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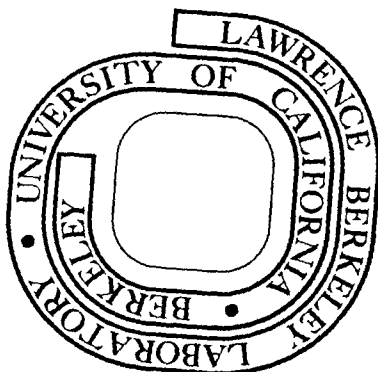
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STRUCTURE-PROPERTY RELATIONS AND THE DESIGN OF Fe-4Cr-C
BASE STRUCTURAL STEELS FOR HIGH STRENGTH AND TOUGHNESS

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ABSTRACT

Some design guidelines for improving strength-toughness combinations in medium carbon structural steels are critically reviewed. From this, quaternary alloy development based on Fe/Cr/C steels with Mn or Ni additions for improved properties is described. Transmission electron microscopy and X-ray analysis reveal increasing amounts of retained austenite in these alloys with Mn content up to 2 w/o and Ni additions at 5 w/o after quenching from 1100° C. A corresponding improvement in toughness properties is also found. Grain refining results in a further increase in the amount of retained austenite. In addition, the excellent combinations of strength and toughness in these quaternary alloys are attributed to the production of dislocated lath martensite from a homogeneous austenite phase free from undissolved alloy carbides.

The question of thermal instability of retained austenite following tempering is considered in detail and it is shown that the decomposition of retained austenite is closely related to the ease of nucleation and growth of cementite. Thus, graphitizing alloying elements such as Ni are beneficial in postponing the decomposition of retained austenite.

I. INTRODUCTION

In our structural alloy steel development group at Berkeley, a fundamental program was initiated about 12 years ago to gain a basic understanding of the influence of first, various alloying elements and heat-treatments on the martensite microstructure, and second, various microstructural parameters on mechanical properties, especially the ambient toughness properties (for example, the plane strain fracture toughness and the impact toughness).⁽¹⁻⁵⁾ In this paper, the influence of quaternary alloy additions on the structure and properties of high purity Fe-4Cr-C steels is investigated and based on this, the design of quaternary Fe-4Cr-C based steels for high strength and toughness is discussed.

Most commercial steels existing today have normally a very complex chemistry based on one or several of the following reasons: (i) elements added in combination give better hardenability than if added individually^(6,7), (ii) several elements are added in combination to exploit the benefits of secondary hardening^(6,8) and/or strengthening from intermetallics such as in very low carbon maraging steels^(9,10), (iii) some elements are added to produce grain refinement^(6,11), and (iv) a few elements are added in order to eliminate/defer the onset of various kinds of embrittlement during tempering of steel⁽¹²⁾ while others are added to suppress H₂ susceptibility.⁽¹³⁾ Often, however, the influence of the individual alloying elements in a complex commercial steel on its microstructure and properties is unknown and thus, in designing commercial steels, empiricism has taken the place of a systematic approach. The need for an understanding of the individual influence of various alloying elements on the structure and properties of much simpler, impurity free experimental alloys clearly exists. It is not always easy to isolate the

individual effects of two alloying elements present in a steel due mainly to the uncertainty of their mutual interaction behavior. Nevertheless, an attempt is made here to study the effects of quaternary additions on the structure and properties of the experimental Fe|Cr|C steel. The ternary Fe|Cr|C steel was chosen mainly because a large volume of information about this steel is already available and because it can possess combinations of properties which are superior to existing complex commercial alloys^(4,1,14,15).

A significant observation made recently^(1,16) using careful methods of transmission electron microscopy is the identification of thin interlath films of retained austenite in alloys apparently having their M_s and M_f temperatures much above room temperature. Since its discovery, several investigators attributed improved fracture toughness properties to the presence of retained austenite^(1,5,17-21). Although in several instances the improvement in toughness properties could not be singly attributed to the retained austenite^(17,18,20), best properties were often associated with microstructures containing large quantities of stable retained austenite^(5,18,20). Almost all the previous work on the influence of austenite on toughness was carried out on commercial steels wherein the complex chemistry and impurities complicate the interpretation. The chemical and mechanical stabilization of austenite as well as its morphology (whether continuous interlath films or discrete islands) could have important repercussions on its influence on the toughness of steel. It is thus one of the important objectives of the current investigation to try to assess unambiguously the role of retained austenite on the mechanical behavior by varying its amount and stability by either heat-treatment or alloying (or both) of the simple experimental Fe-Cr-C alloys. Secondly, in order to improve the toughness-to-strength ratio (which in turn increases

the critical flaw size), steels are usually tempered following quenching and the thermal instability of austenite ensuing tempering could significantly affect the toughness properties. It is thus another objective of this research to study the thermal stability of austenite as a function of type and amount of quaternary alloying.

Since the design of quaternary alloys of optimum composition to further develop the strength and toughness of the base steel constitutes an inherent part of this research, quaternary alloy additions are chosen based on some selection guidelines briefly reviewed in the following section.

II. APPROACH FOR IMPROVING TOUGHNESS-STRENGTH PROPERTIES

The approach adopted for obtaining good combinations of strength and toughness is primarily microstructural control by alloying, heat-treatment or combinations of both. In what follows, the design guidelines for improved mechanical properties are outlined and in the subsequent section, the choice of quaternary alloying based on these principles is discussed.

A. Design Guidelines

i) Carbon Content:

Increasing the carbon content of the steel is by far the most effective and economical way of raising the strength of steel. However, depending on the total alloy content of the steel, it has been shown⁽¹⁴⁾ that above 0.4%C, the steel is susceptible to intergranular cracking. From a fracture mechanics viewpoint, increasing strength without a corresponding increase in toughness would only result in poor utilization of the available strength of steel in

engineering applications where resistance to the propagation of existing cracks is important. At 200,000 psi yield strength level, a minimum of 80 KSI-in^{1/2} plane strain fracture toughness is needed for a critical flaw size of 0.1" if 60-80% of available strength is to be utilized. Above about 0.35%C, martensitic steel acquires a significant contribution to strengthening from substructural twinning. However, as will be discussed shortly, this kind of strengthening is undesirable from a toughness viewpoint. Thus, with a view to designing tough structural steels at a yield strength level of 200,000 psi, the carbon content of all the alloys investigated is maintained at a maximum of 0.3%.

ii) Martensite Substructure

Several investigations in the past^(1,22) revealed that twinned martensites possessed much inferior toughness properties to dislocated martensites when compared at the same strength level (recently summarized in ref. 23). Recent work showed⁽²⁴⁾ that at about 0.3%C in steel, the presence of substructural twinning is also an indication that twinning is the mode of deformation and that it is this combination of substructural and deformation twinning which results in poor toughness. Upon tempering the twinned martensite, extensive undesirable twin boundary precipitation occurs. Twinning was also shown⁽²⁵⁾ to reduce the available number of active slip systems. For these reasons, substructural twinning should be minimized.

iii) Retained Austenite

By increasing the stability of retained austenite to transformation under mechanical stress/strain or under thermal energy, its potential for improved properties can be vastly increased. One of

the simplest ways of increasing the mechanical stability of austenite would be to add an austenite (fcc) stabilizer. The most economical way of doing this is to increase the carbon content. However, the detrimental effects of retained γ in high carbon steels wherein it transforms to twinned martensite have been recognized for a long time. Therefore, fcc stabilizers which do not increase the propensity for twinning should be selected for stabilizing austenite and preventing premature transformation during stressing/straining or tempering.

The present study aims to successfully exploit the austenite for improved properties by

- (1) avoiding excessive carbon enrichment
 - (2) improving stability with fcc stabilizers which do not markedly further increase its tendency for twinning
 - (3) maintaining continuous interlath film morphology wherein the individual martensite crystals are entrapped by austenite
 - (4) maintaining good coherence at the martensite/austenite interfaces
 - (5) increasing the amount of austenite if found beneficial
- iv) Coarse Undissolved Carbides

Coarse undissolved alloy carbides can act as slip barriers resulting in a stress concentration at the carbide/matrix interface.⁽²⁶⁾ This could result in either (i) carbide cracking⁽²⁷⁾ or (ii) interface cracking or (iii) crack nucleation in the matrix due to piled up dislocations. In addition, the carbide/matrix interfaces can provide an easy crack path if the interfacial cohesion is poor. Cox and Low⁽²⁸⁾ demonstrated that during plastic fracture, the resistance to fracture decreased with increasing inclusion size which is attributed to the ease of void nucleation and growth at

coarser particles. Therefore, coarse undissolved carbides can promote brittle fracture and also reduce fracture resistance during plastic fracture and should be eliminated by proper heat treatment. The problem of undissolved coarse carbides becomes particularly acute in alloy steels containing alloying elements which have a stronger carbide forming tendency than iron. Thus, in order to improve the mechanical properties, microstructural control is the basic approach adopted to achieve the following features:

- (i) Maintain dislocated lath martensite.
- (ii) Promote a fine dispersion of carbides in martensite either through auto-tempering or tempering following quenching.
- (iii) Promote stability and occurrence of retained austenite as thin interlath films. This is also necessary to avoid interlath brittle films of carbide.
- (iv) Eliminate coarse undissolved alloy carbides.

Fig. 1 depicts schematically these desirable microstructural features which are achieved in this investigation through a combination of non-conventional heat-treatments and quaternary alloying.

B. Choice of Quaternary Alloying

Although no systematic structure-property correlation exists, it is generally accepted⁽²⁹⁾ that of all the common alloying elements that are often added to medium and low carbon steels, only Mn and Ni improve both toughness and strength as measured by impact and room temperature tests.

Additions of up to 2% Mn to a steel is known⁽³⁰⁾ to increase its hardenability substantially. Nevertheless, excessive additions of Mn are to be avoided for it was shown⁽³⁾ that in medium carbon steels, Mn in excess of 3 w/o leads to large fractions of twinned substructures and secondly, since Mn lowers M_s significantly⁽²³⁾, higher Mn contents result in the suppression of auto-tempering. There are also reports that Mn addition lowers DBTT^(29,31) (Ductile-Brittle Transition Temperature). The influence of Ni is in several respects identical to that of Mn although higher percentages of Ni can be added to a steel without promoting substructural twinning⁽³²⁾ especially in the presence of carbon⁽²²⁾. Importantly, both Mn and Ni are fcc austenite stabilizers and one of the design goals viz., increased stability of austenite, would be accomplished through the addition of Mn or Ni.

Quaternary alloys containing Mn up to 2 w/o and Ni of 5 w/o are thus designed to meet the specific microstructural criteria.

III. EXPERIMENTAL PROCEDURE

Details about the experimental procedure are described elsewhere^(14,15). The chemical compositions of the vacuum melted alloys after homogenization at 1200 C (furnace cooled) are given in Table I. Some of the heat-treatments employed in this investigation are schematically illustrated in Fig. 2. The crack propagation was along the L-T orientation for the Charpy and the plane strain fracture toughness specimens. Wherever the thickness of the fracture toughness specimens was insufficient to yield valid K_{IC} values, a method based on Chells criteria⁽³³⁾ was used to convert the K_Q values into calculated K_{IC} .

IV. RESULTS

A. Transformation Temperatures and Heat-Treatment

The martensite transformation temperatures M_s and M_f and the austenite formation temperatures obtained by dilatometry are tabulated in Table I. The somewhat lower M_s and M_f temperatures in the base Fe|Cr|C steel are attributed to the somewhat higher carbon content of the base alloy over the quaternary alloys. In general, both the M_s and M_f temperatures decreased with the quaternary alloy additions although their difference remained approximately constant around 100°C. Mn and Ni both being strong fcc stabilizers, from Table I one could notice a general trend of lowered A_s and A_f temperatures as well as narrower austenite formation region with additions of Mn and Ni. It will be clear from the discussion presented in subsequent sections that while M_s temperatures measured by dilatometry are fairly precise, the M_f temperatures represent only approximate martensite finish temperatures and they are not a true indication of 100% martensite formation.

It was proposed to characterize initially the influence of various alloy additions on the morphology and substructure of singly treated Fe-4Cr-0.3C base steel. For this an austenitizing temperature of 1100°C and ice water quench were chosen (Fig. 2). This temperature is in the single phase austenite region⁽³⁴⁾ and is high enough to dissolve all the alloy carbides.^(1,34) For the alloy modified with 5% Ni (alloy E), a conventional high temperature austenitization followed by rapid quench resulted in quench cracking.⁽¹⁴⁾ Thus, it was necessary to modify the heat-treatment for this alloy and based on earlier research on the phenomenon of intergranular quench cracking,⁽¹⁴⁾ the modification consisted of

isothermal holding below M_s at 200°C for 1-5 min before finally quenching into water at room temperature (Fig. 2).

Grain-refining double treatments designed with a view to combine the benefits of high temperature austenitization and fine grain size⁽¹⁵⁾ consisted of intermediate low temperature (200°C-1 hr) tempering between the initial high temperature austenitization and final low-temperature grain-refining austenitizing treatment (Fig. 2) at 870°C. In the case of base and Mn-modified alloys, the intermediate tempering treatment was used to promote a fine dispersion of tempered carbides. This dispersion was hoped to augment the preferential nucleation of austenite at carbide/matrix interfaces^(35,36) and thus, serve to bring about a more uniform, fine distribution of austenite crystals during subsequent austenitization. In the case of Ni modified alloys, the need for an intermediate tempering cycle is obviated by the interrupted quench during the initial high temperature austenitization.

B. Microstructural Characterization

(i) Optical Metallography

Optical metallography was carried out with the intention of recording any variations in the gross features of microstructure, e.g., prior austenite grain size, coarse undissolved carbides, etc. with composition and heat-treatment. Fig. 3 shows representative optical micrographs for steels D and E. There were no observable differences in the optical microstructure between the base and modified alloys. The structure represents typical lath martensite occurring in packets (Fig. 3a) although in the 5 Ni modified alloy some indication of transition from lath to plate morphology is discernible (Fig. 3c).

However, as will be shown in a later section, transmission electron microscopy revealed predominately lath martensitic structure even in the 5 Ni modified alloy. There were no undissolved coarse alloy carbides present in any of the single high temperature treated alloys [see for example Fig. 3(a) and (c)] nor could optical metallography resolve any undissolved second phase particles in any of the grain refined steels [Figs. 3(b) and (d)]. However, TEM did reveal the presence of a few submicron size ($\sim 0.25\mu\text{m}$ dia.) nearly spherical undissolved alloy carbides, M_7C_3 in the grain refined structures. These structures did not reveal any proeutectoid or isothermal decomposition products.

The grain sizes of 5 Ni modified alloy closely resembled those of base alloy, viz., $170\mu\text{m}$ for the single high temperature treated specimens and $20\mu\text{m}$ for the grain refined specimens. In every case, double treatments (Fig. 2) caused an approximate tenfold refinement in the grain size compared to single treatments. For the same length of holding at 1100°C , there appears to be a significant austenite grain coarsening with increasing Mn content particularly above about 0.5 w/o Mn. The 2 wt% Mn alloy had about 60-70% larger prior austenite grain size ($\sim 280\mu\text{m}$) compared to the base ternary Fe-Cr-C alloy.

ii) Transmission Electron Microscopy:

Structural characterization by transmission electron microscopy was performed on all the single treated quenched as well as quenched and 200°C tempered conditions of all the alloys but a detailed characterization of the evolution of the microstructure during tempering was limited to the 0.5% Mn and 2% Mn modified alloys in the single

treated condition and for the 5% Ni modified alloy in the double treated condition as it was considered that conclusions from these representative compositions and heat-treatments can be utilized to predict the behavior of other alloys.

a. Structure of as-quenched alloys

The morphology of martensite is of parallel lath type in all the alloys. Two points of significant variation in structure viz., substructure of martensite and precipitation of carbides due to auto-tempering are worth noting. The substructure of Mn modified alloys (up to 2 w/o Mn) remains essentially dislocated (Fig. 4). However, a small percentage ($\sim 10\%$ of the laths examined) of twinning is observed in the 5 Ni modified alloy as shown in Fig. 5(c) through (f). These are the well known $\{112\}_{\alpha}$ microtwins⁽³⁷⁾ and the SAD* pattern, Fig. 5(e), obtained from the BF figure 5(d) is analysed in Fig. 5(f). The amount of auto-tempering decreases with increasing Mn content consistent with decreasing M_s temperature⁽²³⁾ (Table I). In alloys modified with Mn up to 1 w/o both cementite and ϵ -carbide can be found but in the 2 Mn-modified alloy little of any auto-tempered carbides can be found (Fig. 4). In spite of the isothermal hold between M_s and M_f for the Ni-modified alloy, only ϵ -carbide precipitation has been noted. These carbide particles are about 300\AA wide and about 0.5μ long. The "cross-hatched" appearance of ϵ -carbide is also evident in the BF micrograph, Fig. 5(a).

b. Structure of tempered alloys

Tempering at 200°C results in well established $\langle 110 \rangle_{\alpha}$ widmanstatten cementite platelets in all the Mn-modified alloys. Fine, wavy ϵ -carbide precipitates continue to coexist with cementite at this temperature. In the case of Ni-modified alloys, the dominant carbide is ϵ carbide. Fig. 6 shows the widmanstatten carbides in the 2 Mn modified alloy. These cementite platelets are about 200Å wide and 0.5 μ long. Mn appears to promote cementite coarsening in the 200°C tempered structures.

Structural changes occurring at the lath boundaries following 300°C tempering will be dealt with in the next section in connection with retained austenite. The beginning of spheroidization of interlath cementite platelets is evident in several micrographs of the 300°C tempered 2 Mn-modified alloy. In the case of grain-refined 5 Ni-modified alloy, the intralath precipitation consists of a fine distribution of cementite platelets wherein spheroidization can be considered as in very early stages. However, a very fine distribution of spheroidal particles, presumably M_7C_3 , nucleated at dislocations seems to be taking place in Ni-modified alloys following 300°C tempering.

c. Behavior of Retained Austenite

(i) Electron Metallographic Observations

Figs. 7 and 8 illustrate the typical interlath film morphology of the high temperature phase. Of most significance is the conclusion

The abbreviations BF = Bright Field, DF = Dark Field and SAD = Selected Area Diffraction will be used throughout the text.

that there is a monotonic increase in the amount of retained austenite with Mn addition and highest amounts of retained austenite are found in the 5 Ni-modified alloy interrupted quenched to room temperature following single, high temperature austenitization, Fig. 8. It is important to emphasize here that the above conclusion is based on examination of not just one or two micrographs but several micrographs from several thin foils.

The grain refined structures show a similar behavior in the occurrence of retained austenite with quaternary alloying. Moreover, in every alloy there is an increase in the volume fraction of retained austenite in the grain refined structures compared to single treated coarse grained structures. Although the electron metallographic estimation of the volume fraction of retained austenite has its limitations,⁽³⁸⁾ it is estimated that the 2 Mn-modified alloy has about 4 to 5% retained austenite while the 5 Ni-modified alloy shows about 6 to 8% in the single treated condition.

Thermal Stability. The stability of retained austenite is followed as a function of tempering temperature. At 200°C tempering, the retained austenite is stable in all the alloys. Most interesting behavior occurs following 300°C tempering. While the base alloy and the Mn-modified quaternary alloys show no indication of any retained austenite (Fig. 9), the 5 Ni alloy shows substantial amounts of this phase stable following this tempering treatment, Fig. 10. As is clear from Fig. 9, the decomposition of austenite results in the precipitation of coarse interlath stringers of cementite and the thickness of these interlath carbide stringers is a function of initial retained

austenite content, viz., the 2 Mn alloy shows coarser interlath carbides compared to the 0.5 Mn alloy.

In the Ni-modified alloy, the retained austenite present after this treatment is somewhat discontinuous compared to as-quenched morphology and attendant with this, there is some lateral thickening of the austenite films, as revealed in Fig. 10 which may be a result of an attempt to decrease the total α/γ surface area.

ii) X-Ray Analysis

Within the prior austenite grain obviously a single variant of retained austenite crystal orientation exists and therefore, depending on the prior austenite grain size, a monovariant austenite may be contributing to the x-ray diffraction data, a situation similar to the case wherein preferred orientation exists. This and the fact that only small volume fractions of highly deformed austenite phase are present in these alloy steels complicate the detection and accurate analysis of the volume fraction of this phase.^(16,38) Conventional X-ray analysis has failed to resolve the austenite peaks in all the quaternary alloys. However, careful methods of x-ray analysis^(39,40) do reveal retained austenite in these alloys. Figs. 11(a) thru (c) show the volume fraction of this phase as a function of composition and heat-treatment. While much confidence cannot be placed on the absolute numbers, the trend and relative variations in the volume fraction of austenite are quite important. The following important conclusions can be drawn from these plots: the % retained austenite increases with amount of Mn addition (Figs. 11(a) and (b)). Highest amounts of retained austenite are found in the 5 Ni modified alloys (Fig. 11(b)) particularly when held in the

M_s - M_f region, during the quench from austenite phase field when a 3.4% retained austenite is found. Grain-refining increases the amount of retained austenite in the as-quenched structures of all the alloys (compare Fig. 11(a) and (b)). Fig. 11(c) shows the thermal stability of this austenite from which it is clear that in the 2 Mn-modified alloy, the retained austenite undergoes more or less complete transformation at 300°C tempering whereas in the 5 Ni-modified alloy, a major fraction of the original austenite remains stable even after 400°C tempering. Significantly, these x-ray analysis results are in total agreement with those of electron metallographic observations and thus, each one confirms the other.

D. Mechanical Properties

The mechanical properties of the base and quaternary alloy steels are summarized in Tables II through IV. There is a remarkable temper resistance in all the alloys in the tempering range 300-500°C. The 2Mn alloy in the single treated condition exhibits rapid loss of hardness and strength between as-quenched and 300°C tempered conditions.

Significant improvement in the plane strain fracture toughness at a given yield strength is obtained with quaternary alloying of either Ni or Mn, although the 2 Mn-modified alloy shows better toughness values than the 5Ni-modified alloy, especially when compared in the quenched-and-tempered condition, Tables II through IV. The higher Mn alloys are somewhat brittle in the as-quenched condition (ice water quenching) due to the absence of any auto-tempering but following 200°C tempering, these alloys exhibit excellent toughness properties. The substantial improvements in plane strain fracture toughness achieved with quaternary alloying is

also reflected in the plot of K_{IC} vs % Mn or Ni of the grain refined structures, Fig. 12. The improvement in this property shown by the quaternary alloys is particularly significant following the 200°C tempering. Again, the toughness properties of the 5 Ni-modified alloy are somewhat inferior although it should be noted that the 5Ni alloys have higher strengths, Table IV.

The behavior of impact toughness is similar to the behavior of plane strain fracture toughness and the improvement in the impact toughness is particularly significant following 200°C tempering (Fig. 13 (a), Tables II, III). The behavior of the impact toughness for the entire tempering temperature range, viz., up to 600°C is illustrated in Figs. 13 (a) and (b) as a function of composition and heat-treatment. The points of significant importance that emerge from these plots are:

- (i) While the base ternary alloy, the 0.5 Mn-modified alloy and the 5 Ni-modified alloy show only tempered martensite embrittlement,⁽³⁸⁾ the 2 Mn-modified alloy shows two kinds of embrittlement, viz., tempered martensite embrittlement as well as temper embrittlement.⁽⁴¹⁾
- (ii) The embrittlement phenomenon (in impact toughness) occurring in these modified alloys can not be avoided by grain refining. However, the impact toughness values at all temperatures can be improved by grain refinement (Fig. 13 (a)).
- (iii) The temperature of occurrence of tempered martensite embrittlement is a function of composition, Fig. 13(b). In the 2 Mn-modified alloy, it seems to occur around 300°C⁽⁴¹⁾ whereas in the 5 Ni alloy, this temperature is around 400°C.

In order to study the influence of quaternary alloying on the ductile brittle transition temperature (DBTT), the plot of impact energy

vs. testing temperature is obtained for various alloys shown in Fig. 14. It is clear that there is no significant variation in the ductile-brittle transition temperature as a result of Mn addition of up to 2 w/o although the 5 Ni addition showed a substantial lowering of the DBTT (50% Energy Criterion) from about -40°C for the ternary alloy to -70°C for the 5 Ni quaternary alloy. More significantly, however, all the ternary alloying results in a considerable upward shift in the upper shelf energies.

The fracture modes in the quaternary alloys are discussed in detail elsewhere^(38,41) In the highest toughness condition (following 200°C tempering), all the alloys showed typical ductile dimpled rupture.

V. DISCUSSION

A. Influence of Composition and Heat-Treatment on Microstructure

(i) As-Quenched Steels

Martensite structure: The morphology and substructure of ferrous martensites have been subjects of a number of investigations^(2-4, 22, 23 25, 32) and therefore, a detailed discussion of the factors affecting these two important structural parameters will not be attempted here.

In the present investigation all the quaternary alloys revealed predominantly "lath" martensitic structure (Figs. 4 and 5) irrespective of their composition. What is more significant in these structural steels is their substructure, as it is now well established^(23,1) that substructure plays a paramount role in controlling the toughness of steel. Das and Thomas⁽²²⁾ reported that additions of up to 12.5 w/o Ni to a 0.24C steel did not result in any significant twinning. In the present study the base alloy contains 4 w/o Cr and ~ 0.3 w/o C and both Cr and C

are shown⁽¹⁾ to be potential promoters of twinning. Since Ni itself is not a strong promoter of twinning, it is concluded that the observed small amount of twinning in 5 Ni-modified alloys (Fig. 5) can be considered as a result of the indirect effect of Ni through lowering of M_s (Table I) which, in the presence of potential twin promoters, results in twinning. In contrast to the behavior of Ni steels, Huang and Thomas⁽³⁾ found that an upper limit to the addition of Mn to a 0.25 w/o C steel in order to avoid excessive amounts of twinning was a mere 3 w/o. This implies that in the presence of C, Mn is just as much a promoter of twinning as Cr.^(1,3) In the present investigation by limiting the maximum Mn addition to 2 w/o, twinning is avoided.

Retained Austenite: The high temperature fcc austenite phase can be stabilized at room temperature by a variety of mechanisms, some of which are not fully understood. In general, one would expect that elements which are fcc stabilizers should promote retained austenite. However, Thomas and Rao have recently shown⁽⁴²⁾ that in alloys whose bulk M_s and M_f temperatures are above room temperature, austenite can be stabilized at room temperature only in the presence of interstitial C (perhaps also N). Furthermore, Rao et al.⁽¹⁶⁾ have been able to resolve small quantities of retained austenite even in very low-C, unalloyed steels. The fact that the presence of C alone is not a sufficient condition for stabilizing austenite in the as-quenched structures is shown by the work of Clark and Thomas who reported that no resolvable quantities of retained austenite could be found in a medium C steel modified with Mo additions up to 4 w/o. Clearly, the substitutional alloying-interstitial C interactions must also be playing an important role in stabilizing austenite. Interstitial C can stabilize

austenite in several ways: (i) it can physically segregate from the lath martensite to the surrounding austenite and this partitioning can lower the local M_s sufficiently below room temperature whereby austenite is stabilized at room temperature - i.e., "chemical stabilization".⁽⁴³⁾ This kind of stabilization should therefore be particularly effective during slow cooling from the austenitizing temperature, for e.g., air cooling.⁽²⁰⁾ (ii) The second stabilization, known as thermal stabilization is caused again by diffusion of interstitials, C & N, but this time not to achieve partition but to form dislocation atmospheres which inhibit their motion. These pinned dislocations can be in the martensite/austenite interface in which case they would directly inhibit interface motion or they can be in either phase, thus inhibiting stress relaxation in the martensite or austenite. (iii) The third stabilization, known as mechanical stabilization, is concerned with the plastic deformation in austenite accompanying the shear transformation. Edmondson and Ko⁽⁴⁴⁾ and Kelly and Knutting⁽²⁵⁾ studied this phenomenon. Rao and Thomas⁽¹⁴⁾ have considered in detail the question of accommodation of strain resulting from lath martensite formation and concluded that increasing C content increases the dilatation in the martensite lattice and the consequent accommodation in austenite.

In the present investigation not one but several of the above factors might have been responsible for the observed increase in volume fraction with % Mn or Ni addition (Figs. 11(a) and (b)). Increasing Mn addition results in a drop in M_s temperature which therefore discourages migration of C during and after the martensitic transformation. Hence, excessive partitioning of C and the consequent chemical stabilization may not be

the major factor. Similarly, thermal stabilization can also be discounted as the primary reason for the presence of the high temperature phase particularly in the fast-quenched (ice water quench) single-treated specimens consistent with the observation that liquid N_2 refrigeration does not significantly reduce the volume fraction of austenite. However, the fact that most of the C in Mn-modified alloys stayed in solution (as exemplified by the lack of auto-tempering, Fig. 4) results in an increased accommodation strain which could mechanically stabilize the austenite. The addition of 5 w/o Ni results in the same kind of behavior with respect to retained austenite as the Mn-modified alloys, and due to the lowest M_s temperature, the Ni modified alloys show the highest amounts of retained austenite. In the single-treated interrupted-quench structures of Ni-modified alloys, the highest amount of retained austenite is found to result from the promotion of C partitioning and migration to dislocations during the M_s - M_f hold (i.e., chemical and thermal stabilization) in addition to mechanical stabilization. In this connection, an important factor arising from the alloying element-C interaction, which could significantly affect the mobility of C, has to be considered. Alloying elements such as Si, Al and Ni promote graphitization and have carbide-forming tendencies which are either less than that of iron (Ni, Al), or negative (Si). In addition, Ni and Si also raise the activity of C in martensite⁽⁴⁵⁾ and similar behavior is expected of Al⁽¹⁷⁾, whereas exactly the reverse behavior is expected with some of the carbide forming elements. Carbide-formers such as Mn, Cr, Mo, Ti, etc., due to their attractive interaction with C (in increasing order), lower the activity coefficient for C. The result is that Ni, Si and Al can favor C partitioning to austenite and thereby

increase its volume fraction ⁽¹⁹⁾ whereas Mn, Cr, Mo, Ti etc. disfavor C partitioning and this sort of austenite stabilization. The situation with the present alloys is complicated due to the quaternary alloying but it appears that in the 5 Ni-modified alloys, increased amounts of stabilized austenite can also be expected due to the promotion of C partitioning. Apart from composition, one of the important microstructural features that affects the stability of austenite is the prior austenite grain size. In the present investigation the amount of retained austenite in grain-refined alloys is always higher than the corresponding coarse grained structures (compare Figs. 11(a) and (b)). These results are in agreement with earlier work by Brobst and Krauss ⁽⁴⁶⁾ and Leslie and Miller ⁽⁴⁷⁾ on the stabilization of austenite by closely spaced boundaries.

B. Thermal Stability of Retained Austenite

Whereas identification of retained austenite and studies on its stabilization in medium C, low alloy steels are in the very beginning stages, ⁽³⁸⁾ its decomposition following tempering is even much less studied. Most of the earlier studies on retained austenite decomposition were conducted with high C steels (0.55 w/o C) wherein large quantities of austenite are retained. Even here very little careful metallography has been carried out. The austenite decomposition reaction is variously characterized as lower bainitic, upper bainitic or even pearlitic. More recently, however, Speich and Leslie ⁽⁴³⁾ have characterized the decomposition reaction as bainitic. There is practically no work done in the past on the mechanism of decomposition of the specific type of retained

austenite during tempering, viz., the interlath film morphology occurring in the structural steels of interest.

In the present studies, the retained austenite is stable at 200°C tempering in all the alloys (Figs. 8 and 11(c)) but in the Mn-modified alloys the austenite undergoes decomposition following 300°C tempering (Figs. 9 and 11(c)). This is a temperature which is above the bulk M_s temperatures for 1 Mn and 2 Mn alloys and about the same as the bulk M_s temperature for 0.5 Mn modified alloy (Table 1). If the possibility of some segregation and solute enrichment during tempering in austenite is invoked, then the decomposition temperature could lie in the upper bainitic transformation region for all the alloys. What is even more significant is that the decomposition occurs at a temperature where substantial matrix cementite coarsening is also observed.

The elongated carbide stringers occurring at the lath boundaries following the decomposition of retained austenite, Fig. 9, are quite typical of upper bainitic transformation.^(23,4,15) Also, the analysed selected area diffraction pattern of Fig. 9 reveals an orientation relationship between the interlath cementite and matrix which does not conform to the well-established Bagaryatskii orientation relationship. In view of these observations, the present results on the differences in the transformation characteristics of retained austenite in 5 Ni-modified and 2 Mn-modified alloys can be explained as follows. If the retained austenite were to transform by upper bainitic transformation, cementite formation and growth are important. The difficulties involved in the formation and growth of cementite in the presence of graphitizing elements such as Si, Ni, Al are discussed elsewhere.⁽³⁸⁾

The reason why retained austenite would prefer to transform by an upper bainitic transformation appears to be the much lower accommodation necessary for this type of transformation due to the fact that carbide can be precipitated directly from γ . Thus, higher temperatures are necessary in the presence of Ni to transform retained austenite to isothermal decomposition products. In the present study, untransformed retained austenite is observed in 5 Ni alloys at as high temperature as 400°C, Fig. 11(c).

C. Correlation of Microstructure and Mechanical Properties

Since the single treated quaternary and the base alloys are heat-treated so as to dissolve all the alloy carbides (i.e., homogeneous austenite phase before quenching) it will be easier to correlate the mechanical property variations to the microstructural changes. The Mn-modified alloys will be discussed first, and later on, the effect of 5 Ni addition to the ternary alloy will be considered. As shown in Fig. 4 there are no differences in either the martensite morphology or substructure (which is essentially dislocated) as a result of Mn addition up to 2 w/o. The most significant structural change as a result of increasing amounts of Mn addition is the increase in the retained austenite volume fraction (Figs. 11(a) and (b)), and the startling improvement in the impact toughness and plane strain fracture toughness with wt % Mn is evident from Fig. 12. Since fracture properties are of main concern in the present investigation, attention will be focussed on the mechanisms whereby retained austenite could provide resistance to the initiation and propagation of cracks. Suggested

mechanisms of increased crack propagation resistance in the presence of retained austenite include: (i) crack branching, resulting in a more tortuous crack propagation and the consequent increased energy expended, (ii) crack blunting, as a result of plastic flow in austenite resulting in a decrease in stress concentration requiring higher applied stresses for unstable fracture and (iii) transformation induced plasticity (TRIP) in which case, as the name suggests, the transformation of retained austenite to martensite under stress/strain in the plastic zone ahead of a crack relieves the stress concentration. In all the three cases, the effectiveness of retained austenite in providing for improved toughness properties increases with its stability to transformation under mechanical stress/strain.

Besides the above direct effects of austenite on toughness, there are indirect benefits. Retention of austenite at lath boundaries prevents brittle lath boundary carbide formation in the as-quenched as well as quenched-and-tempered structures if the tempering temperature is below instability temperature for austenite. Another significant benefit arising from retention of austenite is that, the γ/α boundary is highly coherent. In contrast, in the absence of γ , the two adjacent laths impinge laterally to form rotation boundary thus creating high energy interfaces for crack propagation and/or segregation and precipitation. (42)

The continuous interlath morphology of retained austenite in the alloys under investigation would prevent propagation of a crack nucleated in the relatively brittle martensite to the adjacent martensite lath, i.e., the networks of retained austenite would help to break the continuity of the brittle phase martensite. Gerberich⁽⁴⁸⁾ proposed a

fracture concept based on critical displacement for treating two phase structures wherein a tough unidirectional phase is dispersed in a relatively brittle matrix. An application of this concept to the microstructure under discussion brings out two very important points: (i) the thicker the austenite films (hence higher the volume fraction), the higher will be its crack blunting ability and (ii) some degree of ductility in martensite is needed in order to prevent brittle failure in martensite even in the presence of austenite. This very nicely explains the observed improvement in fracture toughness and impact toughness values with increasing Mn particularly after 200°C tempering (Fig. 12 and Tables II and III). This occurs because in the higher Mn alloys, auto-tempering did not take place (Fig. 4) due to a low M_s temperature, and a low temperature tempering is necessary in order to induce some plasticity. It has been also reported that such low temperature tempering augments the mechanical stability of austenite.

The advantages of grain refining are discussed in the beginning. In order to combine the benefits of high temperature austenitization, i.e., reduce coarse undissolved alloy carbide volume fraction and maintain a fine γ grain size, double treatments (Fig. 2) are necessary. The increased volume fraction of γ as a result of grain refining is evident from a comparison of Figs. 11(a) and (b) and the corresponding improvement in impact properties of the 2 Mn-modified alloy can be seen from Fig. 13(a). However, as pointed out earlier, electron microscopy did reveal the presence of undissolved alloy carbides and therefore the behavior of grain refined alloys is complex.

In the 5 Ni modified alloy, there are two variations in the microstructure compared to the base alloy, viz., some substructural twinning (Fig. 5) and increased amount of retained austenite, (Fig. 11(b)). The detrimental effects of twinning on toughness have already been discussed and the somewhat poorer toughness properties in this alloy compared to some of the Mn-modified alloys (Fig. 12) is attributed to the presence of substructural twinning. Although the toughness of 5 Ni alloys are somewhat lower than that of the Mn steels, their toughness and strength combinations are quite attractive. By adhering to the design guidelines, microstructures are developed in quaternary alloys which have toughness to strength combinations much superior to the equivalent commercial alloys, shown in Figs. 15 (a) and (b).

VI. SUMMARY AND CONCLUSIONS

Some alloy design considerations for optimizing strength-toughness combinations in high strength structural steels have been critically assessed, and based on these, quaternary alloy additions of Mn and Ni were made to a base Fe-4Cr-0.3C steel. Optimizing heat-treatments were then chosen which resulted in the design of superior experimental steels. The following conclusions have been drawn from this investigation:

- (1). The single high temperature austenitization, viz., 1100°C, produced a homogeneous austenite phase, free from undissolved coarse alloy carbides in all the alloys.
- (2). Additions of up to 2 w/o Mn did not alter the substructure of martensite, which was mainly dislocated. However, the 5 w/o Ni addition to the ternary alloy resulted in about 10% of the martensite laths containing twinned substructure.

tures. This is concluded to be due to the indirect influence of Ni in promoting the twinning propensity of C and Cr.

- (3). There is a monotonic increase in the volume fraction of interlath retained austenite with Mn. The stabilizing mechanisms for austenite are discussed and it is concluded that chemical stabilization resulting from excessive C segregation cannot be the dominant stabilizing mechanism to account for the observed increase in retained austenite. The 5 w/o Ni addition resulted in the highest amount of retained austenite following M_s - M_f hold. This is attributed to enhanced roles of both thermal and chemical (C segregation) stabilizations in this treatment.
- (4). There is roughly a ten-fold refinement in grain size following the grain-refining double treatments and the volume fraction of retained austenite increased in all the alloys compared to their single treatments.
- (5). Both fracture toughness and impact toughness increased with Mn additions. This is attributed to the increased amount and stability of retained austenite. Grain refining further increased the toughness properties in the 2 Mn and 5 Ni modified alloys due to the combined influence of increased retained austenite and fine grain size. For the 5 Ni modified alloy, the somewhat inferior toughness properties are attributed to the small but significant fraction of substructural twinning in these alloys. The higher amount

of retained austenite in this alloy appears to have compensated for this loss in properties as the 5 Ni alloys did show superior strength-toughness combinations.

- (6). Tempered Martensite Embrittlement (TME) occurs in the range 300-400°C depending on alloy composition and is coincident with decomposition of interlath retained austenite into stringers of coarse cementite at these boundaries. Grain-refining, although ineffective in eliminating TME, nevertheless reduces its severity. This is concluded to be due to the mutually opposing tendencies of fine grain size and increased retained austenite following grain refinement.
- (7). The decomposition reaction of retained austenite following tempering is concluded to be upper bainitic in the alloys investigated and graphitizing elements such as Ni, Al and Si which destabilize M_3C are beneficial in postponing the onset of TME to 400°C and above.

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TABLE I.

ALLOY COMPOSITIONS AND TRANSFORMATION TEMPERATURES

Alloy Designation	Composition (wt%)					Measured Temp. (°C)			
	C	Cr	Mn	Ni	Fe	M _s	M _f	A _s	A _f
A	0.29	4.0	---	---	Bal.	270	170	726	808
B	0.24	4.0	0.54	---	Bal.	305	190	728	762
C	0.24	4.1	1.0	---	Bal.	274	167	700	735
D	0.25	4.0	1.93	---	Bal.	253	164	655	685
E	0.27	3.8	---	5.0	Bal.	210	110	641	656

TABLE II.

MECHANICAL PROPERTIES OF SINGLE TREATED, COARSE GRAINED STEELS

Alloy	Tempering Temperature (°C)	0.2% Offset YS (KSI) Δ	UTS (KSI) Δ	% Reduction in Area	% Elongation Total (Uniform)	K_{IC} KSI-in $1/2\sqrt{\nabla}$	Charpy-V-Notch Energy ft-lbs Δ
Fe-4Cr-0.3C	as-quenched	195	240	35.4	8.0 (3.0)	71	18
	200	189	230	45.5	11.0 (4.0)	76.5	30
	300	173	208	45.2	10.0 (3.3)	----	15
	400	169	202	48.3	11.0 (3.3)	----	15.5
	500	155	175	52.4	13.5 (4.4)	----	19.5
	600	110	129	78.6	17.0 (5.2)	----	36.5
+ 0.5 Mn	as-quenched	192	233	34.0	9.0 (3.5)	92.5	14.0
	200	175	214	47.0	11.0 (3.5)	117 (150)*	35.0
	300	170	204	50.0	10.8 (3.3)	----	14.0
	400	163	195	51.0	11.3 (3.6)	----	15.5
	500	150	172	60.0	13.5 (4.2)	----	19.5
	600	104	125	71.0	18.2 (5.4)	----	36.5
+ 2.0 Mn	as-quenched	207	265	33.0	8.5 (3.5)	59	3.4
	200	195	235	36.0	6.5 (2.5)	126 (180)*	40.0
	300	177	212	19.0	-----	----	18.5
	400	160	195	45.0	11.5 (4.0)	----	14.5
	500	150	175	24.0	12.5 (4.0)	----	4.0
	600	105	125	64.0	17.0 (6.0)	----	10.2

Δ 1KSI = 6.89 MPa
 ∇ 1KSI-in $^{1/2}$ = 1.11 MPam $^{1/2}$
 Δ 1ft-lb = 1.356 N-M

* K_Q values only, calculated K_{IC} in brackets.

TABLE III.

MECHANICAL PROPERTIES OF GRAIN REFINED (DOUBLE TREATED) STEELS

Alloy	Tempering Temperature (C)	0.2% Offset		% Reduction in Area	% Elongation Total	K _{IC} KSI-in 1/2∇	Charpy-V-Notch Energy ft-lbs _Δ
		YS (KSI) _Δ	UTS (KSI) _Δ				
Fe-4Cr-0.3C	as-quenched	180	230	24.0	9.4	66.0	20.0
	200	187	227	32.0	9.0	----	20.5
+ 0.5 Mn	as-quenched	185	230	48.2	13.3	74.5	23.5
	200	186	222	49.1	13.7	82.5	32.5
+ 1.0 Mn	as-quenched	177	228	47.4	13.7	85.0	29.1
	200	185	223	50.0	13.9	110.0	40.0
+ 2.0 Mn	as-quenched	189	242	38.7	11.0	84.0	30.5
	200	184	230	50.8	15.4	126.0*	49.5
	300	182	215	58.5	14.6	----	29.5
	400	177	204	59.1	15.4	----	24.5
	500	161	180	60.3	21.0	----	17.0
	600	108	127	72.6	23.3	----	28.0

_Δ 1KSI = 6.89 MPa
_∇ 1KSI-in^{1/2} = 1.11 MPam^{1/2}
_Δ 1ft 1b = 1.356 N-M

*K_Q only

TABLE IV.

MECHANICAL PROPERTIES OF 5 Ni MODIFIED ALLOYS

Treatment	Tempering Temperature (°C)	0.2% Offset		% Reduction in Area	% Elongation Total (Uniform)	K IC KSI-in 1/2∇	CVN Impact Energy ft-lbsΔ
		YS (KSI)Δ	UTS (KSI)Δ				
Single Treatment M _s -M _f holding	as-quenched	195	275	25.0	9.0 (5.5)	89.5	19.5
	200	187	234	-	12.0 (5.0)	123.0	43.5
Coarse grained Structure	as-quenched	200	280	44.5	11.1	75.0	27.0
	200	193	242	57.5	15.8	102.0	41.9
	300	183	218	58.7	15.3	-----	41.0
	400	181	215	59.5	16.0	-----	39.0
	500	172	195	64.0	18.1	-----	48.5
	600	114	137	75.0	24.0	-----	117.0

Δ 1KSI = 6.89 MPa

∇ 1KSI-in^{1/2} = 1.11 MPam^{1/2}

Δ 1ft lb = 1.356 N-M

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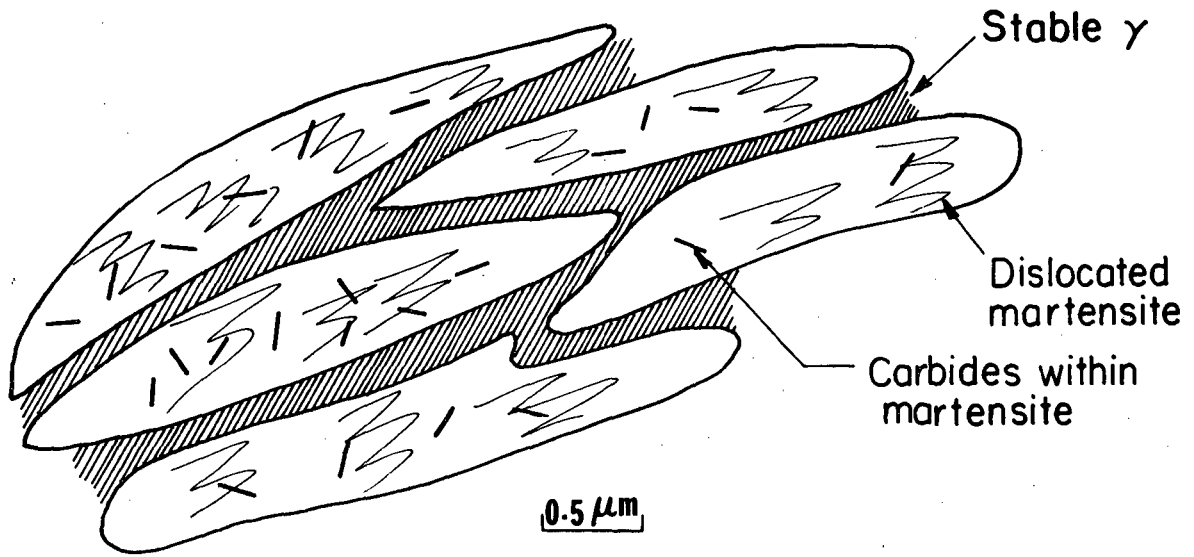
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FIGURE CAPTIONS

- Fig. 1. Schematic showing desired duplex microstructure.
- Fig. 2. Schematic of heat-treatments employed in this study.
- Fig. 3. Optical micrographs of as-quenched steels: (a) and (b) are for 2 Mn modified alloy and (c) and (d) are for 5 Ni modified alloy. (a) and (c) are from single high-temperature treated specimens whereas (b) and (d) are from grain-refined specimens.
- Fig. 4. BF micrographs (a) and (b) show the dislocated lath martensite structure devoid of any auto-tempered carbides in the as-quenched coarse-grained structure of 2 Mn modified alloy.
- Fig. 5. BF micrographs (a) and (b) reveal the dislocated lath martensite while (c) and (d) show the presence of some substructural twinning in the 5 Ni-modified alloy single treated and interrupted quenched to room temperature. Twinning reflections from (d) are shown in the SAD of (e) and suitably indexed in (f).
- Fig. 6. BF (a), DF (b), SAD pattern (c) and the corresponding indexed pattern (d) revealing widmanstätten cementite in the 200°C tempered 2 Mn-modified alloy.
- Fig. 7. Extensive retained austenite in the as-quenched 1 Mn single treated alloy. (a) BF and (b) DF micrographs revealing austenite in bright contrast.
- Fig. 8. Extensive retained austenite in the 5 Ni alloy (coarse grained) is revealed in the BF (a) and DF (b) micrographs. (c) is the DF micrograph of retained austenite from a different area of the specimen. The strong austenite reflections (subscript 'a') observed in the quaternary alloys can be seen from the indexed SAD pattern shown in (d).

- Fig. 9. Decomposition of retained austenite into interlath stringers of cementite in 300°C tempered 2 Mn alloy. (a) BF, (b) DF, (c) SAD, and (d) analysis of this carbide.
- Fig. 10. (a) BF, (b) DF of austenite, (c) SAD showing austenite reflections analyzed in (d) in 300°C tempered 5 Ni alloy (fine grained).
- Fig. 11. Variation in the X-ray volume fraction of retained austenite (a) with Mn in single treated alloys, (b) in grain refined alloys (also shown is the retained γ in single treated, M_s - M_f quenched 5 Ni alloy) and (c) with tempering temperature in 2 Mn and 5 Ni modified alloys.
- Fig. 12. K_{IC} vs. w/o quaternary alloying for the grain-refined structures.
- Fig. 13. Comparison of impact energy as a function of tempering temperature for (a) the coarse and fine grained structures of the 2 Mn alloy and (b) the grain-refined 2 Mn and 5 Ni alloys.
- Fig. 14. Ductile-brittle transition curves for the base and quaternary steels.
- Fig. 15. Comparison of toughness to strength relations in experimental quaternary alloys and equivalent commercial alloys. (a) Charpy impact energy vs. tensile strength and (b) plane strain fracture toughness vs. tensile strength.

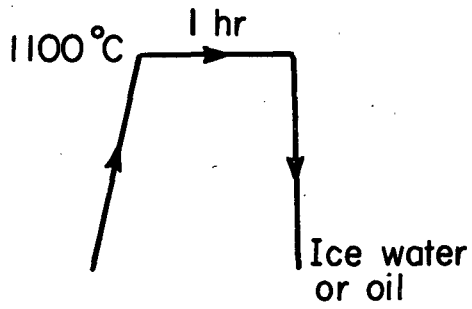


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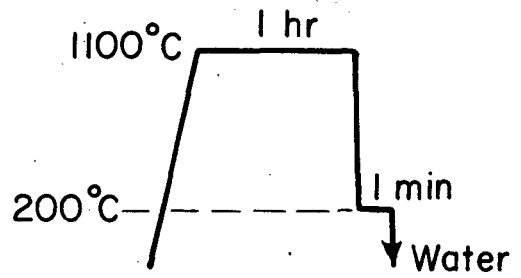
Fig. 1

SINGLE HEAT TREATMENTS

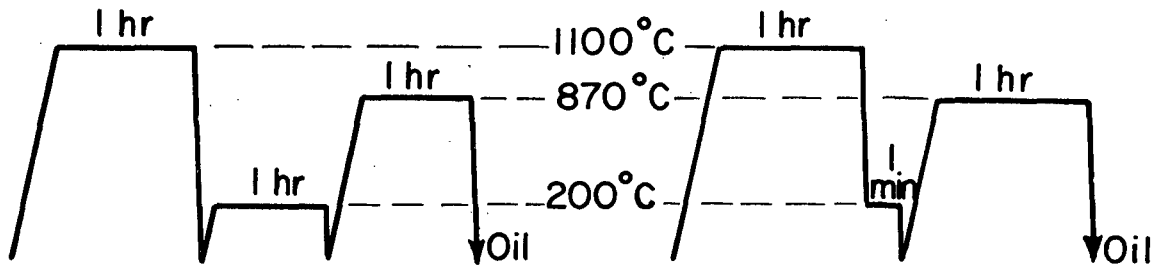
Base and Mn Steels



Ni Steels



GRAIN REFINING DOUBLE TREATMENTS

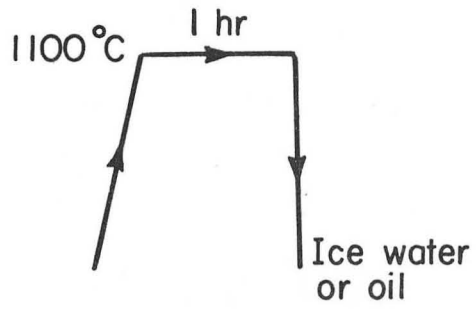


XBL 768-7315

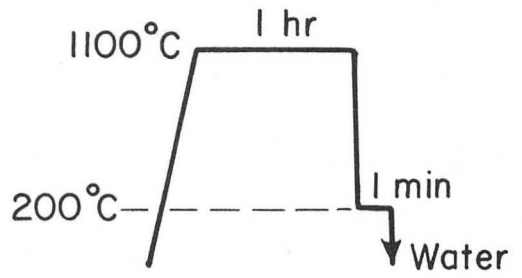
Fig. 2

SINGLE HEAT TREATMENTS

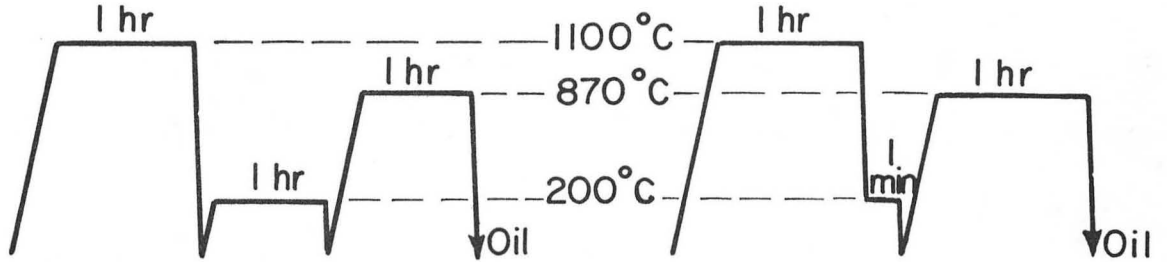
Base and Mn Steels



Ni Steels

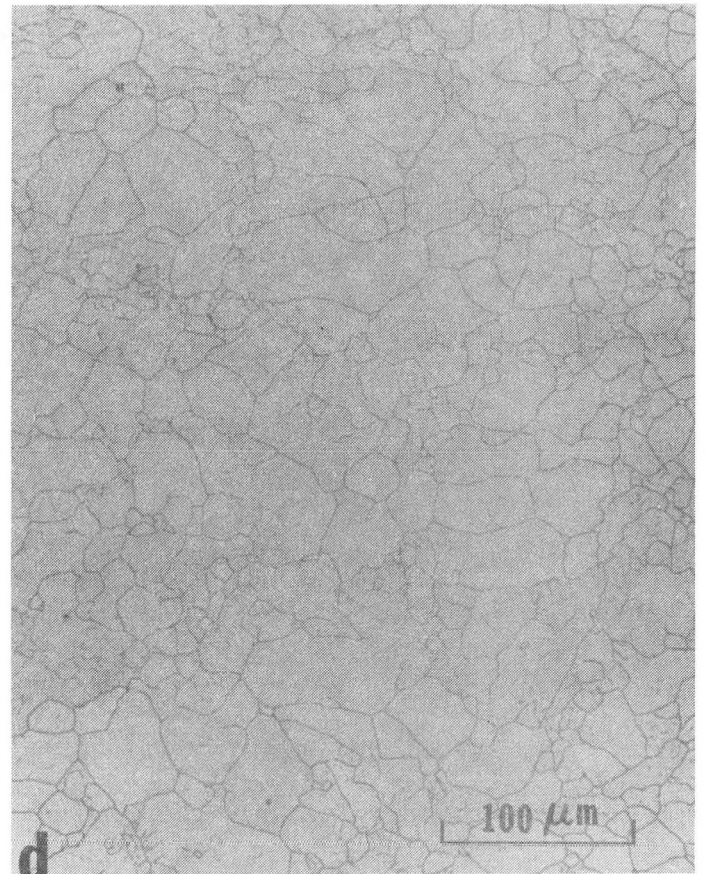
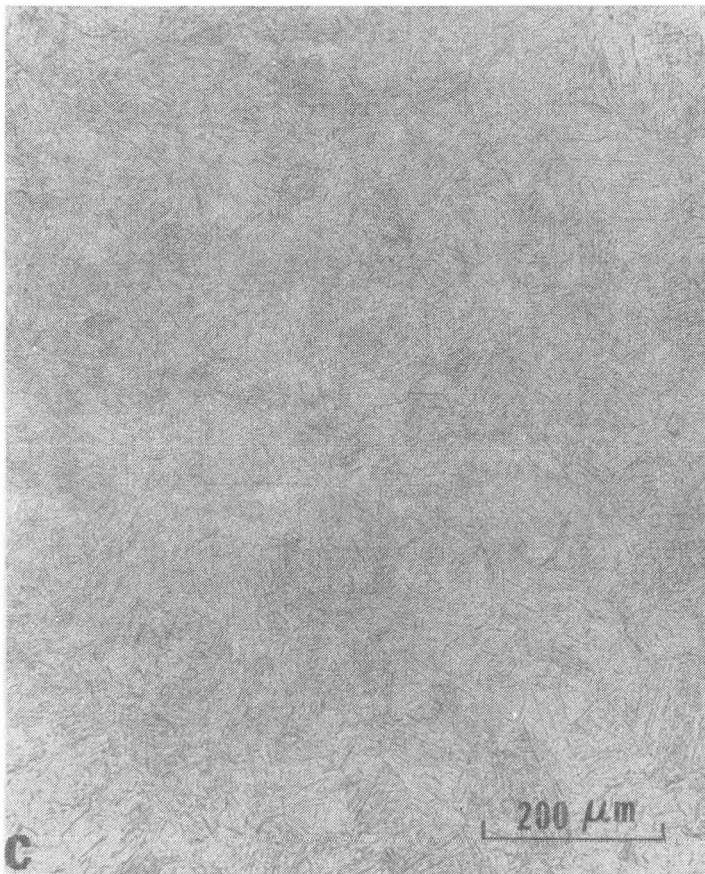


GRAIN REFINING DOUBLE TREATMENTS



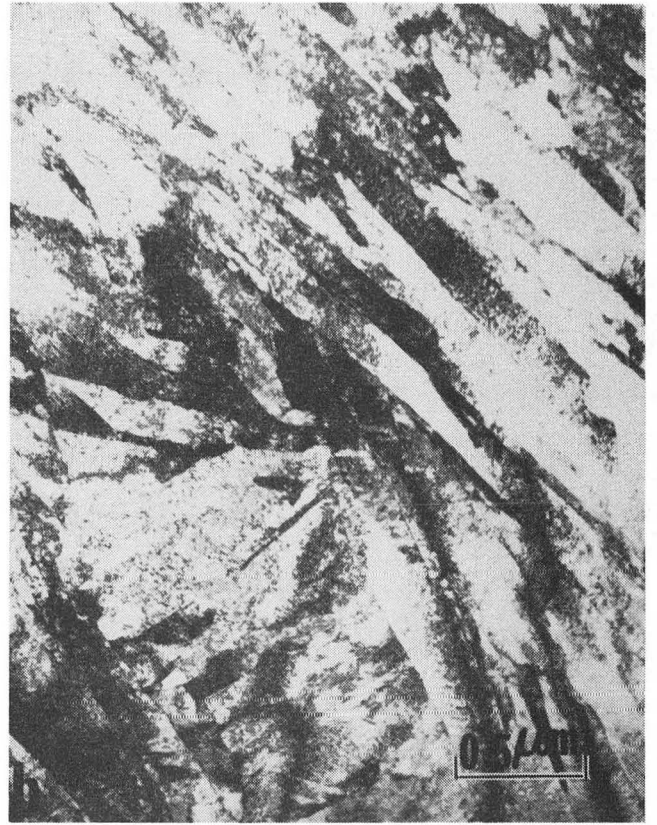
XBL 768-7315

Fig. 2



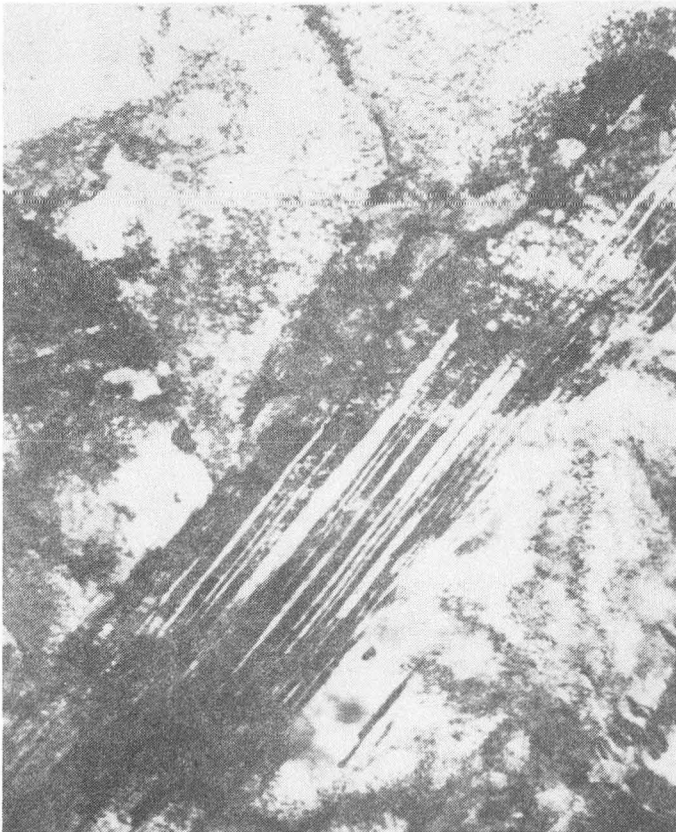
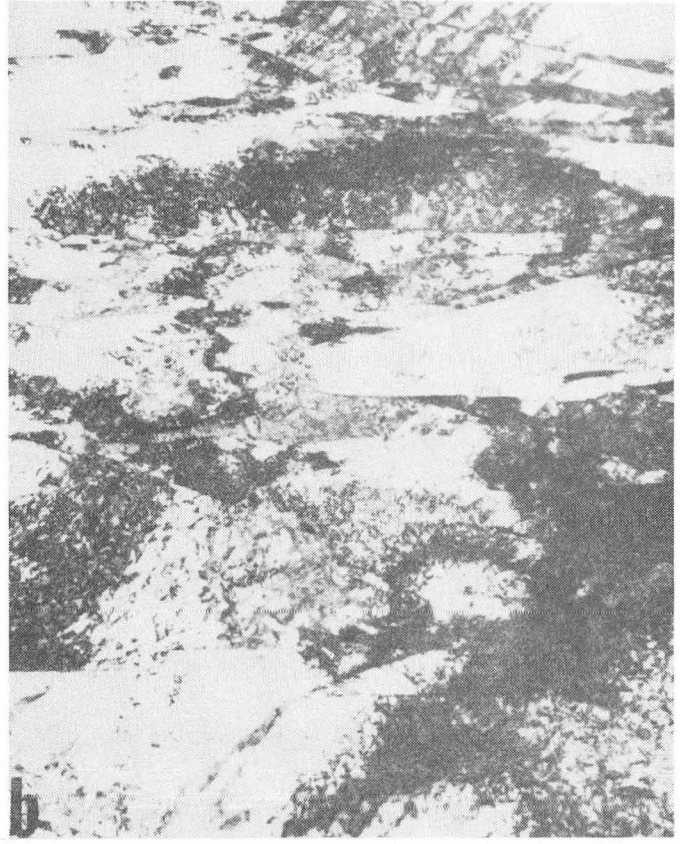
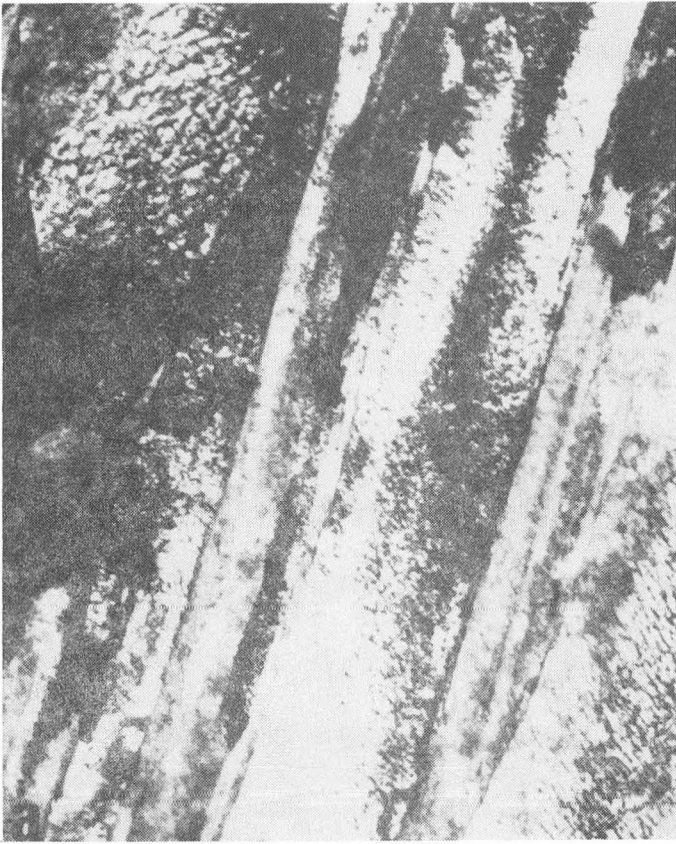
XBB-782-1185

Fig. 3



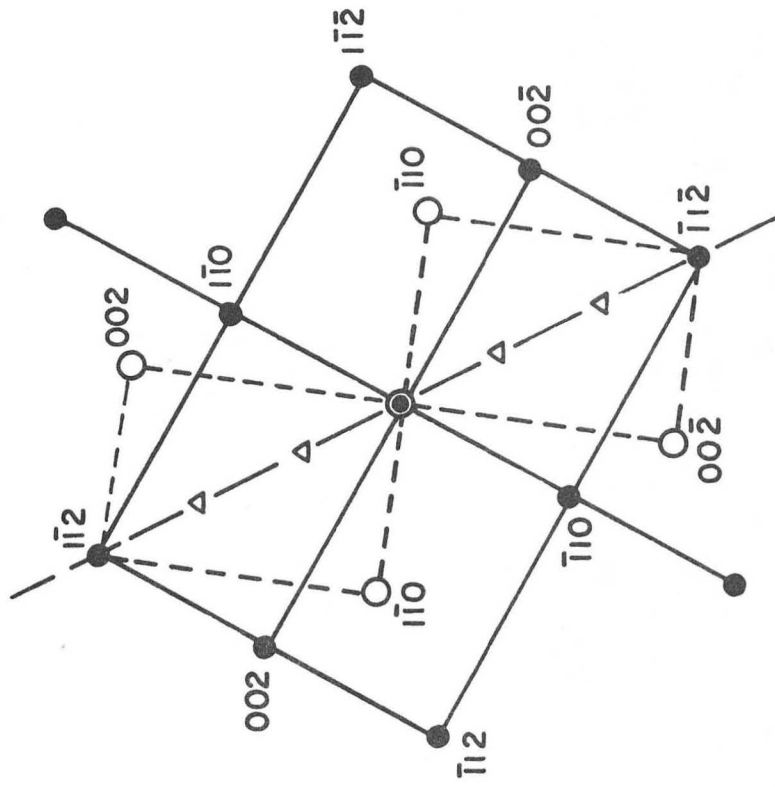
XBB 768-7131

Fig. 4



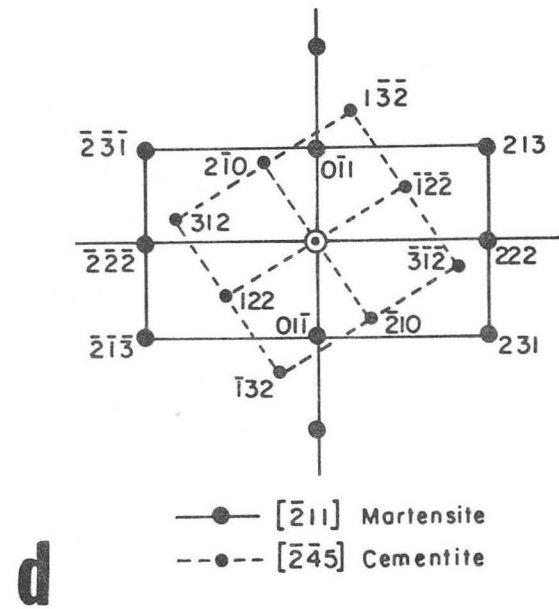
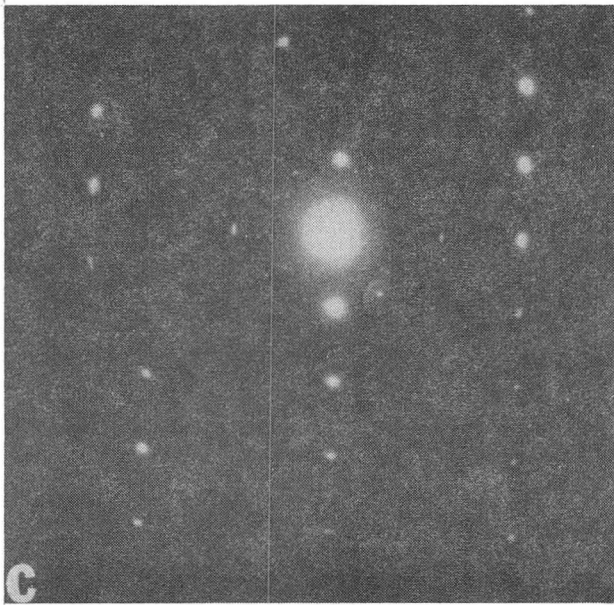
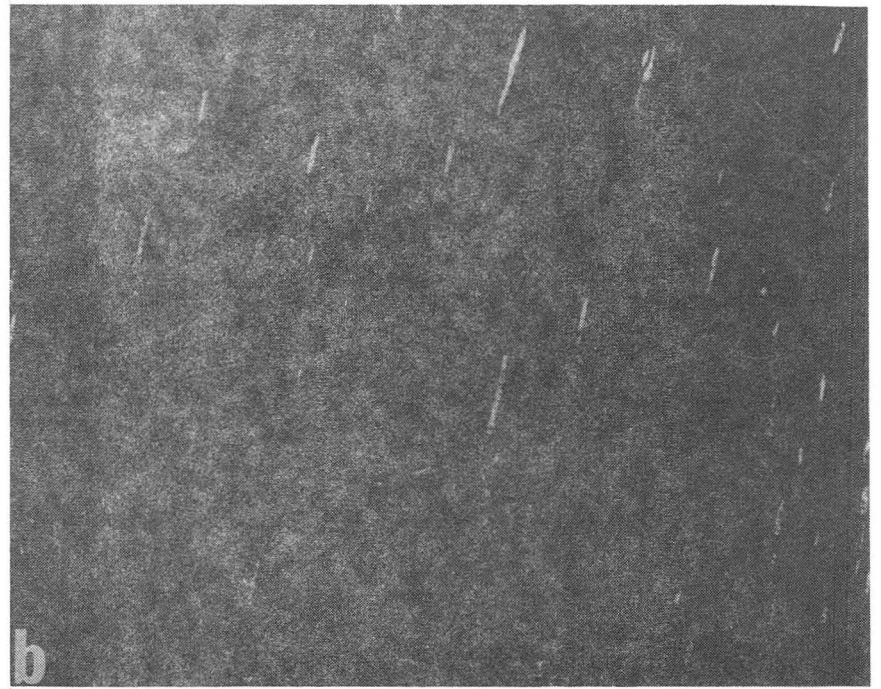
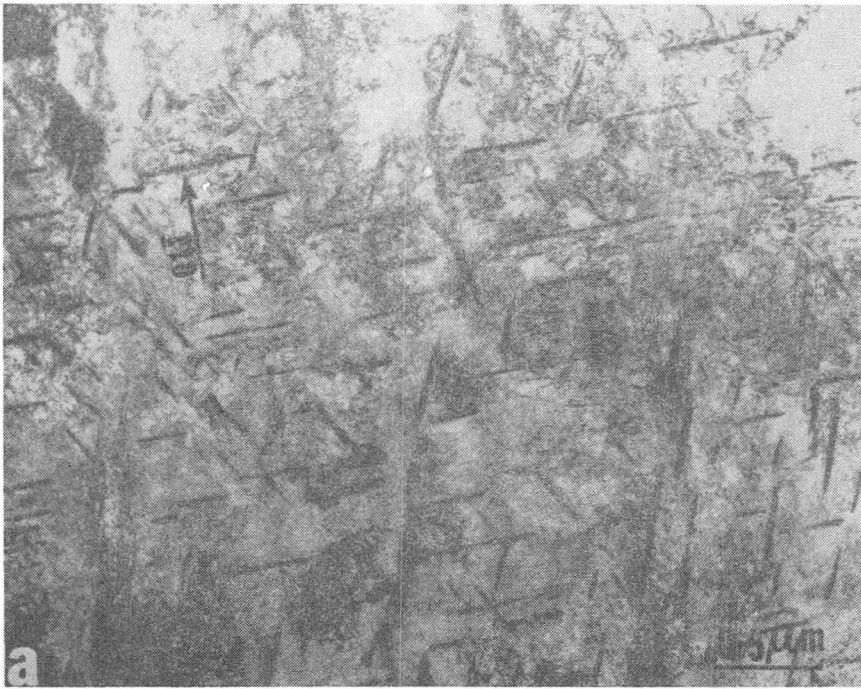
XBB-768-7133

Fig. 5(a-d)



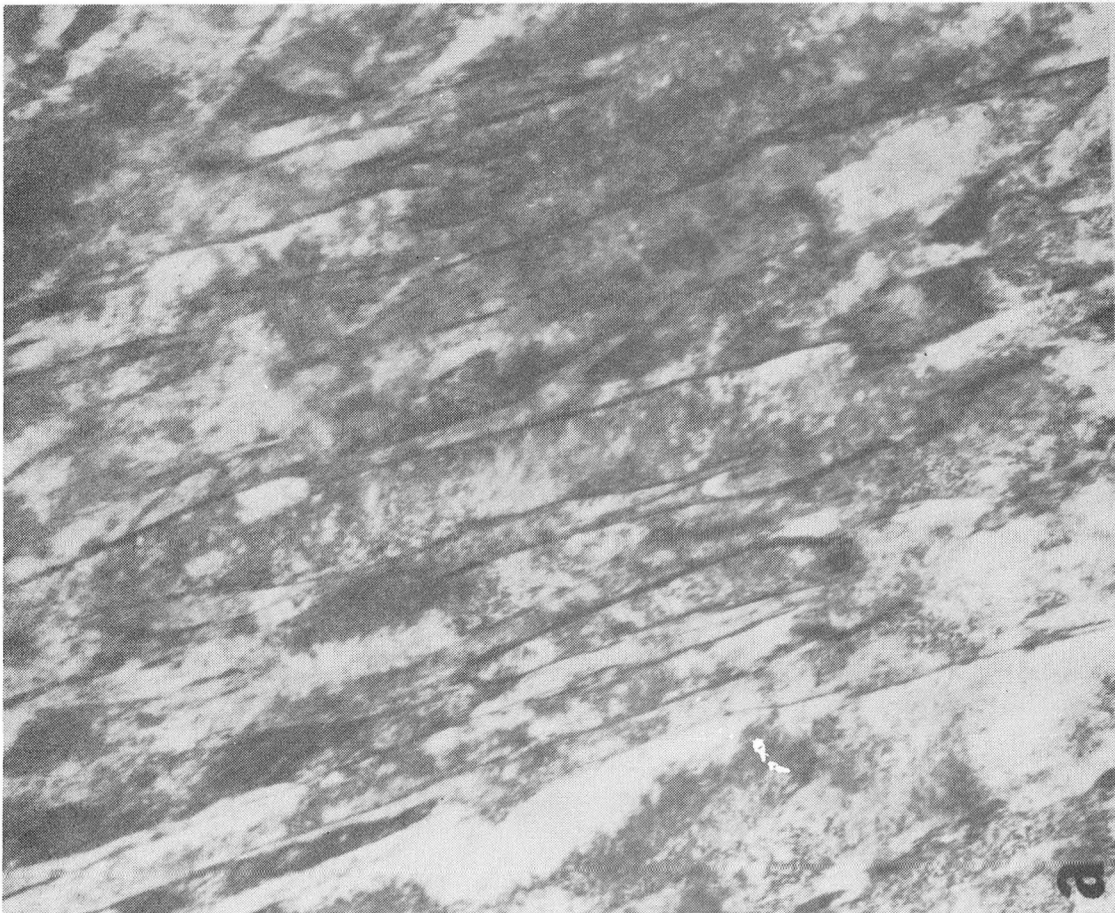
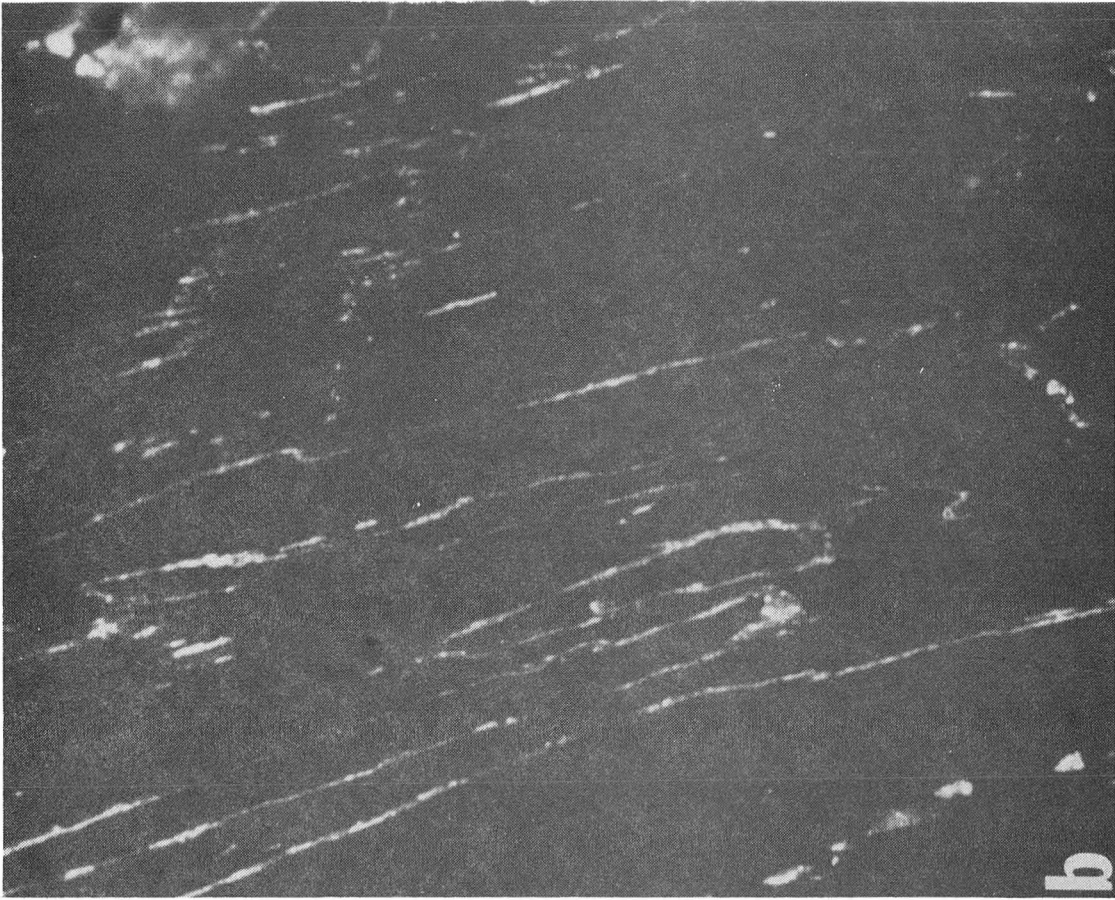
XBB-782-1179

Fig. 5(e-f)



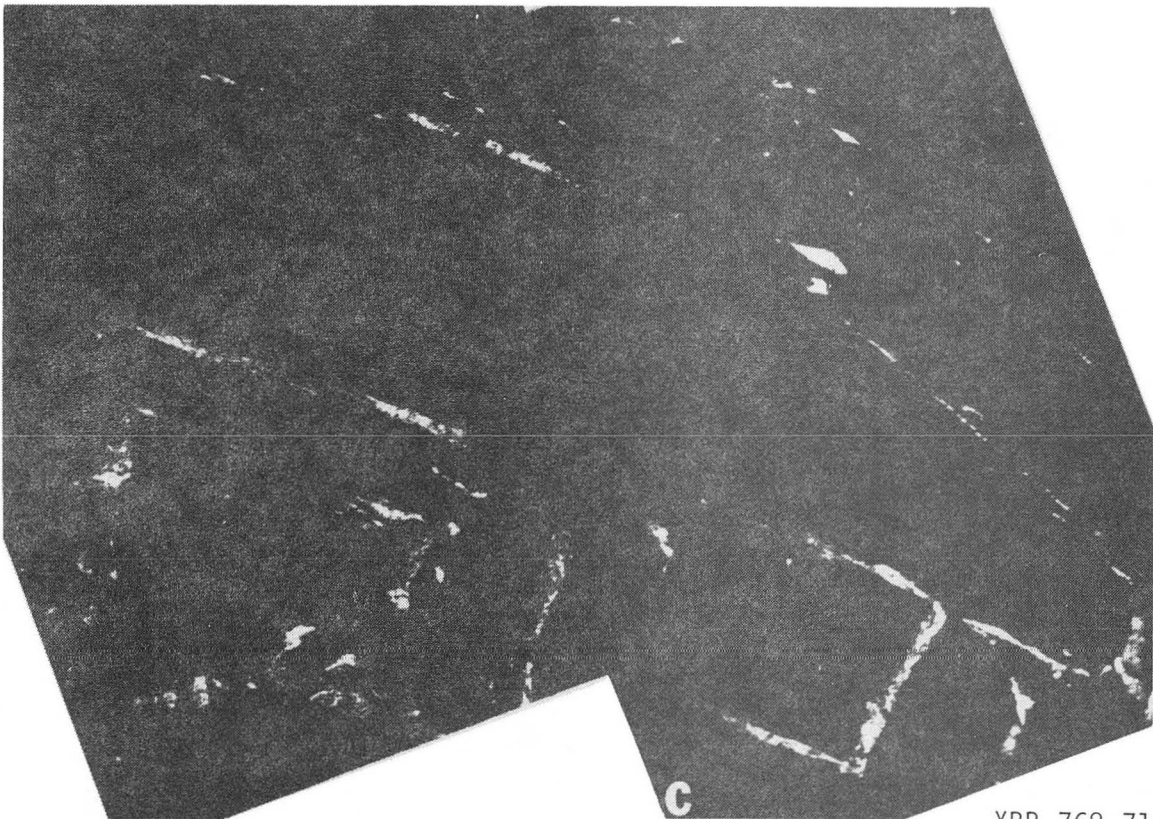
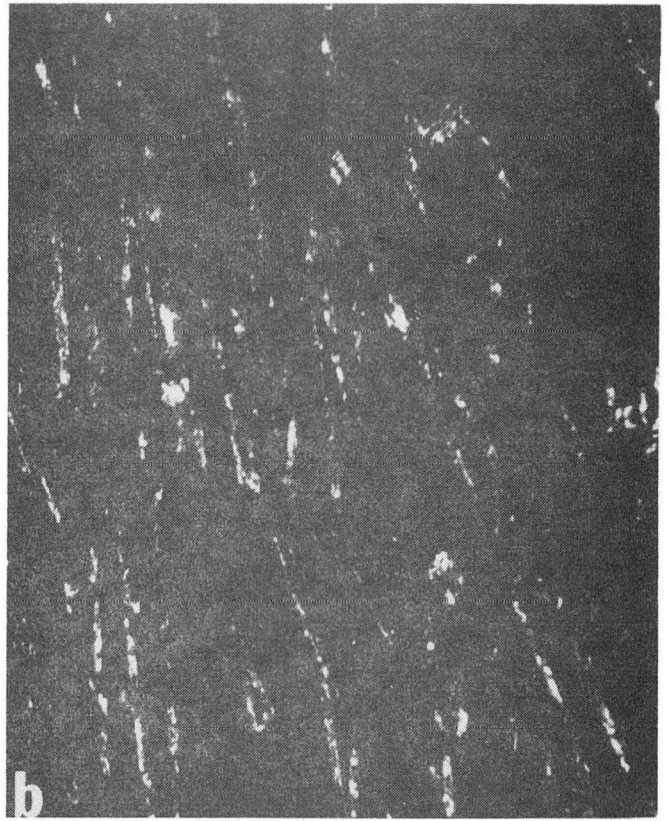
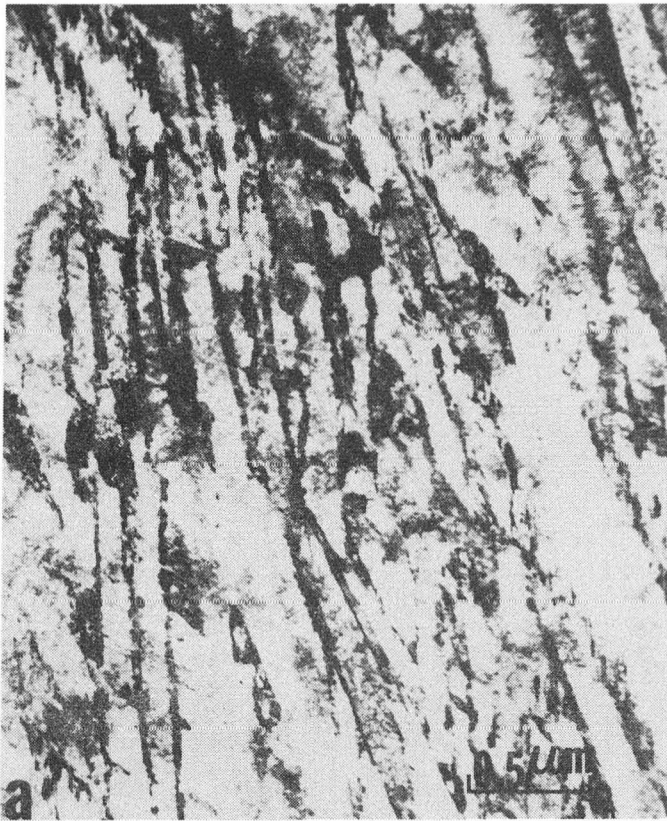
XBB-782-1175

Fig. 6



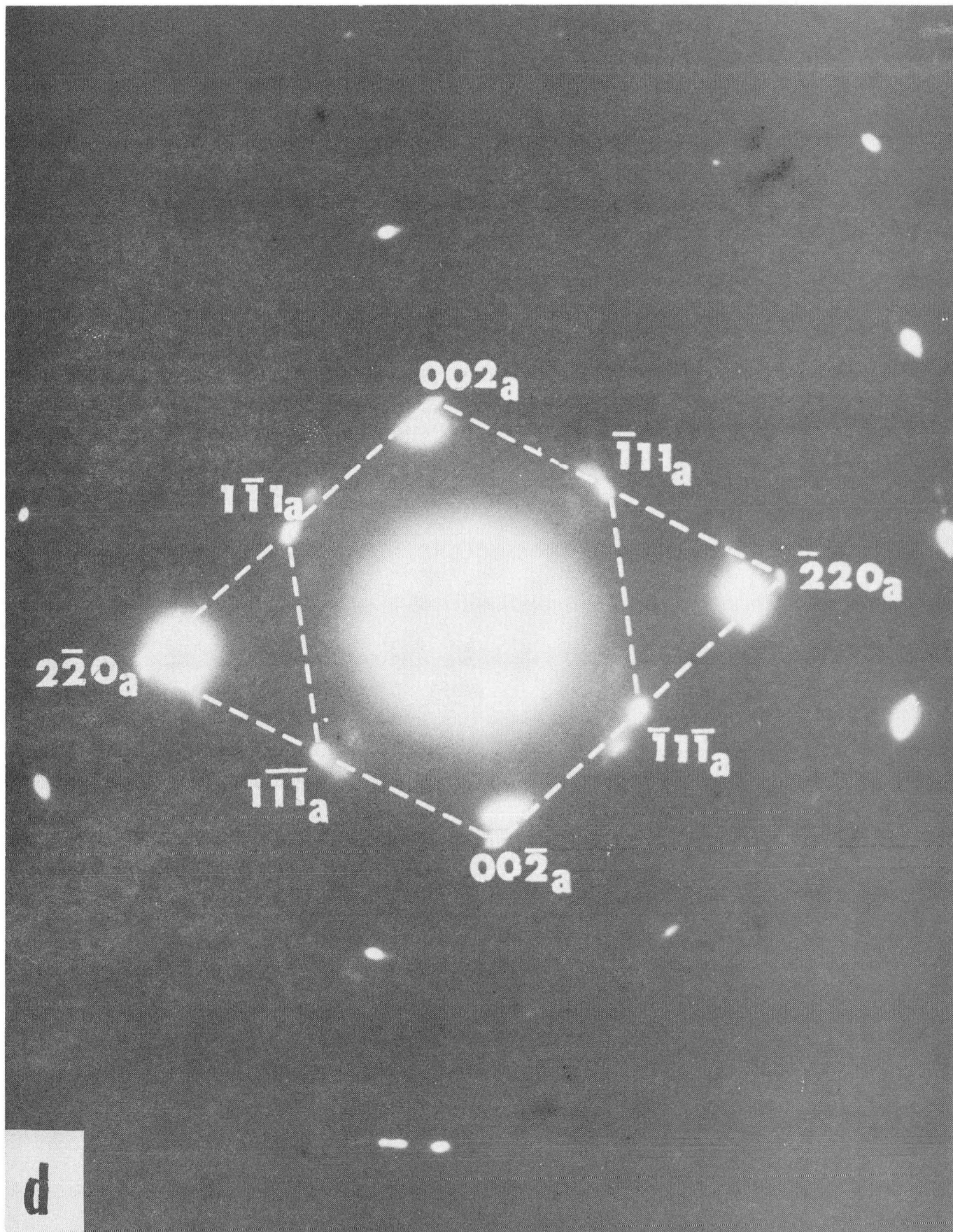
XBB 782-1055

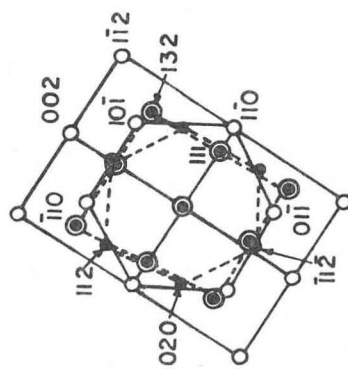
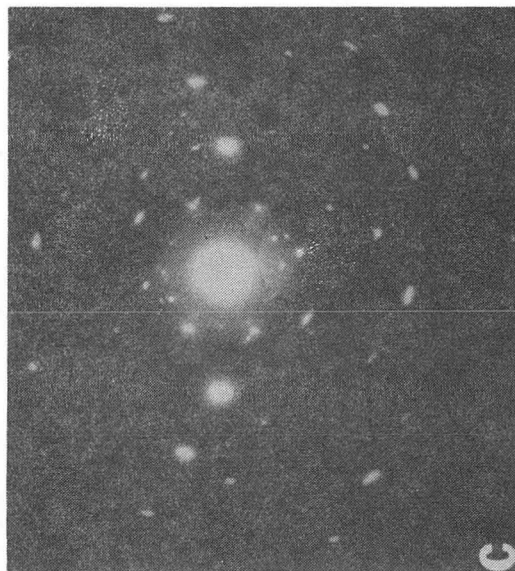
Fig. 7



XBB-768-7130

Fig. 8(a-c)



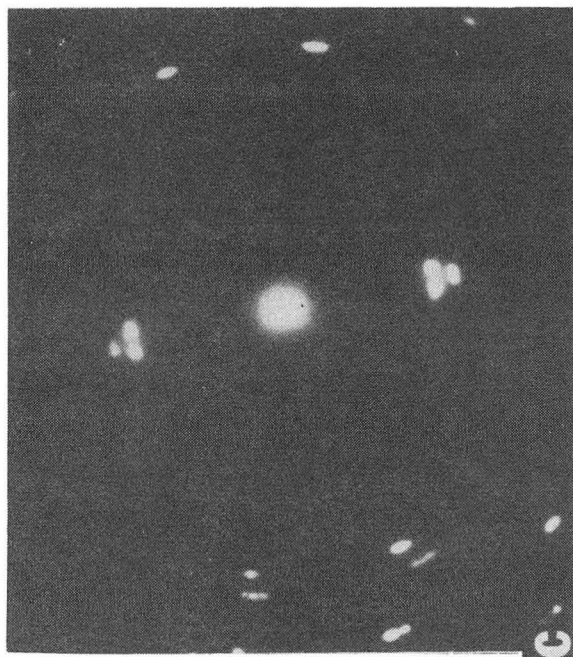
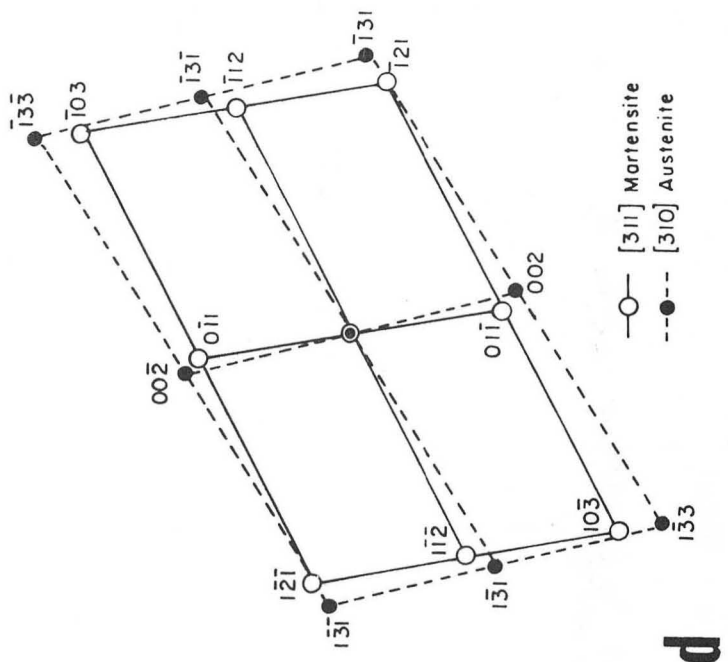


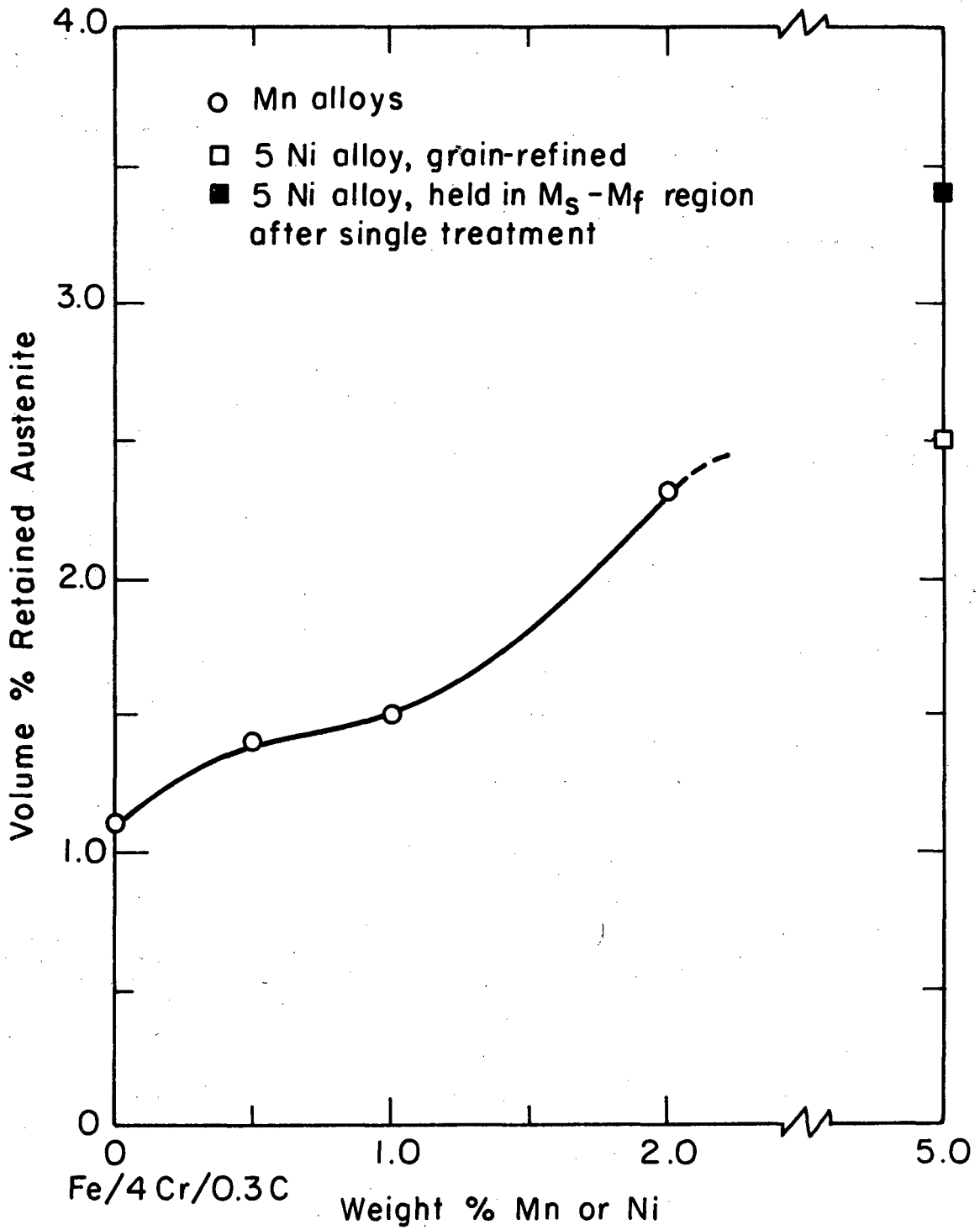
○— [111], [110] Martensite
●--- [201] Cementite
● [112] Cementite

d

XBB 782-1174

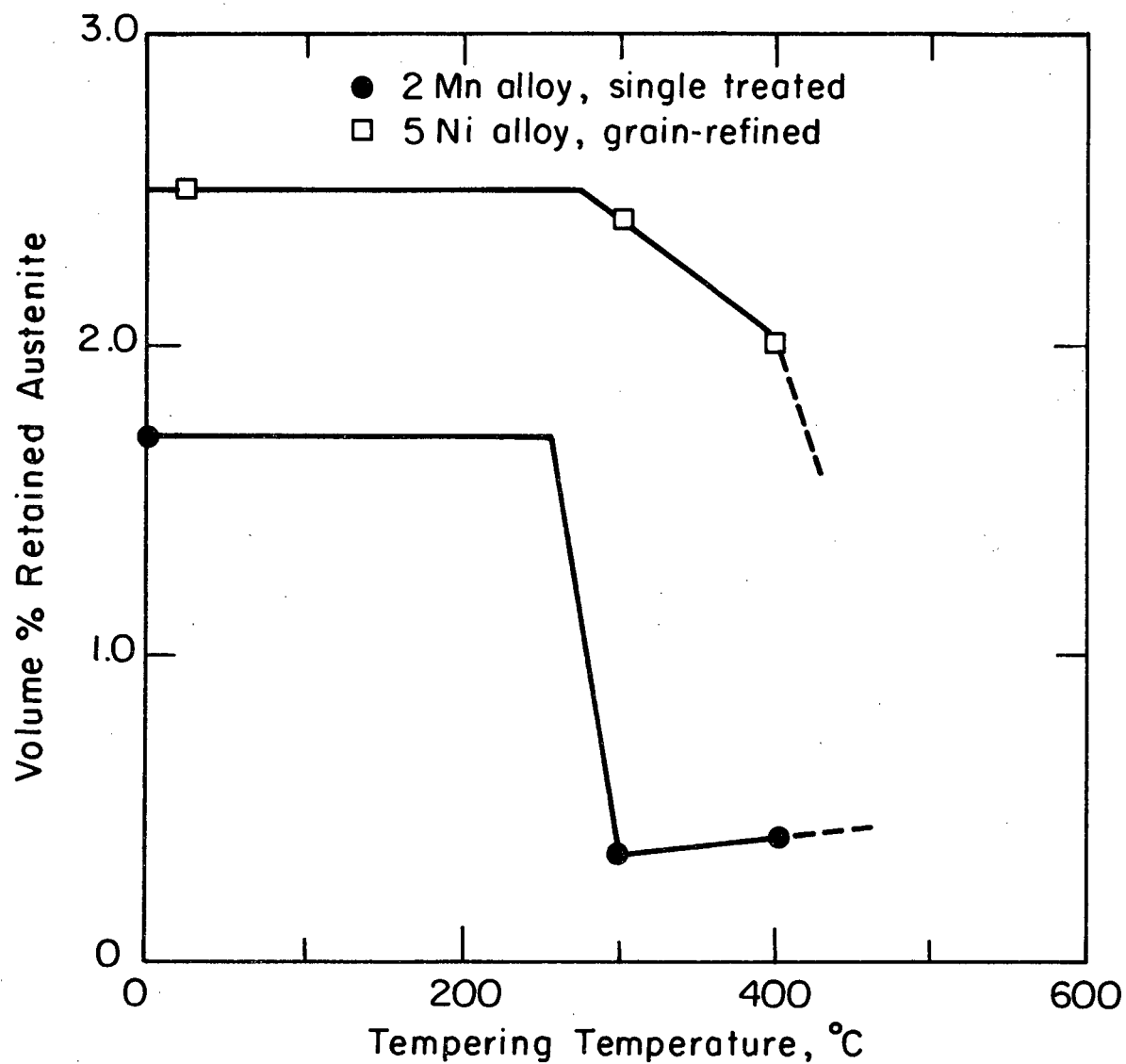
Fig. 9





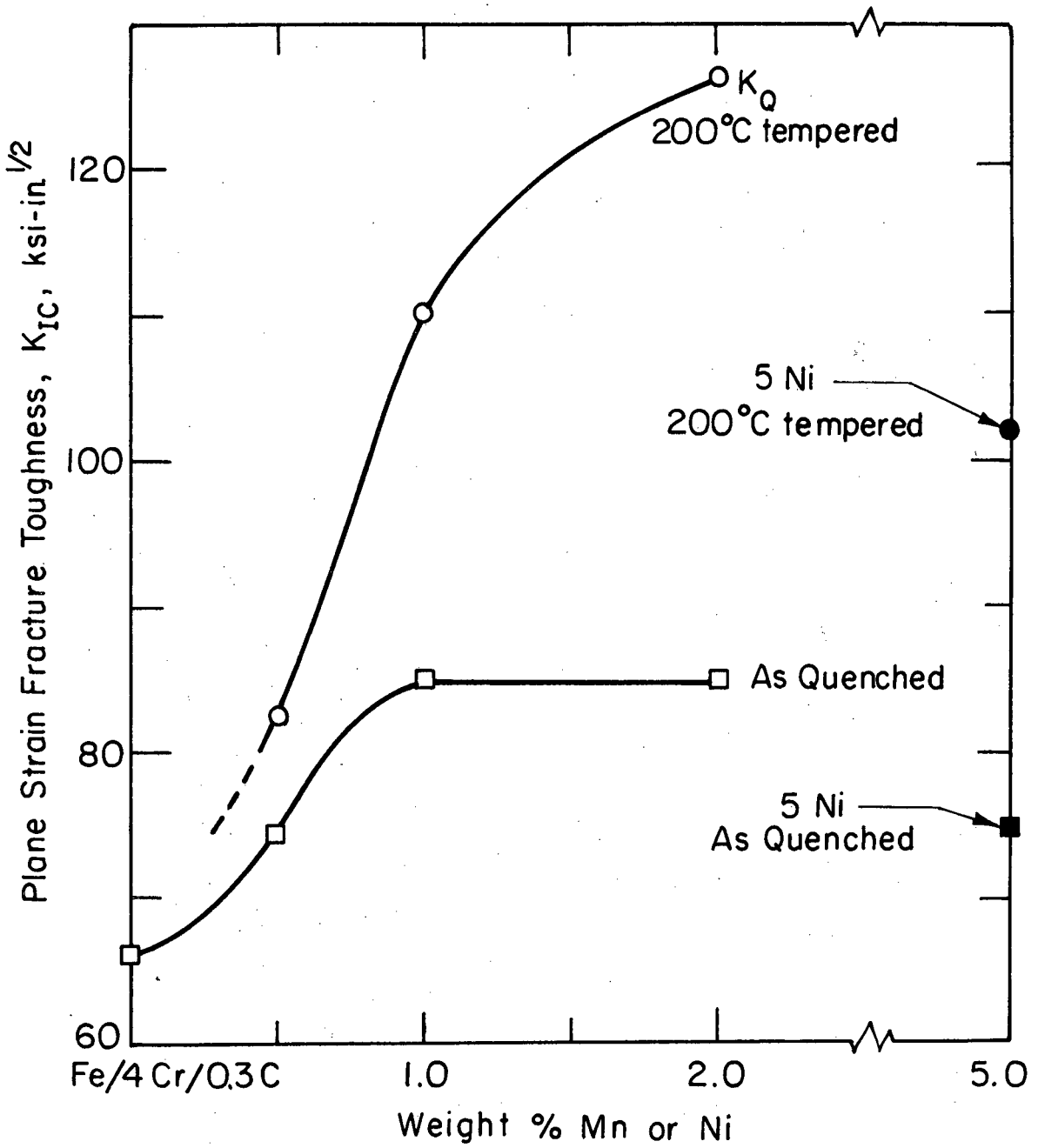
XBL 78I-4426

Fig. 11(b)



XBL781-4425

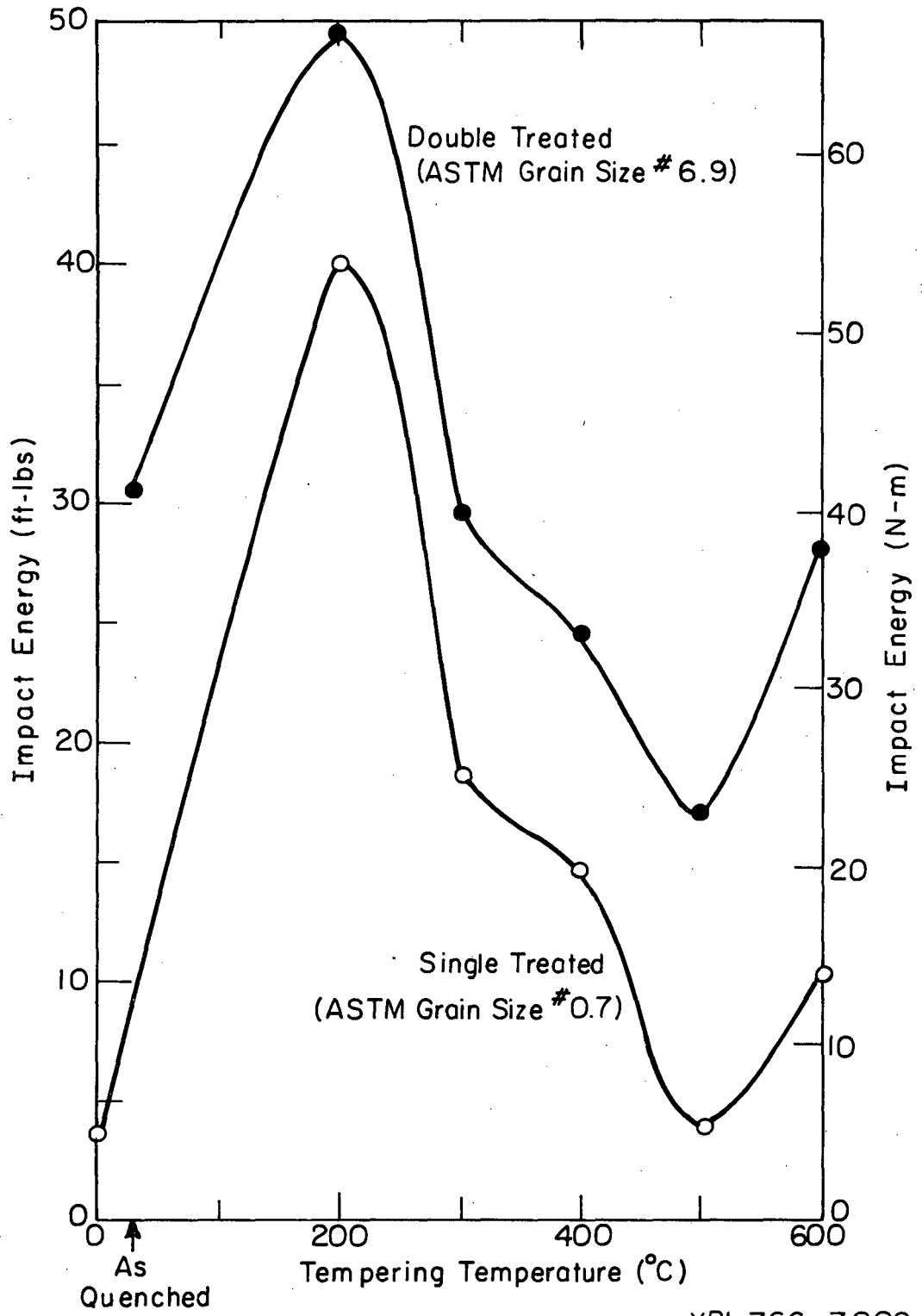
Fig. 11(c)



XBL 781-4437

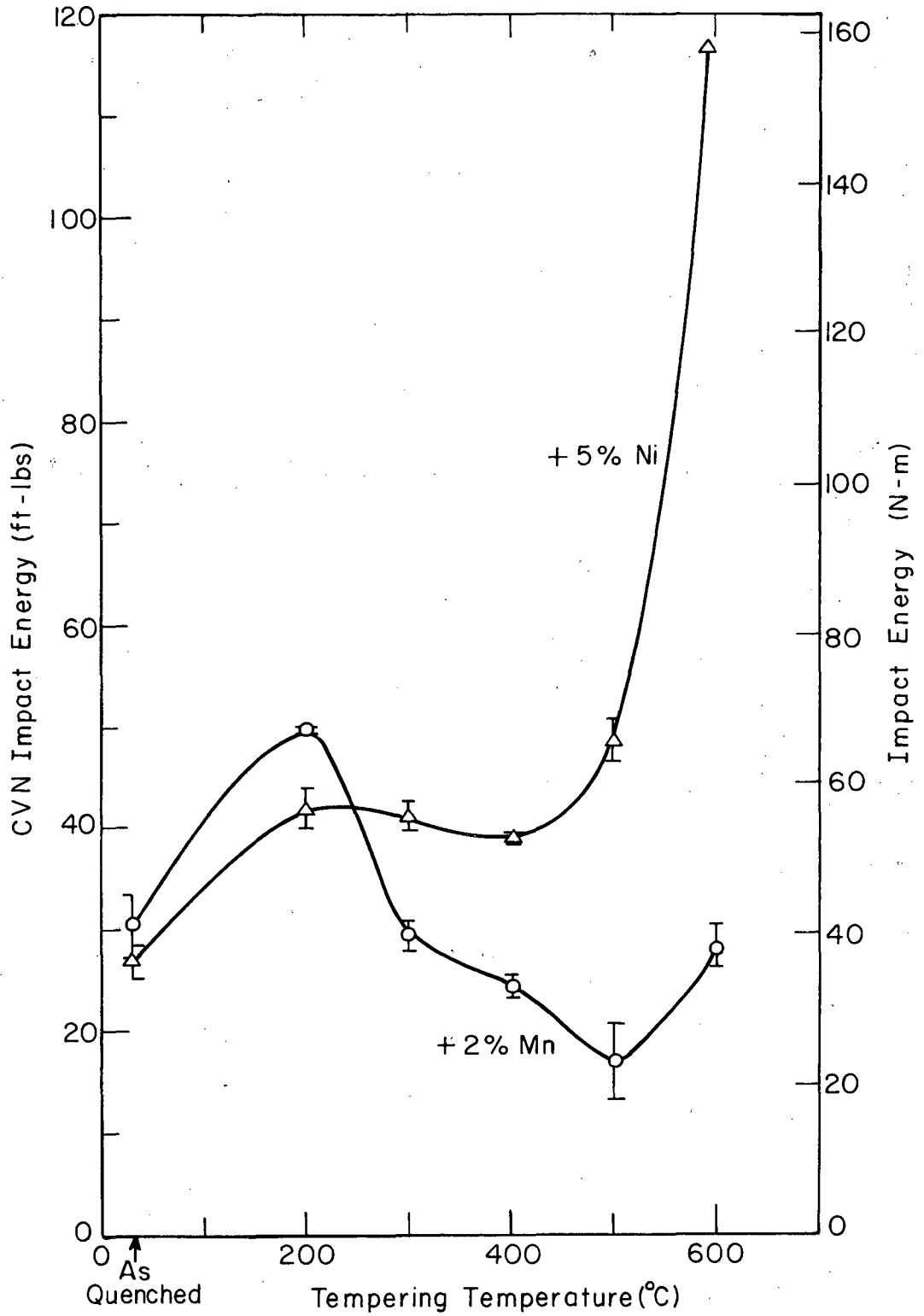
B.V.N.Rao &
G.Thomas

Fig.12



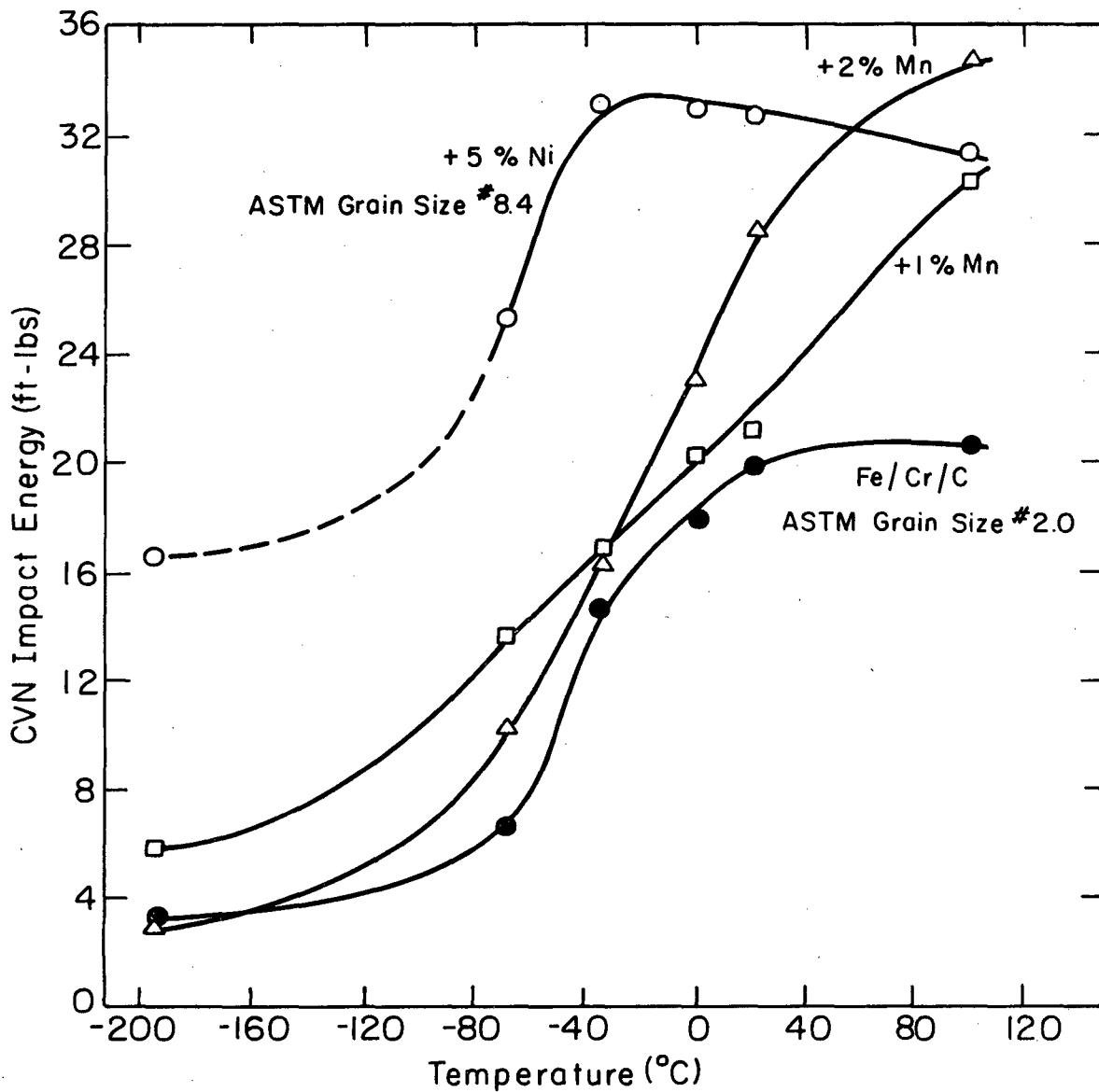
XBL 766-7002

Fig.13(a)



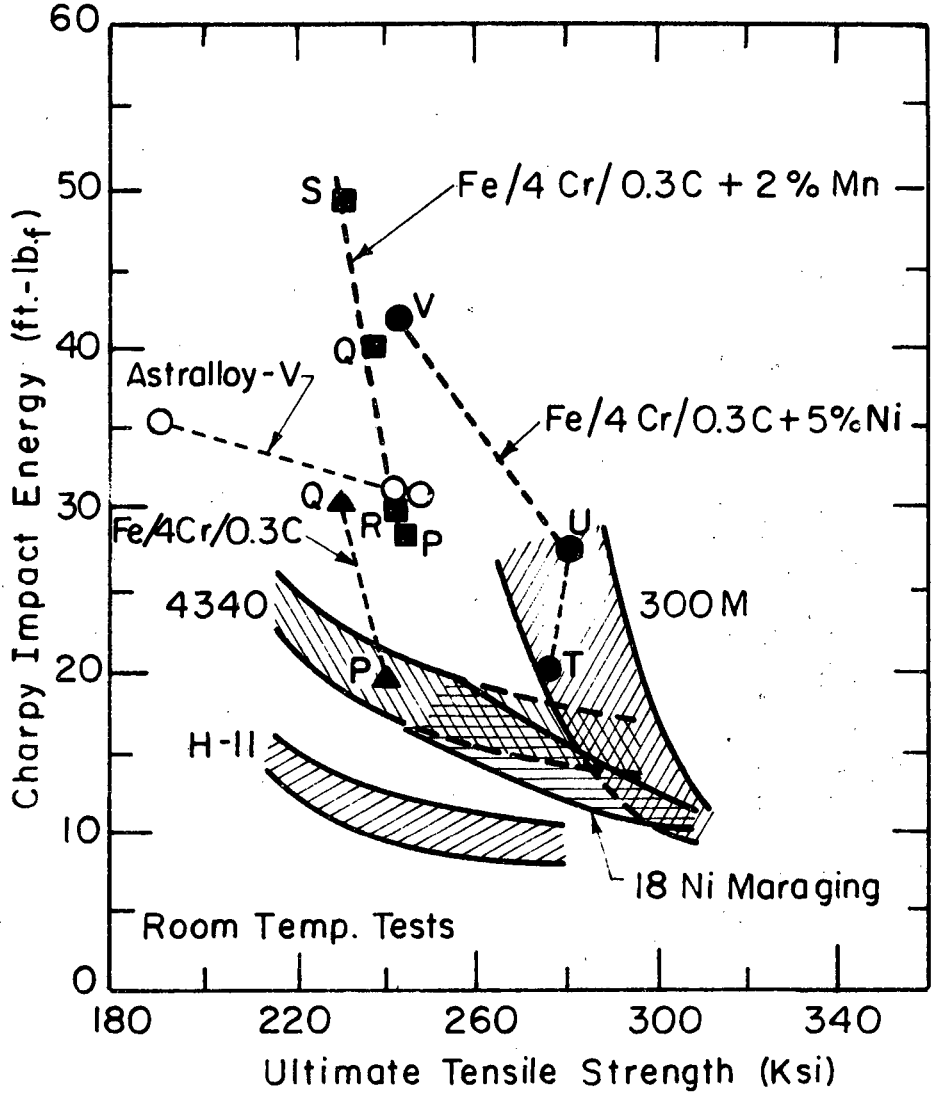
XBL 766-7006

Fig.13(b)



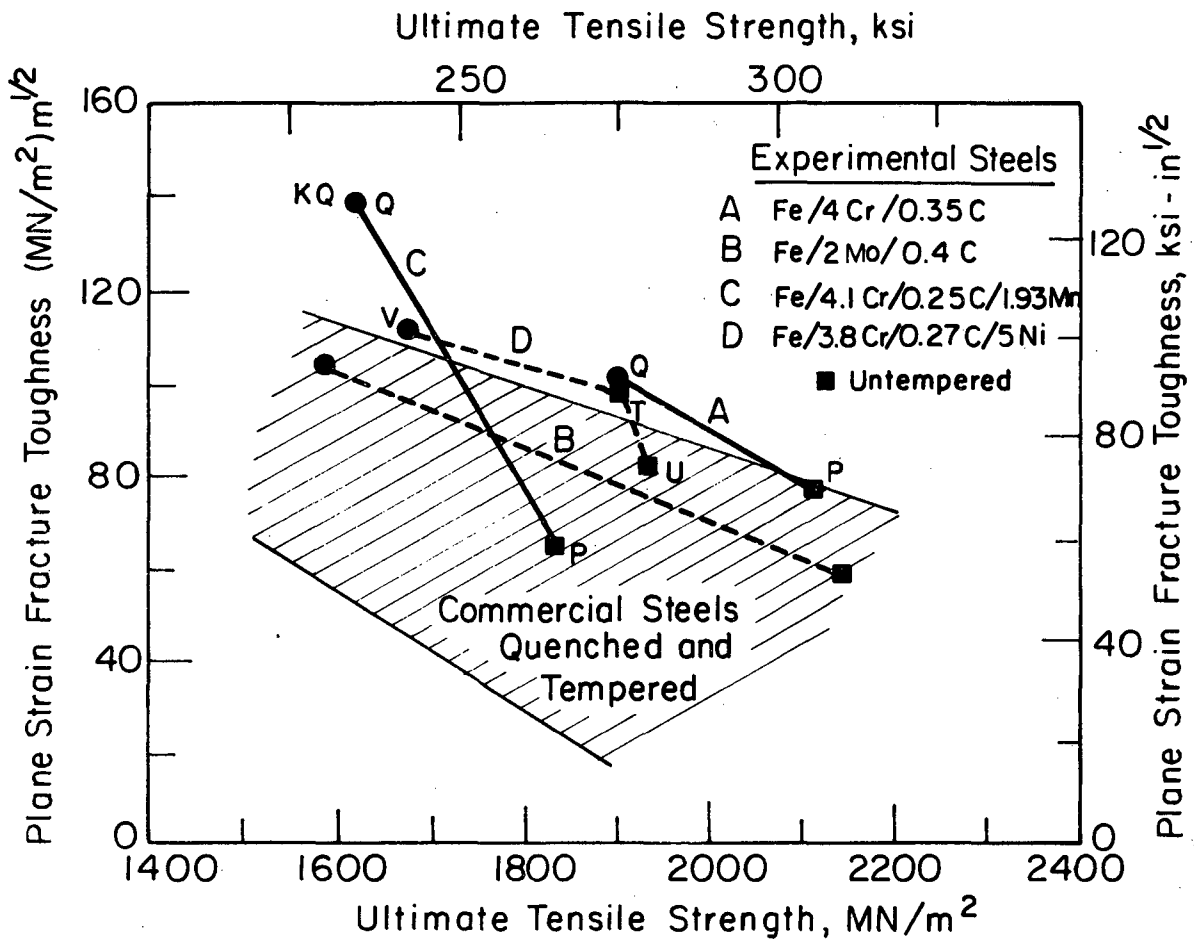
XBL 766-6999

Fig. 14



XBL 768-7314 A

Fig.15(a)



XBL 7710-6803

Fig. 15(b)

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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