformation heterogeneity is expected to increase the inherent susceptibility of these alloys to cryogenic intergranular fracture.

Transitions to brittle fracture modes commonly occur as the test temperature is decreased. Perhaps the best examples of deformation characteristics which promote brittle fracture are those associated with low-temperature deformation. Changes in deformation characteristics at low temperatures can be directly associated with the increased difficulty of thermally-activated deformation processes, or with changes in phase stability or deformation modes.

Decreased deformation temperatures are known to increase macroscopic flow stresses and work-hardening rates (WHR's). On a microscopic

scale, reductions in thermally-activated dislocation motion limit the ease with which arbitrary shape changes can be accommodated. Dislocation generation and operation on many independent slip systems are required for the accommodation of strain at grain boundaries and the relaxation of stress concentrations at crack tips. The decreases in SFE with decreasing temperatures can also be significant. Low SFE's are known to inhibit dislocation cross-slip in fcc materials and may result in higher WHR's and increasingly planar deformation modes.

The high-Mn alloys investigated here exhibit marked deformation heterogeneity. Planar deformation bands are observed on pre-polished tensile specimens (see Figs. 43-45) as well as on some of the exposed grain boundaries examined on fracture surfaces in the SEM (see Fig. 42). The deformation bands extend from one grain boundary to the next. These features indicate concentration of deformation at the intersections of the deformation bands with the grain boundaries in these alloys.

The SFE is expected to largely influence the mode of deformation in high-Mn alloys. The creation of an intrinsic stacking fault through the extension of a Shockley partial dislocation becomes easier as the SFE is reduced. The stacking faults formed upon deformation of these alloys fully extend between grain boundaries. An fcc deformation twin is created when an intrinsic fault forms on each neighboring plane, while formation of an intrinsic fault on every other neighboring plane produces a region of hcp structure. The mechanism of deformation-induced ϵ martensite formation has been observed to occur by the overlapping of stacking faults in austenitic alloys [80,81].

It is not surprising then that the SFE should strongly influence the deformation mode of austenitic alloys. Remy and Pineau have shown that the deformation structures in Co-Ni [89] or Fe-Mn [82] alloys are temperature (and SFE) dependent. At high temperatures, deformation occurs by slip and dislocation cells are observed. As the deformation temperature and associated SFE's decrease, deformation-twinning is observed and becomes more abundant with further decreases in temperature. At still lower temperatures (and SFE's), deformation-induced ϵ formation occurs. Deformation-twinning or both twinning and ϵ martensite formation occur during tensile deformation of the high-Mn alloys at 77K.

The deformation modes in low-SFE alloys increase the planarity of deformation. Both the deformation twins and ϵ martensite plates function as obstacles to deformation on other $\{111\}_\gamma$ planes. While the passage of slip or twin bands through existing twins can be accommodated plastically [15], energetically unfavorable dissociation reactions are necessary which require the development of stress concentrations [82,90]. Deformation twinning and ϵ martensite formation [1,89-93] are both known to increase WHR's in fcc alloys.

Important stress concentrations are also produced at twin tips. A sharp twin arrested at a grain boundary is effectively equivalent to a pile-up of Shockley partial dislocations along the twin-tip front. The stress field due to twin impingement at grain boundaries is believed to directly result in the nucleation of intergranular microcracks in some materials [38,90,94,95].

Low-SFE materials such as high-Mn alloys are thus inherently more susceptible to intergranular fracture. The difficulty of cross-slip reduces the number of active slip systems and contributes to increasingly planar deformation. Deformation-twinning or ϵ formation also increase the macroscopic WHR's and localize slip to narrow deformation bands. In addition to large grain boundary stress concentrations at deformation ledges from accommodation of localized deformation, twin-tips are potential nucleation sites for intergranular microcracks. Thus high-Mn alloys are inherently susceptible to intergranular fracture from the standpoint of both low grain boundary cohesion and deformation heterogeneity.

While the dispersal of deformation in low-SFE materials such as high-Mn alloys is heterogeneous, quantification of the actual stress concentrations and micro-mechanical behavior is beyond the scope of this work. The deformation characteristics of binary, ternary, and quaternary alloys are qualitatively compared in the next section.

3. Control of intergranular fracture. While the native properties of binary Fe-Mn austenitic alloys promote a transition to intergranular fracture at cryogenic temperatures, the transition temperature is sensitive to both alloy and process modifications. Intergranular fracture is suppressed at 77K in Fe-Mn-Cr-C-N alloys such as alloys J and C, or through controlled cooling of quaternary alloys such as alloy Q1. The control of intergranular fracture is expected to result from remedial changes in deformation behavior and grain boundary chemistries.

The onset of brittle fracture is stress-controlled. Actual fracture stresses, however, are several times larger than the tensile strengths of these materials. Therefore the influence of the deformation behavior on stress concentrations is important. Variations in the deformation behavior due to alloy modifications were investigated from both macro- and micro-mechanical viewpoints.

It is generally expected that the resistance to brittle fracture should scale inversely with yield strength. However, chemistry modifications of Fe-Mn binary alloys increase both the yield strengths and cryogenic impact resistances. The strain-hardening coefficient (n) is another important macroscopic variable. Although the 77K yield strength of binary Fe-30Mn is relatively low, its high n -value results in the development of high flow stresses and the potential for development of high stress concentrations.

An important determinant of the n -value is the γ phase stability. While all of the experimental alloys are fully-austenitic in the as-annealed condition, deformation-induced ϵ formation occurs in binary Fe-30Mn. The amount of ϵ formed during deformation decreases linearly with increasing N content, but is apparently independent of the Cr content. As an interstitial addition, carbon is expected to behave similarly to nitrogen with respect to changes in austenite stability. However, neither the Cr or C additions are observed to have a significant influence on the austenite stability. Also, while the cryogenic mechanical properties generally improve in alloys with increasing austenite stability, the stabilization of austenite does not ensure ductile behavior at cryogenic temperatures. In addition to the embrittlement of high-N

alloys, it is known that Fe-Mn binary alloys become increasingly susceptible to intergranular fracture at high Mn contents although these conditions lead to increased austenite stability.

The high WHR of binary Fe-30Mn is associated with the deformation-induced $\gamma \rightarrow \epsilon$ transformation. The potency of ϵ plates as barriers to slip on other $\{111\}_{\gamma}$ planes is well-documented [1,93]. The addition of N is very effective in stabilizing the γ against ϵ formation, and in ternary Fe-Mn-N alloy T3 the increased γ stability lowers the n-values significantly. Further alloy modifications such as higher N contents or Cr additions have only minor effects on the measured n-values. Yet the DBTT decreases significantly with these additions. Thus while the lower n-values are considered to inhibit brittle fracture, they cannot fully account for the observed improvements in the DBTT.

The influence of chemistry modifications on the micro-mechanical behavior during tensile deformation was examined through identification of active deformation modes and qualitative analysis of the slip dispersal. Deformation in these alloys occurs by slip, ϵ formation, and twinning modes. Beyond the effectiveness of N additions in stabilizing the austenite against ϵ formation, however, no significant changes in deformation mode were observed due to alloy chemistry modifications. Deformation twinning is observed after 15 percent elongation in both ternary alloy T3 and quaternary alloy Q1.

The slip dispersal, as characterized from the surface relief of tensile-deformed samples also remains qualitatively similar for the stable austenitic alloys. Planar deformation bands which intersect grain boundaries at either ends dominate the observed surface contrast. Stress concentrations at the grain boundaries are evident from the slip extrusions observed on the surfaces of fractured grain boundaries (see Fig. 42).

All of the high-Mn experimental alloys exhibit deformation behavior characteristic of low-SFE materials. The SFE of Fe-Mn binary alloys reaches a minimum at approximately 20 wt. percent Mn which corresponds to a maximum ϵ content [96,97]. Although N additions inhibit ϵ formation they can also decrease the SFE in austenitic alloys [73,78]. The addition of chromium may also lower the SFE of austenitic stainless steels, although its effect is relatively minor [98]. Nickel is one of the few elements known to increase the SFE of Fe-based austenitic alloys [98,99]. While the influence of C and N additions on the SFE of austenitic stainless steels may be small [100], C has been observed to promote cellular dislocation structures [101] while N does not [102].

The marked beneficial influence of chemistry modifications on control of the DBT in high-Mn alloys are expected to result at least partially from improved deformation characteristics. However, neither the anticipated influences of lower SFE's or the observed changes in the deformation characteristics of the fully-austenitic alloys with alloy chemistry modifications can support mechanisms for the control of intergranular fracture.

The grain boundary chemistries and resultant interfacial cohesion are also expected to be important determinants of the transition to

intergranular fracture. Grain boundary chemistries are altered by both alloy chemistry and process modifications. Alloy chemistry modifications through quaternary additions of N and Cr decrease the DBTT of Fe-30Mn alloys. Additions of C to quaternary alloys further improve the cryogenic ductility. The grain boundary segregation of B during slow-cooling treatments is also associated with increased resistance to intergranular fracture. In the order of increasing remedial influences, grain boundary segregations of N, B, and C are predicted by pair-potential theory [62] to increase the grain boundary cohesion.

Ternary N additions to Fe-30Mn, however, promote intergranular fracture in Charpy impact specimens at 77K. This can be attributed at least in part to the increased flow stresses with increasing N contents. Alternatively the distribution and state of precipitation of the N largely influence its role in controlling the transition temperature. There are many situations in which N is associated with the promotion of intergranular embrittlement.

In mild or low-alloy steels, high impurity levels of N are known to result in intergranular embrittlement [103]. The embrittlement is believed to result from the grain boundary precipitation of nitrides. In high-N austenitic stainless steels, sensitization treatments (such as aging at 700°C) also result in cryogenic intergranular embrittlement associated with nitride precipitation at grain boundaries [24]. The intergranular embrittlement of high-Mn alloys exposed to the furnace atmosphere during annealing is associated with N enrichment at the grain boundaries, as observed by AES analysis. However, no nitride precipitation is expected at the annealing temperature of 1000°C. The improvement in grain boundary cohesion from N additions predicted by pair-potential theory is based on non-interaction among solute atoms. This is obviously not the case for nitride precipitates. Also, if N atoms at the interface are in molecular versus atomic form, a severe embrittlement should result due to the negligible resistance to creation of a free surface. The distribution of N at the grain boundary is therefore important.

Chromium additions of 5 percent to Fe-Mn-N alloys significantly lower the DBTT. No beneficial influence on the grain boundary cohesion is expected directly, but Cr is known to strongly interact with N. The N solubility in these alloys, for example, increases from 0.12 wt. percent in Cr-free Fe-30Mn to 0.22 wt. percent with the addition of 5 wt. percent Cr. Nitrogen is also known to precipitate as Cr-rich compounds during aging [103-105]. Thus Cr encourages N redistribution resulting in the localization of N to Cr atoms. Solute redistributions due to the interaction of N and Cr may influence dislocation motion as well as grain boundary cohesion.

Nitrogen enrichment at the grain boundaries is observed by AES in as-quenched ternary and quaternary alloys (see Table 12). This accumulation of N is considered to occur at the annealing temperature. It is generally observed that N solubility in Fe decreases at high temperatures. For example, the accumulation of N in a high-N austenitic stainless steel (Nitronic 40) during vacuum annealing at 1250°C (1523K) results in pore formation from vaporization at the grain boundaries [106]. Chromium is also weakly segregated to the grain boundaries in

quaternary alloy Q2. Although Cr is not expected to directly enhance cohesion its affinity for such elements as N and O may be beneficial. The Cr enrichment at the grain boundaries is present after either quenching or slow-cooling from the annealing temperature, while N redistribution during slow-cooling treatments eliminates the N enrichment.

Carbon additions to quaternary Fe-Mn-Cr-N alloys significantly improve the cryogenic impact resistance and inhibit intergranular fracture. The segregation behavior of C could not be measured by AES, however, due to high levels of in-situ adsorption. The presence of carbon is predicted by pair-potential theory to strongly increase cohesion. There is also experimental evidence in the literature supporting increases in grain boundary cohesion due to C additions. While there is evidence of grain boundary site competition between C and embrittling elements such as P [107], recent work by Suzuki et al. [108] support the remedial influence of C as an intrinsic cohesion-enhancer.

The cooling rate from the annealing temperature also influences the degree of intergranular embrittlement. At least part of the improvement with reduced cooling rates can be attributed to changes in grain boundary chemistry. One significant change is the absence of N enrichment at the grain boundaries in a quaternary Fe-Mn-Cr-N alloy after an intermediate air-cooling treatment (see Table 10). Another is the segregation of B to the grain boundaries. Although B is present at trace impurity levels in the bulk, grain boundary B concentrations exceed 1 at. percent in the air-cooled condition. Boron is perhaps the most widely recognized remedial segregant and is associated with increased resistance to intergranular fracture in many alloys, from ferritic Fe-Mn [52,53] to Ni_3Al intermetallics [54-56]. Both pair-potential theory and the quantum calculations of Briant and Messmer [64] predict that B increases the interfacial cohesion of steels. The effectiveness of B as an alloying addition, however, is limited by the presence of relatively large C and N concentrations which are used as strengthening agents in high-Mn alloys, and would reduce the solubility of boron.

In summary, both alloy chemistry and processing modifications are isolated which improve the resistance of high-Mn steels to cryogenic intergranular fracture. The significant improvement in the DBTT of a quaternary Fe-Mn-Cr-N alloy relative to ternary Fe-Mn-N alloys suggest a synergistic effect of Cr and N additions. Changes in grain boundary cohesion are expected to largely control the resistance of these alloys to intergranular fracture. The transition behavior in quaternary Fe-Mn-Cr-N is sensitive to post-anneal cooling rates which result in grain boundary chemistry modification through B segregation and decreased N levels. The addition of carbon, regarded as a cohesion-enhancer, is especially effective in increasing the resistance of high-Mn alloys to intergranular fracture.

VI. CONCLUSIONS

A. Sources of Intergranular Embrittlement.

A transition to intergranular fracture occurs in high-Mn austenitic steels with decreasing temperature. While the onset of intergranular fracture is normally associated with an extrinsic source of embrittlement, the results of the present research show that the high-Mn austenitic steels are inherently susceptible to intergranular embrittlement. The principal results may be summarized as follows:

Grain Boundary Cohesion.

Decreases in grain boundary cohesion with the addition of Mn to Fe-based alloys are predicted from measurements of Mn segregation behavior using the thermo-chemical and pair-potential models for solute effects on the ideal work of fracture. AES analysis shows the absence of Mn segregation to the grain boundaries, while preferential sputtering of Mn with respect to Fe indicates a strong tendency for the surface segregation of Mn. These results support the intrinsic embrittling influence of Mn additions in steels.

AES analysis shows no indication of the segregation of embrittling impurity species to the grain boundaries (impurity concentrations of 0.1 at.% are readily detectable). Although sulfur is present in many AES spectra, its presence is always associated with Mn-rich inclusions.

Deformation Behavior.

Heterogeneous deformation conducive to the creation of grain boundary stress concentrations is prevalent in high-Mn steels. Deformation is highly planar in nature and localized into narrow bands which fully extend between grain boundaries. In addition to slip localization, deformation-twinning occurs in fully-austenitic high-Mn alloys.

Deformation ledges present on the as-fractured grain boundaries due to localization of slip indicate the presence of high grain boundary stress concentrations.

B. Mechanical Property and Fracture Mode Control

The influence of alloy chemistry and processing modifications on the cryogenic mechanical properties and control of intergranular fracture in high-Mn austenitic steels have been investigated. The principal results may be summarized as follows:

Chemistry Dependence.

The ductile-to-brittle transition temperature, which is associated with increasing amounts of intergranular fracture, increases with N content in ternary Fe-Mn-N alloys.

The ductile-to-brittle transition temperature decreases, and the resistance to intergranular fracture increases with the addition of Cr in Fe-31Mn-5Cr-0.16N.

Carbon additions to Fe-31Mn-5Cr-N alloys result in fully-ductile impact behavior at 77K.

Nitrogen additions to binary Fe-30Mn increase the room temperature and 77K yield strengths at a rate of 80 ksi (560 MPa), and 320 ksi (2200 MPa) per wt.% N, respectively.

Chromium additions significantly increase the nitrogen solubility in Fe-30Mn alloys. The maximum nitrogen content retained increases from 0.12 to 0.22, to at least 0.36 wt. percent nitrogen in 0.5, and 12 percent Cr alloys, respectively.

Nitrogen additions stabilize the austenite with respect to deformation-induced epsilon martensite formation.

Processing Dependence.

Although inclusion contents apparently control the impact toughness of fully-austenitic alloys in the ductile regime, they are not of primary importance in determining the transition to intergranular fracture.

Grain coarsening treatments reduce the cryogenic impact toughness of Fe-Mn-N alloy T3 due to promotion of intergranular fracture, despite decreases in yield strength. In ductile Fe-Mn-Cr-N alloy Q1, increases in grain size increase the 77K Charpy impact energy while grain refinement leads to transition behavior associated with the relatively large increases in yield strength.

Reduced cooling rates from the annealing temperature increase the cryogenic impact toughness of the Cr-containing alloys. The improvement in ductility can be recovered in rapidly-quenched material through isothermal aging at 500°C.

Boron segregation to the grain boundaries during slow-cooling treatments is anticipated to enhance the resistance to intergranular fracture through improved grain boundary cohesion.

RECOMMENDED RESEARCH

The intrinsic susceptibility of alloys such as the high-Mn steels to intergranular fracture is an area worthy of further investigation. A few areas of particular interest to the author are listed below:

The influence of grain boundary chemistry on the grain boundary structure and the interaction of matrix slip dislocations with the grain boundaries.

The chemistry and strain-rate dependence of dislocation substructural development.

Isolation of intergranular crack initiation sites and relation to the deformation structure.

The role of Ni in improving the cryogenic toughness of high-Mn austenitic steels.

Determination of the distribution of carbon in high-Mn austenitic steels using an ultra-clean AES system.

The susceptibility of high-Mn alloys to other potential intergranular embrittlement phenomena such as stress corrosion cracking and high-temperature embrittlement.

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Alloy	Composition, wt.%									
	Fe	Mn	Cr	Ni	Si	N	C	S	P	O
T1	bal.	30	-	-	-	0.025	0.006	0.009	<0.005	0.019
T2	bal.	30	-	-	-	0.048	0.008	0.009	<0.005	0.031
T3	bal.	30	-	-	-	0.122	0.006	0.010	<0.005	0.003
Q0	bal.	27	4.5	-	-	-	-	-	-	-
Q1	bal.	31	5	-	-	0.158	0.003	0.014	<0.005	0.006
Q2	bal.	31	5	-	-	0.223	0.001	0.012	<0.005	-
Q3	bal.	31	5	-	-	0.361	0.002	0.016	<0.005	-
J	bal.	33	5	-	0.58	0.124	0.140	0.011	<0.005	0.011
K	bal.	23	13	5	0.30	0.210	0.046	0.011	<0.005	0.031
C	bal.	31	5	-	-	0.119	0.120	-	-	0.036
S	bal.	31	5	-	0.54	0.145	0.009	-	-	0.040

XBL 8611-4546

Table 1. Experimental alloy designations and compositional analyses.

Melt Addition				Final Melt Chemistry			
Mn	Cr	N	Fe	Mn	Cr	N	Fe
31.5	-	0.2	bal.	30.4	-	0.12	bal.
31.5	-	0.4	bal.	30.7	-	0.12	bal.
31.5	5.1	0.2	bal.	30.7	4.9	0.16	bal.
31.5	5.1	0.4	bal.	31.0	5.0	0.22	bal.
31.5	12.2	0.4	bal.	31.3	12	0.36	bal.

XBL 8611-4545

Table 2. Melt additions and final alloy compositions.

77K Tensile Properties

Alloy	Yield Strength ksi, (MPa)	Tensile Strength ksi, (MPa)	Elongation* %
C	95 (655)	155 (1070)	64
S	96 (660)	135 (930)	17
J	100 (690)	>165 (1140)	>60
K	111 (765)	194 (1340)	55

* from 1 in (25 cm) guage length

XBL 8611-4544

Table 3. 77K tensile properties: alloys C,S,J, and K.

Typical as-annealed grain sizes*

* mean intercept length grain size
of 12mm plate

Alloy	Grain size, μm
T1	79
T2	66
T3	38
Q1	57
Q2	62
Q3	39
J	63
K	66
C	85
S	81

XBL 8611-4543

Table 4. Mean-linear-intercept grain sizes.

Treatment (Fe-31Mn-5Cr-0.16N)	77K Charpy Impact Energy, Joules
40% Cold roll + 950°C/6 min —>brine quench	25
1225°C/48 hrs —>brine quench	23
1000°C/1 hr—>brine quench	41
1000°C/1 hr —>air cool	183
1000°C/1 hr —>furnace cool	80

XBL 8611-4542

Table 5. Thermal history dependence of the 77K Charpy impact energy in alloy Q1.

Treatment * (Fe-31Mn-5Cr-0.14N)	Charpy Impact Energy, Joules
as water-quenched	95
+600°C/30 min → air cool	156
+600°C/30 min → water quench	146
+600°C/16 hrs → water quench	45
+750°C/30 min → water quench	37
+450°C/30 min → water quench	129
1000°C/1 hr → air cool	165

*initial condition: 1000°C/1 hr → water quench

XBL 8611-4541

Table 6. Influence of isothermal aging temperature on the 77K Charpy impact energy.

Cooling Rate Influence on LNT Charpy Impact Values

Alloy Composition	LNT Charpy Impact Value, [Joules]		
	ice brine quench	water quench	air cool
Fe-30Mn-0.12N	16	15	13
Fe-31Mn-5Cr-.16N	41	92	183
Fe-31 Mn-5Cr-.22N	8	23	49
Fe-31Mn-12Cr-0.36N	-	24	45
Fe-33Mn-5Cr-.6Si-0.14C-0.12N	165	191	224
Fe-31Mn-5Cr-0.5Si-0.14N	38	72	92
Fe-31Mn-5Cr-0.12C-0.12N	138	144	155

XBL 8611-4540

Table 7. Influence of cooling rate on the 77K Charpy impact energy for several alloys.

AES Surface Analysis, Alloy Q2

Condition	Surface Chemical Composition, At%		
	Oxygen	Mn	Cr
as-fractured	10	25	5.5
overnight in vacuum	17	28	5
oxygen-dosed	47	34	1.3

XBL 8611-4539

Table 8. Dependence of apparent Mn content at the fracture surface on measured surface oxygen content.

Sputtering Induced Compositional Changes in Fe-30Mn

Condition	Survey Region	Composition, At.%	
		Fe	Mn
as fractured	intergranular	bal.	31.2
	transgranular	bal.	31.4
Ar⁺ sputtered	intergranular	bal.	20.8
	transgranular	bal.	21.0

XBL 8611-4538

Table 9. Mn content measured by AES at grain boundary and transgranular regions of the as-fractured and Ar⁺ sputtered surfaces of binary Fe-30Mn.

Auger Electron Spectroscopy Fracture Surface Analysis

Heat Treatment	Survey Region	Chemical Composition, At.%				
		Fe	Mn	Cr	N	B
1000 °C/1 hr →WQ	intergranular	61.5	31.5	5.7	1.5	0.1
	transgranular	63.0	31.4	5.3	0.9	-
1000 °C/1 hr →500 °C/10 min →air cool	intergranular	60.9	31.4	5.7	0.9	1.1
	transgranular	63.1	31.1	5.3	0.9	-
1000 °C/1 hr →500 °C/36 hrs →air cool	intergranular	60.5	31.7	6.0	1.5	0.6
	transgranular	59.9	36.1	5.3	1.0	0.1

XBL 8611-4537

Table 10. AES compositional analysis comparisons of as-fractured grain boundaries and transgranular fracture regions for three cooling treatments in alloy Q2.

AES Fracture Surface Analysis

Specimen ID		Chemical Composition, At. %			
		Fe	Mn	Cr	N
Alloy T3	intergranular	bal	33.6	-	1.0
	transgranular	bal	32.6	-	0.8
Alloy C	intergranular	bal	31.2	4.1	0.9
	transgranular	bal	31.6	4.2	0.7

XBL 8611-4536

Table 11. AES compositional analysis comparisons of as-fractured grain boundaries and transgranular fracture regions for water-quenched alloy C and alloy T3.

AES Fracture Surface Analysis
Furnace-exposed alloy Q2

Distance from exposed surface, mm	Grain Boundary Chemistry, At%				
	Fe	Mn	Cr	N	O
0.05	bal	32	4.6	2.4	(4.8)
0.15	bal	32	4.7	1.1	(4.1)
0.3	bal	29	5.2	1.4	(4.6)
0.4	bal	30	4.5	1.1	(4.9)
0.7	bal	33	4.9	1.2	(4.2)

XBL 8611-4535

Table 12. AES compositional analysis of as-fractured grain boundaries near the furnace-exposed surface of alloy Q1.

XBL 8110-6792

Fig. 1. Charpy v-notch impact specimen dimensions.

Fig. 2. Flat tensile specimen dimensions.

NOTE: Tolerances ± 0.010 except as noted

XBL 698-1155

XBL 812-5241

Fig. 3. Schematic of the ultra-high vacuum chamber for AES analysis.

XBL 812-5242

Fig. 4. AES in-situ fracture specimen dimensions.

Fig. 5. Charpy impact energy verses temperature for binary Fe-31Mn, and ternary Fe-Mn-N alloys T1, T2, and T3.

Fig. 6. SEM fractographs of Fe-30Mn-0.12N Charpy impact specimen tested at: a) room temperature, b) 183K and c) 77K.

XBB 860-8609

Fig. 7. SEM fractographs of 77K Charpy impact specimens: a) alloy T1, b) alloy T2, c) alloy T3.

Room Temperature Charpy Impact Energy & Number of Inclusions vs. Oxygen content

XBL 8611-4509

Fig.8. Room temperature Charpy impact energy and inclusion spacing verses residual alloy oxygen content.

XBL 8611-4527

Fig. 9. Room temperature yield and ultimate tensile strength verses nitrogen content.

XBL 8611-4528

Fig. 10. 77K yield and ultimate tensile strength verses nitrogen content.

a.

b.

XBL 8611-4524

Fig. 11. Tensile elongations: a) room temperature, b) 77K.

XBB 869-7318

Fig. 12. SEM fractographs of alloy T2 tensile specimen tested at:
a) room temperature, and b) 77K.

XBL 858-3361

Fig. 13. Charpy impact energy verses temperature for: a) quaternary Fe-Mn-Cr-N alloys Q1, Q2, and Q3, (above), b) alloy Q0.

b

XBL 8611-4526

**Ductile-to-Brittle Transition Temperature (DBTT)*
vs. Nitrogen Content**

* Charpy impact energy (Cv) < 0.5 Cv (room temperature)

XBL 8611-4525

Fig. 14. Ductile-to-brittle transition temperature verses nitrogen content.

XBB 869-7319

Fig. 15. SEM fractographs of 77K Charpy impact specimens:
a) alloy Q1, b) alloy Q2.

XBB 869-7320

Fig. 16. SEM fractographs of alloy Q0 Charpy impact specimens tested at: a) room temperature, b) 77K.

XBB 860-8608

Fig. 17. SEM fractograph of alloy Q3 Charpy impact specimen tested at 77K.

XBB 869-7321

Fig. 18. SEM fractograph of alloy Q1 tensile specimen tested at 77K.

Fig. 19. Charpy impact energy verses tensile yield strength for binary Fe-30Mn, alloys T3, Q1 at room temperature, 148K, and 77K.

XBL 8611-4510

Fig. 20. Charpy impact energy verses temperature for alloy J, and alloy K.

XBB 869-7322

Fig. 21. SEM fractographs of 77K Charpy impact specimens:

a) alloy J, b) alloy K.

Fig. 22. Charpy impact energy verses temperature for alloy C, and alloy S.

XBB 869-7324

Fig. 23. SEM fractographs of 77K Charpy impact specimens:

a) alloy C, b) alloys S.

a

b

XBB 860-8603

Fig. 24. Optical micrographs of as-annealed alloys (Keller's etch): a) alloy T3, b) alloy Q1.

XBB 869-7325

Fig. 25. SEM fractographs of alloy Q1 Charpy impact specimens tested at 77K: a) brine-quenched, b) water-cooled, c) air-cooled.

XBB 869-7326

Fig. 26. SEM fractograph of furnace-cooled alloy Q1 Charpy impact specimen tested at 77K.

Influence of Aging Time at 500°C on LNT Charpy Impact Values
Fe-31Mn-5Cr-0.16N, water quenched + aged

XBL 8611-4511

Fig. 27. 77K Charpy impact energy of alloy Q1 verses aging time at 500°C.

XBL 8611-4531

Fig. 28. Grain size dependence of the 77K yield strength in alloys T3, and Q1.

148K Charpy Impact Energy vs. Grain Size
Fe-30Mn-0.12N

d = mean intercept length grain size

XBL 8611-4532

Fig. 29. Grain size dependence of the 148K Charpy impact energy of alloy T3 in the brine-quenched and air-cooled conditions.

77K Charpy Impact Energy vs. Grain Size
Fe-31Mn-5Cr-0.16N

Fig. 30. Grain size dependence of the 77K Charpy impact energy in air-cooled alloy Q1.

XBB 860-8606

Fig. 31. SEM fractograph of grain-refined alloy Q1 Charpy impact specimen tested at 77K.

Fig. 32. Volume fraction epsilon martensite (ϵ) verses nitrogen content in tensile specimens tested at 77K.

XBL 8611-4533

Fig. 33. Volume fraction epsilon martensite (ϵ) verses nitrogen content in alloys ground through 600 grit SiC paper at room temperature.

XBL 8611-4514

Fig. 34. True-stress verses true-strain for 0-2% strain at 77K: binary Fe-30Mn, alloys T3, Q0, Q1, Q2, and Q3.

Fig. 35. True-stress verses true-strain for 0-2% strain at 77K: alloys J, C, S, and K.

XBL 8611-4515

XBL 8611-4516

Fig. 36. Complete true-stress verses true-strain tensile flow curves at 77K: binary Fe-30Mn, Fe-35Mn, alloys T1, T3.

XBL 8611-4517

Fig. 37. Complete true-stress verses true strain tensile flow curves at 77K: alloys Q0, Q1, Q2, and Q3.

XBL 8611-4518

Fig. 38. Complete true-stress verses true-strain tensile flow curves at 77K: alloys J,C,S, and K.

Fig. 39. Strain-hardening coefficient (n) verses true-strain at 77K: binary Fe-30Mn, Fe-35Mn, alloy T1, T3.

Fig. 40. Strain-hardening coefficient (n) verses true-strain at 77K: alloys Q0, Q1, Q2, and Q3.

XBL 8611-4520

Fig. 41. Strain-hardening coefficient (n) verses true-strain at 77K: alloys J, C, S, and K.

XBB 869-7327

Fig. 42. SEM fractograph of deformation ledges on grain boundaries of 77K notch-impact specimen: a) alloy Q2 (above).

XBB 869-7328

Fig. 42: b) alloy Q2.

XBB 869-7329

Fig. 42: c) alloy T3.

100 μm

Fig. 43. Optical surface contrast on pre-polished surfaces deformed from 0-2% total tensile strain at 77K: a) binary Fe-30Mn, b) alloy T3, c) alloy Q1.

XBB 869-7330

Fig. 44. Optical surface contrast on pre-polished surfaces deformed from 2-4% total tensile strain at 77K: a) binary Fe-30Mn, b) alloy T3, c) alloy Q1.

XBB 869-7331

Fig. 45. Optical surface contrast on pre-polished surfaces deformed from 15-17% total tensile strain at 77K: a) binary Fe-30Mn, b) alloy T3, c) alloy Q1.

XBB 869-7332

100 μm

Fig. 46. Optical micrograph of tensile specimen polished and etched after 2% strain: a) binary Fe-30Mn, b) alloy T3, c) alloy Q1.

XBB 869-7333

Fig. 47. Optical micrograph of tensile specimen polished and etched after 4% strain: a) binary Fe-30Mn, b) alloy T3, c) alloy Q1.

XBB 869-7334

Fig. 48. Optical micrograph of tensile specimen polished and etched after 15% strain: a) binary Fe-30Mn, b) alloy T3, c) alloy Q1.

XBB 869-7335

XBB 860-8604

Fig. 49. TEM of alloy Q1 deformed 10% in tension at 77K:

a) bright-field image (above), b,c) bright-field and corresponding dark-field image from twinning reflection, d) selected-area diffraction pattern and indexed sketch.

XBB 860-8605

XBL 8611-4547

Fig. 50. Typical AES survey of a grain boundary in alloy T3.

a

b

XBB 869-7337

Fig. 51. a) AES sulfur map, b) corresponding SEM micrograph.

Fig. 52. Expanded AES spectra comparing the as-fractured grain boundary boron content with that from a transgranular region.

XBB 869-7328

Fig. 53. Furnace-exposed alloy Q1: a) SEM fractograph of 77K Charpy impact specimen, b) optical micrograph of secondary intergranular cracking in 77K tensile specimen.

XBL 8611-4522

Fig. 54. 77K Charpy impact energy verses 77K tensile yield strengths for all experimental alloys.

XBB 860-8607

Fig. 55. SEM fractograph of alloy T3 Charpy impact specimen tested at 77K.

Remedial/Embrittlement Plot

XBL 8611-4529

Fig. 56. Remedial/embrittlement plot predictions from pair-potential theory (after Seah [62]).

XBL863-7561

Fig. 57. Charpy impact energies verses temperature for Fe-35, 40, and 45Mn binary alloys (after Xue [10]).