

NOTICE
This report was prepared at the account of work sponsored by the United States Government neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

LBL-3982

HEAT-TREATMENT, MICROSTRUCTURE AND MECHANICAL
PROPERTIES OF EXPERIMENTAL HIGH STRENGTH Fe-4Cr-0.4C STEELS

B. V. Narasimha Rao*, R. W. Miller*† and G. Thomas*

Department of Materials Science and Engineering, College of Engineering,
and Center for the Design of Alloys, Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

ABSTRACT

As part of a continuing experimental program on alloy design of structural steels, the present investigation is concerned with the heat-treatment, microstructure and mechanical properties of martensitic and lower bainitic Fe/4Cr/0.4C steels which are normally brittle after conventional treatments. New double heat-treatments have been designed in order to avoid intergranular cracking in the as-quenched structures and to take advantage of both a higher austenitizing temperature and fine austenite grain size. These treatments involve high temperature (1100°C) austenitizing during the first solution treatment followed by either interrupted quenching (Ms-Mf range) or isothermal transformation to produce lower bainite. Finally, the steels are given a 900°C grain refinement treatment. Lower bainite was obtained by isothermally transforming austenite just above the Ms temperature. Tempering after the martensitic and bainitic treatments was also done in an attempt to improve the toughness of the material.

The strength and toughness properties of as-quenched martensitic structures are somewhat superior while these properties of lower bainitic

* B. V. Narasimha Rao and R. W. Miller are Graduate Students and G. Thomas is Professor of Metallurgy, University of California, Berkeley.

† R. W. Miller is now at Rockwell International, Materials Testing Division, Downey, California.

structures are comparable to those of a plain 0.4C steel. The properties of the nearly 100% bainite structure were unaffected by the cooling rate from the transformation temperature. Elimination of intergranular cracking produced toughness properties in quenched and tempered martensites which are far superior to those of lower bainite at the same strength level. It has also been shown that the toughness properties of as-quenched double-treated steels are superior to single treated steels. The chromium appeared to have a strong influence on the nature and morphology of carbides, as the bainitic as well as the martensitic structures showed marked temper resistance in the tempering range 200 to 500°C.

INTRODUCTION

In a continuing program on alloy design of experimental structural steels^(1,2), the present investigation of the structure and properties of lower bainite and martensite of the simple ternary Fe-4Cr-0.4C steel is taken up since a similar martensitic alloy, but with a lower carbon content, viz., 0.35%, yielded superior mechanical properties even in the untempered condition⁽³⁾. The increase of carbon from 0.35 to 0.4% has the potential of economically raising the yield strength of the steel to 300 ksi, but the steel is then prone to embrittlement, hence the challenge is to eliminate such embrittlement.

Though a considerable amount of research in the past^(2,4,5) has been directed to the design and development of strong, tough new steels through often expensive adjustments in composition, comparatively little work has been done on the effective use of modifications in conventional heat treatment practices so as to produce desirable morphological and sub-structural features. It is only recently that it has been demonstrated^(3,6,7) that the plane strain fracture toughness of the steel can be greatly improved by employing high temperature austenitization. However, such austenitizing practice leads to an increased amount of carbon and other alloying elements in solution due to better dissolution of alloy carbides and also a very large austenite grain size (ASTM grain size number <0.5). These two factors have been shown⁽⁸⁾ to promote intergranular quench cracking in the present Fe-4Cr-0.4% steel. While high austenitizing temperatures are shown to contribute favorably to the plane strain fracture toughness properties of some steels, the impact toughness and elongation properties of these steels were either unaffected or

were somewhat inferior to those of low temperature treated (commercial practice) steels⁽⁷⁾. In addition, the potential usefulness of finer austenite grain size in increasing the yield strength⁽⁹⁾, decreasing the severity of segregation of embrittling constituents⁽¹⁰⁾ and lowering of ductile-brittle transition temperature^(9,11,12) cannot be beneficially exploited by using a high austenitizing temperature. Thus, the aim of the present investigation is to eliminate intergranular cracking and at the same time combine the beneficial effects of high austenitizing temperature and fine grain size through suitable modifications in heat-treatment practices in an attempt to impart reasonable toughness to a steel at strength levels exceeding 300 ksi.

Studies comparing the toughness of bainite and martensite structures have provided mixed results. In steels containing <0.4%C, tempered martensite possesses better toughness properties compared to lower bainite at the same strength level⁽¹⁾. The inferior toughness properties of tempered martensites with C content \geq 0.4% as compared to lower bainite of the same steel has been attributed to twinning and the consequent twin boundary carbide precipitation in martensites⁽⁵⁾. However, no attempts have been made to improve the ever worsening intercrystalline cohesion in martensitic structures due to transformation strains at these high carbon levels and then compare the properties of these steels to those of lower bainitic steels. Thus, it is also the aim of the present study to investigate the toughness properties of quench-crack free martensitic structures compared with those of bainitic structures which could be produced conventionally without quench cracking.

EXPERIMENTAL PROCEDURE

The alloy steel investigated had the following composition (in wt. pct.) after homogenization at 1200°C for 48 hrs. in a vacuum furnace.

Cr	C	Fe	Ms (°C)	Mf (°C)
4.6	0.43	Bal	~320	~220

The martensite start and finish temperatures for the alloy were measured by dilatometric as well as magnetic permeability methods. All austenitizing treatments were carried out in vertical tube furnaces under a constant flow of Ar gas. Initially, oversized tensile, charpy and K_{IC} specimens were cut and final machining was done under flood cooling after heat-treatment. All isothermal transformations were carried out by quenching into a salt pot located directly below the furnace containing agitated salt maintained at the required temperature. In the case of some room temperature quenched specimens, a few tempering treatments at 200°C, 400°C and 600°C for 1 hr. were also carried out by immersing the specimen in a salt pot maintained at the required temperature and quickly quenching into water at the end of the treatment. For the martensitic treatments, an austenitizing temperature of either 1100° or 1200°C was employed during the first solution treatment and a 900°C austenitization was employed during the final grain refinement treatment. Figure 1 shows schematically the various heat-treatments that were adopted.

In order to determine the heat-treatment necessary for obtaining the desired lower bainite structure, (viz., no interlath embrittling carbides), a time-temperature-transformation (T-T-T) diagram was mapped out as shown in Fig. 2. This was accomplished by optical and electron metallographic studies. The bainite transformation temperatures were chosen on the basis of obtaining complete transformation at as low a

temperature as possible without interference from martensite formation. For the mechanical property measurements of the bainitic steels, specimens were austenitized for 1 hr. at 1200°C. Tempering treatments for 1 hr. at 500, 400, 350 and 300°C were performed on some of the lower bainitic specimens following the room temperature quench.

Microstructural features were documented by optical as well as transmission electron microscopic observations. Thin foils for electron microscopy were obtained from bulk, heat-treated fracture toughness test specimens after completion of testing. About 25 mils. thick slices were cut from K_{IC} specimens. After removing any oxide scale, the specimens were chemically thinned to less than 5 mils. at room temperature in a solution of 4-5 ml. HF in 100 ml. H_2O_2 . 2.3mm discs were spark cut from these and then sanded down to about 2 mils. thick. These thin foils were finally electropolished in a twin jet electropolishing apparatus at room temperature using a solution of 75 gm. CrO_3 , 400 ml. CH_3COOH and 21 ml. distilled water. The polishing voltage varied from 25 to 35 volts. Thin foils so obtained were examined in a Siemens Elmiskop IA electron microscope at an accelerating voltage of 100 kV.

X-ray analysis was used to measure the amount of retained austenite and it was concluded that the amount of retained austenite, if present, was too small to be detected by this method (~1-2%).

Mechanical properties were determined through tensile tests, plane strain fracture toughness tests and Charpy-V-Notch impact tests, all conducted at room temperature. Round, 1/4 in. tensile specimens were tested on a 300 kip capacity MTS machine at a cross-head speed of 0.04 in/min. Plane strain fracture toughness values were obtained by testing standard compact tension crack-line loaded toughness specimens. Initially, in the case of martensitic steels, a very conservative estimate of thickness requirements to satisfy ASTM specifications for plane strain condition [thickness $> 2.5 \left(\frac{K_{IC}}{y} \right)^2$] was made and thus, the first specimens for a number of treatments were much thicker than the second ones. The 300 kip MTS machine was again used for fatigue pre-cracking the specimens to a minimum crack length of 0.05 in which were subsequently tested in the same machine to obtain the fracture toughness data. All fracture surfaces of K_{IC} specimens were examined using a JSM-U3 scanning electron microscope at an operating voltage of 25 kV.

RESULTS AND DISCUSSION

Mechanical Properties

It has been shown⁽⁸⁾ that conventional austenitizing and quenching treatments lead to intercrystalline cracking in the as-quenched structures of the present steel. With an aim to ideally combine the benefits of eliminating undissolved alloy carbides and also to obtain a fine, uniform austenite grain size, multiple heat-treatments have been designed. The initial solution treatments for these have been so designed as to minimize the transformation strains (and the consequent impingement stresses at two growing martensite packets) by either a) isothermal transformation to lower bainite (as for D6 in Fig. 1) or b) interrupted quenching to

the M_s - M_f range to produce auto-tempered martensite with some stabilized lath boundary films of austenite (as for C3 in Fig. i). Following these solution treatments, all the specimens were subjected to a 900°C grain refinement treatment before finally transforming to produce martensite. The tensile and CVN impact properties of the specimens subjected to these treatments are given in Table I. Table II reports the valid plane strain fracture toughness results after some of the treatments. It is seen that the fracture toughness properties of specimens transformed initially to lower bainite (D6 in Tables I and II) are inferior to those of initially interrupted quench (martensite range) specimens (C3 in Tables I and II) although the difference is not marked. For comparison purposes, mechanical properties of specimens subjected to single 900°C austenitizing treatment are also included in Tables I and II (E1 and E2) and it is clear that specimens subjected to this commercial treatment exhibited the lowest toughness properties at comparable strength levels.

Increasing the austenitizing temperature to 1200°C (treatment K2 in Tables I and II) during the first solution treatment did not produce any pronounced changes in the properties: the plane strain fracture toughness values were almost the same while there was a small drop in tensile strength of 1200°C treated specimens (K2) as compared to the 1100°C treated specimens (C3).

Also prolonging the holding time at 900°C during the grain refinement treatment from 30 min. to 60 min. did not result in any appreciable difference in the toughness properties (compare C9 and C3 in Table II).

With a view to investigating the possibility of improving the toughness of the steel while not suffering a serious drop in strength, interrupted

quenching to 265°C in the martensite transformation range has been carried out after the second austenitizing treatment (C7 and D5). This resulted in a rather significant improvement in the elongation and K_{IC} fracture toughness values although there was a small drop in tensile strength as compared to that of room temperature quenched specimens. Thicker specimens (C71 in Table II) showed the highest fracture toughness. However, it is doubtful that these fracture toughness values correspond to the strength values obtained for this treatment from thinner specimens (.0.55" thick). (see also Fig. 2 for kinetics.) Interrupted quenching to 200°C i.e. below the M_f temperature (specimen G5) did not improve the toughness of the steel over the directly room temperature oil-quenched specimens. Quenching to this temperature would have resulted in almost 100% martensite and little tempering (See Fig. 2).

Since lower bainite in this steel could be produced after a single high temperature austenitizing treatment without intergranular quench cracking, an attempt was made to study and compare the properties of this structure with those of the martensitic structure. Table III gives the results of the room temperature mechanical properties of single 1200°C treated specimens consisting of lower bainite. Two bainitic transformation temperatures were tested, viz., 360°C and 330°C. These temperatures were chosen near the M_s because it has been shown by others^(13,14) that the lower the bainitic transformation temperature, the more favorable are the properties. This fact was confirmed in the present investigation. At 330°C, the yield and ultimate strengths increased by as much as 10% over the specimens transformed for the same length of time at 360°C. Toughness and elongation results were generally low with no significant

differences between the two transformation temperatures. Modifications in the basic isothermal heat-treatment were studied to investigate possible means of improving the properties. These modifications include, in addition to the transformation temperature, length of isothermal holding, rate of cooling following isothermal transformation, and tempering of the final bainitic structures. After 15 min. of isothermal transformation, the period of rapid bainitic growth was over before the austenite was completely transformed. Longer times were studied to see if the remaining austenite would transform in a reasonable length of time. Transformation times of up to 60 min. resulted in no significant change in the strength. Slower cooling rates from the isothermal temperature resulted in no change in the strength or impact toughness of material. Tempering temperatures of 300°C, 350°C and 400°C seemed to have little effect on the strength, whereas the toughness decreased from a value of 37 to 28. After 500°C tempering, however, a substantial decrease in tensile strength occurred for specimens transformed at either 330°C or 360°C while the Charpy impact value remained unchanged. The Charpy impact transition curve for specimen 1-B (Table III) was plotted in Fig. 3 and it appears that at 100°C the upper shelf of the transition curve had been reached. Even at this temperature, the structure showed very poor impact toughness.

The tempering behavior of doubly treated martensitic specimens (C3 and D6 in Fig. 1) is plotted in Fig. 4. Both the specimens C3 and D6 showed little change in elongation, CVN impact energy and yield strength in the tempering range 200-400°C. Tempering at 600°C resulted in a very rapid recovery of impact toughness and elongation with a concomitant drop in yield and ultimate tensile strengths (Fig. 4). The plane strain

fracture toughness values for the lower bainite and martensite structures (0440) are compared as a function of yield strength in Fig. 5. Figure 6 compares the Charpy impact energy as a function of the yield strengths of the two structures. Also plotted in Fig. 5 are properties for a 4Cr-0.35C martensite steel from an earlier investigation⁽³⁾ for comparison (0435). From these plots, it is clear that at the same strength level tempered martensite possesses much better toughness properties as compared to lower bainite in this alloy.

Microstructure

1) Structure of Beneficial Duplex Martensitic Treatments with Final Oil Quench to Room Temperature.

Optical metallographic examination revealed that the prior austenite grain size of the doubly treated martensitic specimens (ASTM grain size #8) is an order of magnitude smaller than the single treated bainitic specimens (ASTM grain size #0)⁽⁸⁾. Transmission electron microscopic investigation of the martensitic structures revealed that the substructure is a mixture of dislocated and twinned martensite although their amounts varied with treatment. There was no apparent difference in the as-quenched microstructures of doubly treated specimens subjected to either initial lower bainitic (D6) or initial interrupted quenching (C3) treatments as shown in Fig. 7. Figure 7(a) and 7(c) clearly reveal the packet martensitic structure consisting of parallel laths of treatments C3 and D6 respectively. A packet boundary where the laths from two adjacent packets impinge can also be seen in Fig. 7(c). Fig. 7(d) shows the presence of twinning in these specimens. Thin foils made from thicker K_{IC} specimens (viz., D61 and C31 in

Table II) revealed some undissolved carbides of roughly spherical shape (as in Fig. 7(b) marked by arrow) along with a profuse amount of auto-tempered $\{110\}_m$ Widmanstätten carbides Fig. 7(b). Microscopic examination of thin foils made from thinner K_{IC} specimens revealed, however, that there were no undissolved carbides; and as expected, an increase in the amount of twinning and a substantial decrease in the amount of auto-tempering. In contrast, the structure of the single 900°C austenitized specimens (treatment E2 in Fig. 1) consisted of essentially dislocated lath martensite wherein undissolved carbides are frequently observed.

Interlath films of retained austenite were observed in all the as-quenched specimens and a detailed account of its identification is given elsewhere^(15,16). Even after refrigeration in liquid N_2 there is no noticeable decrease in the amount of retained austenite in these specimens⁽¹⁶⁾. Such refrigeration should result in a substantial decrease in the amount of retained austenite if the major stability of γ is either chemical stabilization due to solute enrichment of austenite or thermal stabilization^(17,18) due to dislocation pinning in γ by carbon precipitation. On this basis, the stability of γ in this steel must be due to mechanical stabilization.^(19,20)

2) Structure of Beneficial Duplex martensitic Treatments With Final Interrupted Quenching to Martensite Range

Holding at 265°C for 3 min. during the final quench resulted in a duplex structure consisting of lower bainite and lath martensite, shown in Fig. 8. The amount of lower bainite varied with specimen thickness from about 40% in thicker specimens (D51 and C71 in Table II) to 10% in

in thinner specimens (D52 and C72 in Table II). (Also see Fig. 2.)

Figure 8(c) reveals the presence of some twinning in these specimens although it was by no means widespread or present in large quantities. There is a striking difference in the morphology of carbides in room temperature quenched and tempered specimens (see later section) and interrupted-quenched specimens (C7, D5). The carbides precipitated in specimens C71, C72 and D51 (Table II) were more numerous and hence direct identification by diffraction analysis was possible. In these specimens, frequently, twin related laths were present. The carbides precipitated within the laths during isothermal holding and surprisingly, showed no preference for twin related lath boundaries (Fig. 9). Twinning in the matrix occurred on $\{112\}_m$ and the orientation relationship between the orthorhombic cementite and ferrite (Fig. 9) shown was

$$\begin{array}{l} [2\bar{1}0] \text{ carbide} \quad || \quad [311] \text{ matrix} \\ (001) \text{ carbide} \quad || \quad (112) \text{ matrix} \end{array}$$

This is verified to correspond to one of the variants of the Bagaryatski orientation relation between ferrite and cementite in tempered martensite as reported earlier⁽²¹⁾. These carbides appear to be spheroidized in the 3 min. holding at 265°C. Precipitation of cementite along twin boundaries in martensite was frequently observed in thinner K_{IC} specimens.

3) Structure of Tempered Martensite

Tempering specimens after the C3 and D6 treatments at 200°C resulted in substantial $\{110\}_m$ widmanstatten cementite precipitation shown in Fig. 10(a). Some $\{100\}_m$ carbides can also be seen in Fig. 10(a). The retained austenite from the as-quenched structures remained untransformed

{Figs. 10 (b) and (c)} after tempering at 200°C. These films of γ apparently prevented lath boundary carbide precipitation. Twin boundary cementite precipitation was, however, identified and is similar to that reported earlier⁽³⁾.

Upon tempering at 400°C, the intralath Widmanstätten carbides appear to be dissolving {Fig. 11(a)} while a new spherical carbide (about 150Å large) precipitation at the lath boundaries, presumably from the existing austenite films, seems to have already started {Figures 11(b), 11(c) and (d)}. This new carbide could not be identified in this investigation, but Seal and Honeycombe⁽²²⁾ identified it as Cr_7C_3 . They explained that the formation of Cr_7C_3 at the lath boundaries even before general intralath Cr_7C_3 precipitation is due to the higher carbon concentration of retained austenite and that general precipitation of Cr_7C_3 within the laths subsequently takes place during the re-resolution of cementite which provides the carbon. The present results seem to substantiate these suggestions. Tempering at 600°C resulted in precipitation of a fine dispersion of intralath spherical carbides. (about 300Å large), presumably Cr_7C_3 (Fig. 12). However, the $\{110\}_m$ plate shaped carbides still existed even after tempering at 600°C (Fig. 12). Substantial recovery of martensite substructure and some recrystallization were also noticeable in these structures.

4) Structure of Single Treated Lower Bainitic Specimens

Optical metallography was used to follow the progress of the bainite transformation during isothermal holding to map out the T-T-T diagram (Fig. 2). The start of the bainitic transformation was characterized by nucleation of bainite at the grain boundaries. Growth seemed to proceed to the interior of the grain with needles branching from parent needles.

Upon transformation for 70 min. at 350°C, small, irregularly shaped regions identified as martensite could be seen. As a means of distinguishing the martensite regions from the unetched bainite regions, specimens 5-A and 4-B (Table III) were tempered at 500°C upon completion of isothermal transformation. During the austenite to ferrite plus cementite transformation, carbon diffuses away from the growing bainite needles to concentrate in the untransformed austenite regions. Upon quenching, these relatively high carbon containing austenite regions transform to martensite which is thus supersaturated with carbon. After tempering at 500°C the cementite in these regions precipitates and is revealed as dark, irregularly shaped areas (Fig. 13).

The typical lower bainite morphology in all the treatments was similar to that reported earlier^(1,5) and consisted of an even distribution of cementite particles in a ferritic matrix aligned unidirectionally at 50 to 60° to the main axis of the ferrite plate, shown in Fig. 14. The microstructure of the specimens isothermally transformed just above the Ms temperature, viz., at 330°C, revealed no evidence of interlath carbides or retained austenite (Fig. 14(a)). After 15 min. of isothermal holding at this temperature, the bainite transformation was nearly complete with better than 95% of the structure bainitic and the remainder being martensite. Figs. 14(c) and (d) show the martensite regions trapped between the bainite plates. These regions are characterized by the appearance of microtwins {Fig. 14(c)} and a high dislocation density. Fig. 14(d) also illustrates a wavy carbide structure branching out from the martensite leading to the speculation that these carbides may have precipitated directly from the prior austenite as in upper bainite even at this low temperature⁽²³⁾. The appearance of this kind of morphology may be

due to carbon enrichment in these localized regions. The level of carbon concentration in these areas may have been greater than 0.5% due to the diffusion of carbon to austenite during the bainite transformation. At this high carbon level, the cementite was able to precipitate directly from the austenite⁽²⁴⁾. Even after increasing the transformation temperature to 360°C, the structure remained largely lower bainitic with small carbides aligned across the ferrite plates although, at this temperature, some of the bainite formed with long, irregular carbides following the growth direction of the plate {Fig. 14(b)}. Evidence of interlath carbides was also detected by dark field imaging of the carbide diffraction spots.

CORRELATION OF MICROSTRUCTURE AND MECHANICAL PROPERTIES

The lower bainite structure represents a relatively uniform mixture of carbide and ferrite. Also in the initial interrupted quenching treatment a uniform mixture of widmanstatten carbides and ferrite is obtained.⁽¹⁶⁾ Thus, with either of the two initial structures, the preferential nucleation of austenite at carbides⁽²⁵⁾ would be high, resulting in a uniform, fine austenite grain size at the end of the second low temperature austenitizing treatment. Since in both cases the carbide is cementite and not chromium carbide⁽²⁶⁾ the dissolution rate in γ would be much faster. Thus, as expected, the tensile properties of steels C3 and D7 are almost identical.

The strength level of martensitic specimens is somewhat higher than the reported strength level of similar medium carbon steels.⁽⁷⁾ This can not be attributed to the presence of Cr since Cr is known to be not very effective as a solid solution strengthener in ferrite. In the

present steel partial contribution to yield strength could have resulted from the fine grain size.⁽⁹⁾ Although Cr is an ineffective solid solution strengthener, it does promote substructural twinning.⁽³⁾ In the present investigation twinning was present in all the steels although its amount varied from treatment to treatment. It was observed quite frequently in steels C3 and D7. Many earlier investigators^(19,3,27) have already pointed out the strengthening resulting from twinning. Similarly, the deleterious effects of twinning on toughness properties of steel have been discussed by some authors, especially in the presence of carbon.^(1,19,27,29) Thus, if martensite deforms by twinning, then microcracks may result at the intersections of these twins with those already present in the structure.⁽³⁰⁾ If twinning is indeed detrimental to toughness properties of medium carbon steel, then the properties of the martensitic steels should be far inferior to the properties of the same steel in the lower bainitic condition.⁽⁵⁾ However, it is clear from the plots of Figs. 5 and 6 that the mechanical properties of martensitic microstructure are far superior to the single treated coarse grained lower bainitic steel and the CVN impact energy and K_{IC} fracture toughness values of martensitic microstructure are more than double the corresponding values for lower bainite at the same strength level. Before specific conclusions can be made, one other important factor has to be considered. The plotted properties of martensite in Figs. 5 and 6 correspond to fine γ grain size whereas the plotted values for lower bainite correspond to very coarse γ grain size. It is

possible that because of the much finer γ grain size and the consequent finer packet size⁽⁸⁾ in specimen C3, the impact energy values correspond to upper shelf values whereas for the coarse lower bainitic structure, the CVN energy values correspond to lower shelf values.

However, the measured upper shelf energy for lower bainite was only about 13 ft. lbs. (Fig. 3). Thus, even if we use these upper shelf values for lower bainite, the toughness properties of these steels are far inferior to those of tempered martensite in the present Fe/4Cr/0.4C steel for a given strength. At about the carbon levels where lower bainite is shown to be superior to tempered martensite by earlier investigators⁽⁵⁾ intercrystalline cohesion at the prior γ grain boundaries becomes increasingly poor. The crack propagation will in those cases tend to be along this low energy crack path, i.e., intergranular. Thus, unless efforts are made to reestablish this cohesion in martensitic steels, any comparison made only on the basis of internal microstructure will be doubtful.

It has been shown⁽²²⁾ that secondary hardening in the temperature range 250 to 400°C is a function of both carbon and Cr content of the steel. At 0.4%C it has been suggested⁽²²⁾ that significant secondary hardening occurs at as low as 3% chromium content and that even higher Cr and C contents are needed in order to actually observe a raise in yield strength upon tempering in this temperature range. In the present investigation there was an arrest in the CVN energy and elongation values upon tempering in the 200-400°C range (Fig. 4) and it is argued that secondary hardening is not very prominent in the present steel on the basis that there was actually a small drop in yield strength

in this temperature range. All that one can say is that the secondary hardening in this alloy may be just sufficient to offset any change in properties that accompanies tempering of a plain carbon steel in this range. Also, it is observed that while the intralath Widmanstatten carbides appear to be dissolving, there was simultaneously, precipitation of spheroidized carbides, presumably Cr_7C_3 , at the interlath boundaries. This might mean that the total alloy content of ferrite remains unaltered in this temperature interval and thus the DBTT (Ductile Brittle Transition Temperature) is maintained. Upon tempering at $600^\circ C$, rapid coarsening of the intralath and interlath Cr_7C_3 carbides results in depletion in ferrite matrix of both Cr and C⁽²²⁾. This results in a rapid lowering of transition temperature^(31,32) and the consequent dramatic improvement of toughness but a drop in strength level.⁽³⁾

Specimens E1 and E2 (Table I) which are single treated at $900^\circ C$ showed much inferior CVN energy values as compared to specimen C3 even though their grain sizes are very much alike. In the former, grain boundary decoration by precipitates which lowers the surface energy and thus increases DBTT^(11,12) has been noted. On the same basis interlath precipitation of carbides can partially account for the arrest in CVN energy values in the $250-400^\circ C$ tempered specimens. As has already been pointed out, a very small amount of retained austenite has been conclusively identified in all steels. While it is possible that it could have a positive contribution to the CVN energy values, it is not clear at the moment how exactly the fracture toughness properties after the various treatments are influenced by such small quantities of retained austenite.

The bainitic properties of this alloy had, at best, yield strengths of 190 ksi and 250 ksi U.T.S. This strength level conforms well with the findings of other researchers for a fully transformed bainitic steel with 0.4% C⁽³³⁾. The lower transformation temperature of 330°C produced a finer structure than the 360°C structure. A smaller packet size in the lower temperature specimen may (also) have accounted for the increased strength as suggested by Naylor and Krahe⁽³⁴⁾. The absence of interlath carbides in the structure transformed at 330°C also could have contributed to the superior properties. However, the toughness remained about the same after the two transformation temperatures. The alloy showed greater temper resistance than a plain carbon steel indicating the possible influence of mild secondary hardening on the properties as discussed before.

The appearance of parallel ridges on some areas of the fractured surfaces of the lower bainitic steel (Fig. 15) leads to the speculation that these corresponded to the bainite plates. Measurement of the spacing and length of these ridges showed that their size agrees quite well with the size and spacing of bainite plates in optical micrographs. If the crack path follows the plate boundary, as this infers, then the size and distribution of these bainitic transformation units would have a great influence on the strength and toughness of the bulk specimen. Poor as the toughness properties are in the lower bainitic condition, they still are far superior to those of Fe-4Cr-0.35C lower bainitic structure reported by Raghavan⁽²⁷⁾. In the latter, the M_s temperature was relatively high and interference from upper bainite or tempered martensite in the microstructure occurred.

Since a 100% lower bainite structure could not be attained in the present investigation, it is not clear what effect the untransformed regions had on the mechanical properties of this alloy. In the regions that were untransformed during the isothermal treatment, there was evidence of a high carbon concentration due to diffusion of carbon ahead of the growing ferrite-austenite interface. It is believed that in an alloy of similar carbon level, but with a lower M_s temperature, the diffusion of carbon during the bainitic transformation could be lowered since lower transformation temperatures would then be allowed. These lower transformation temperatures may then result in a more complete bainite transformation. With a decrease in the localized regions of high carbon concentration, there would be a corresponding decrease in the amount of martensite in the structure. It is believed that eliminating these brittle martensite-carbon regions could improve the toughness of the lower bainite structure.

CONCLUSIONS

Based on the present study on Fe/4Cr/0.4C Steel, the following conclusions can be drawn:

1. The strength level of the crack-free as-quenched martensitic structures was somewhat higher than that of similar 0.4C martensitic steels while the fracture toughness values corresponded to those reported earlier. The strength level of lower bainitic structure was high and comparable to that of the same structure in a high strength 0.4C plain steel.
2. The toughness properties of doubly treated martensitic specimens were superior to those of single conventionally treated specimens.

The impact toughness was more than doubled while there was about 25% gain in K_{IC} fracture toughness after some double treatments.

3. Elimination of intergranular cracking produced toughness properties in quenched and tempered martensites which were far superior to those in the lower bainite condition even at this carbon content (0.4%) and with appreciable amount of twinning in martensite. The impact energy and K_{IC} fracture toughness values of the tempered martensites were more than double those of lower bainite at the same strength level.

4. Once intergranular cracking was eliminated, increasing austenitizing temperature to above 1100°C during the first solution treatment did not result in any improvement in mechanical properties of martensite.

5. The quenched and tempered martensitic specimens possessed better combination of properties than specimens which were interrupted-quenched to the same strength level.

6. A 100% lower bainitic structure could not be attained. Besides bainite, the structure also contained a small amount of small irregularly shaped regions of martensite with relatively high carbon concentration. The effect of these nonbainitic regions on the mechanical properties was unclear.

7. The bainitic and martensitic structures of this alloy showed high resistance to tempering in the range of 250 to 500°C possibly due to the mild secondary hardening effect of Cr.

8. The best results were obtained by double treatment to produce grain refined martensite. The corresponding microstructure consists of

Mostly dislocated martensite and stabilised interlath untransformed austenite with no embrittling interlath carbides. The latter is particularly detrimental and must be eliminated e.g. by avoiding upper bainite and tempering where the interlath retained austenite is unstable and transforms to ferrite and carbide ($\sim 300^{\circ}\text{C}$ and above).

9. From the alloy design standpoint, increasing the carbon from 0.35 to 0.4% resulted in a drastic lowering of intercrystalline cohesion in the as-quenched structures in addition to its influence in elevating transition temperature and increasing twinned substructures. While there was an immediate gain in strength from the increase in carbon, even after complex heat-treatments, the toughness properties of the present alloy (in its martensitic condition) were only close to but never superior to those of Fe-4Cr-0.35C steel.

ACKNOWLEDGMENTS

The alloy used in this investigation was graciously supplied by Republic Steel Corporation. This work was done under the auspices of the U.S. Energy Research and Development Administration through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory.

REFERENCES

1. G. Thomas, Iron and Steel International, 1973, 46, 451.
2. V. F. Zackay, E. R. Parker, J. W. Morris and G. Thomas, Mat. Sci. and Eng., 1974, 16, 201.
3. J. McMahon and G. Thomas, Proc. Third Intl. Conf. on Strength of Materials, "Microstructure and Design of Alloys", Cambridge, Inst. of Metals (London), 1973, 1, 180.
4. D. Huang and G. Thomas, Met. Trans., 1971, 2, 1587.
5. S. K. Das and G. Thomas, Trans. ASM, 1969, 62, 659.
6. V. F. Zackay, E. R. Parker, R. D. Goolsby and W. E. Wood, Nature Physical Science, 1972, 236, 108.
7. G. Y. Lai, W. E. Wood, R. A. Clark, V. F. Zackay and E. R. Parker, Met. Trans., 1974, 5, 1663.
8. B. V. Narasimha Rao and G. Thomas, Mat. Sci. and Eng., 1975, 20, 195.
9. R. A. Grange, Met. Trans., 1971, 2, 65.
10. G. Clark, R. O. Ritchie and J. F. Knott, Nature Physical Science, 1972, 236, 108.
11. A. H. Cottrell, Trans. AIME, 1958, 212, 192.
12. N. J. Petch, Phil. Mag., 1958, 3, 1089
13. K. J. Irvine, F. B. Pickering, JISI, 1963, 34, 518.
14. R. F. Heheman, V. J. Luhan and A. R. Troiano, Trans. ASM, 1957, 49, 409.
15. B. V. Narasimha Rao, J. Y. Koo and G. Thomas, EMSA Proceedings, 1975 Claitor's Publishing Division, p. 30.
16. B. V. Narasimha Rao, M. S. Thesis, University of California, Berkeley, LBL-3794, 1975.

17. G. S. Ansell, S. J. Donachie and R. W. Messler, Jr., Met. Trans., 1971, 2, 2443.
18. E. J. Klier and A. R. Troiano, Metals Technology, 1945, 12, 1.
19. P. M. Kelly and J. Nutting, JISI, 1961, 197, 199.
20. B. Edmondson and T. Ko., Acta Met., 1954, 2, 235.
21. G. R. Speich and W. C. Leslie, Met. Trans., 1972, 3, 1043.
22. A. K. Seal and R. W. K. Honeycombe, JISI, 1958, 188, 9.
23. D. H. Huang, Ph.D. Thesis, Univ. of Calif., LBL-3713, 1975.
24. F. B. Pickering, Symposium: Transformation and Hardenibility, Climax Moly., Ann Arbor, 1967, 115.
25. G. R. Speich and A. Szirmai, Trans. AIME, 1960, 245, 1063.
26. T. Lyman and A. R. Troiano, Trans. ASM, 1946, 37, 402.
27. M. Raghavan and G. Thomas, Met. Trans., 1971, 2, 3433.
28. M. Raghavan, M. S. Thesis, Univ. of Calif. UCRL-19132, 1969.
29. M. Raghavan, D. Eng. Thesis, Univ. of Calif., Berkeley, LBL-477, 1972.
30. D. Hull, Acta Met., 1960, 8, 11.
31. J. A. Rinebolt and J. W. Harris, Jr., Trans. ASM, 1951, 43, 1175.
32. W. C. Leslie, R. J. Sober, S. G. Babcock and S. J. Green, Trans. ASM, 1969, 62, 690.
33. L. J. Klinger, W. J. Barnett, R. P. Forlumbert and A. R. Troiano, Trans. ASM, 1954, 44, 1557.
34. J. P. Naylor and P. R. Krahe, Met. Trans., 1974, 5, 1699.

TABLE CAPTIONS

- TABLE 1. Room temperature tensile and impact toughness properties of martensitic treatments.
- TABLE 2. Room temperature plane strain fracture toughness properties of martensitic structure.
- TABLE 3. Room temperature mechanical properties of single treated steel with lower bainitic structure.

TABLE I

A. Initial Interrupted Quenching to M_s - M_f Range

Heat-treatment	0.2% offset Yield Strength ksi (MNm ⁻²)	Ultimate Tensile Strength ksi (MNm ⁻²)	% Elongation in 1.25" gauge		CVN Impact Energy ft-lbs (NM)
			Uniform	Total	
C3, as-quenched	260 (1791)	340 (2343)	1.5	1.5	10.0 (13.6)
C3, 200°C tempered	236 (1626)	297 (2046)	4.4	9.0	15.0 (20.4)
C3, 400°C tempered	222 (1530)	245 (1688)	2.7	9.5	15.5 (21.1)
C3, 600°C tempered	128 (882)	148 (1020)	3.2	10.5	80.0 (108.8)
C7	233 (1605)	316 (2177)	3.8	6.1	11.6 (15.8)
C9	265 (1826)	330 (2274)	1.2	1.2	--
G6	215 (1481)	307 (2115)	4.4	7.8	--
G5	247 (1702)	326 (2246)	3.6	5.1	--
K2	255 (1757)	324 (2232)	3.0	3.5	6.1 (8.3)

B. Initial Lower Bainitic Treatment

D6, as-quenched	260 (1791)	330 (2274)	2.5	2.5	6.8 (9.2)
D6, 200°C tempered	243 (1674)	295 (2033)	2.8	6	15.0 (20.4)
D6, 400°C tempered	225 (1550)	246 (1695)	1.6	6.5	15.5 (21.1)
D6, 600°C tempered	128 (882)	146 (1006)	3.5	11.0	80.0 (108.8)
D5	242 (1667)	302 (2081)	2.6	4.4	11.0 (15.0)

C. Single Cycle 900°C Austenitizing Treatment

E1 (30 min. holding)	245 (1688)	330 (2274)	2.8	2.8	3.8 (5.2)
E2 (60 min. holding)	260 (1791)	330 (2274)	1.8	1.8	3.7 (5.0)

TABLE II

Heat-treatment	Test Specimen #	Thickness of Specimen (inches)	P_m/P_0	Plane Strain Fracture Toughness K_{IC} (ksi-in ^{1/2}) (MNm ⁻² -m ^{1/2})	K_{IC}/γ -s (in ^{1/2})
C3	C31	0.862	1.00	42.3 (46.4)	0.16
	C32	0.581	1.00	33.00 (36.2)	0.13
D6	D61	0.830	1.11	36.5 (40.1)	0.14
	T1C31	0.861	1.00	52.5 (57.6)	0.22
C3 (200°C tempered)	T1C32	0.581	1.00	51.0 (56.0)	0.22
	T1D61	0.830	1.02	52.1 (57.2)	0.21
D6 (200°C tempered)	T2C31	0.862	1.00	61.2 (67.2)	0.28
	T2D61	0.832	1.00	58.1 (63.8)	0.25
D6 (400°C tempered)	G71	0.862	1.00	77.6 (85.2)	0.33
	G72	0.581	1.00	39.1 (42.9)	0.17
D5	D51	0.830	1.00	58.8 (64.6)	0.24
	K21	0.581	1.00	33.6 (36.9)	0.13
K2	K22	0.581	1.03	32.9 (36.1)	0.13
	G51	0.581	1.00	33.2 (36.5)	0.13
G5	G52	0.581	1.00	34.7 (38.1)	0.14
	C91	0.581	1.00	34.8 (38.2)	0.13
C9	C92	0.581	1.00	36.0 (39.5)	0.14
	G61	0.581	1.00	45.8 (50.3)	0.21
G6	E21	0.504	1.00	27.8 (30.5)	0.11
	E22	0.504	1.00	28.5 (31.3)	0.11

TABLE III

Specimen	Isothermal Heat Treatment			Tempering Temp. °C	Yield Strength ksi (MNm ⁻²)	Ultimate Tensile Strength ksi (MNm ⁻²)	Uniform Elongation %	K _{IC} ksi-in ^{1/2} (MNm ⁻² -m ^{1/2})	Charpy V-notch ft-lbs (N-m)
	Time	Cooling Rate							
1-A	360°C	15 min.	H ₂ O Quench	--	165 (1137)	230 (1585)	5 *	35(38.4)	6.6 (9.0)
2-A		30 min.	H ₂ O Quench	--	162 (1116)	220 (1516)	4.7 *	--	6.6 (9.0)
3-A		60 min.	H ₂ O Quench	--	168 (1158)	220 (1516)	2.5 *	--	7.5 (10.2)
4-A		15 min.	Air Cool	--	178 (1226)	230 (1585)	5 *	--	6.5 (8.8)
5-A		15 min.	H ₂ O Quench	500	172 (1185)	201 (1385)	3.5 *	--	7 (9.5)
1-B	330°C	15 min.	H ₂ O Quench	--	192 (1323)	250 (1723)	3.5 *	37(40.6)	7 (9.5)
2-B		60 min.	H ₂ O Quench	--	193 (1330)	234 (1612)	4.7	35(38.4)	5.5 (7.5)
3-B		15 min.	Air Cool	--	190 (1309)	250 (1723)	4.3	--	6 (8.2)
4-B		15 min.	H ₂ O Quench	300	186 (1282)	245 (1688)	3.0	28(30.7)	
5-B		15 min.	H ₂ O Quench	350	187 (1288)	240 (1654)	2.5 *	28(30.7)	
6-B		15 min.	H ₂ O Quench	400	187 (1288)	235 (1619)	3.5 *	29.(31.8)	
7-B		15 min.	H ₂ O Quench	500	180 (1240)	210 (1447)	2.5 *	--	6.5 (8.8)

*Failed before onset of necking

- Fig. 1. Schematic illustration of heat-treatments employed to produce martensitic structure.
- Fig. 2. Isothermal transformation diagram for the steel.
- Fig. 3. Charpy impact transition curve of the lower bainitic specimen 1-B (Table 3).
- Fig. 4. Plot of mechanical properties of C3 and D6 vs. tempering temperature.
- Fig. 5. Plot of plane strain fracture toughness vs. yield strength.
- Fig. 6. Plot of Charpy impact energy vs. yield strength.
- Fig. 7. (a) and (c) illustrate the typical morphology and substructure of martensite of treatments C3 and D6 respectively, (b) illustrates the carbide morphologies in as-quenched structures of C3 and D6 and (d) reveals the presence of twinning in these specimens.
- Fig. 8. (a) and (b) B.F. and D.F. pictures showing lower bainite structure in foils obtained from thicker K_{IC} specimens of C7 and D5 treatments, (c) reveals presence of substructural twinning in martensite of these specimens and (d) illustrates extensive tempering in martensite and the numerous, thick $\{110\}_m$ widmanstätten cementite.
- Fig. 9. Carbide precipitation in martensite in interrupted-quenched specimens of C7 and D5. (a) is the B.F., (b) is the D.F. from a twin reflection, (c) is the D.F. from a carbide reflection, (d) is the SAD pattern and (e) is the analysis of the pattern. The twinning plane of the twin related laths is $(\bar{1}21)_m$.

Fig. 10. Typical 200°C tempered microstructures of treatments C3 and D6. (a) is the B.F. showing carbide precipitation and (b) and (c) are B.F. and D.F., respectively, revealing untransformed austenite.

Fig. 11. Typical 400°C tempered structures of C3 and D6. (a) shows $\{110\}_m$ carbides with irregular interfaces indicating they may be dissolving (b) illustrates lath boundary carbide precipitation (indicated by arrow), presumably from the break-up of existing austenite films. (c) and (d) also reveal preferential precipitation of spherical carbides at lath boundaries in B.F. and D.F. respectively.

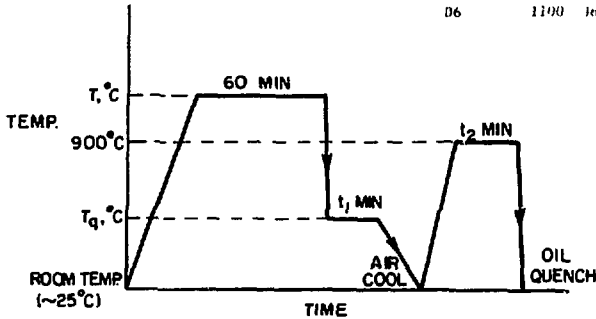
Fig. 12. Carbides in specimens tempered at 600°C.

Fig. 13. Tempered martensite wedged between plates of bainite.

Fig. 14. Bainite at 330°C, transformation time 15 min., (b) is bainite at 360°C, (c) and (d) martensite regions trapped between bainite plates.

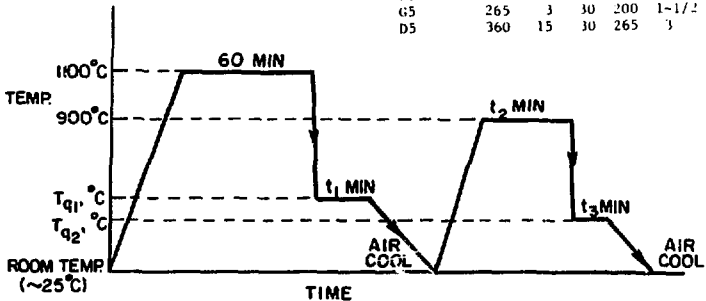
Fig. 15. (a) Fractograph of lower bainitic Charpy impact specimen (see Table 3) and (b) is the fractograph of lower bainitic treatment 1-B.

Heat-treatment	T	t _q	t ₁	t ₂
C3	1100	265	3	30
C9	1100	265	3	60
K2	1200	265	3	30
D6	1100	160	15	30



(c)

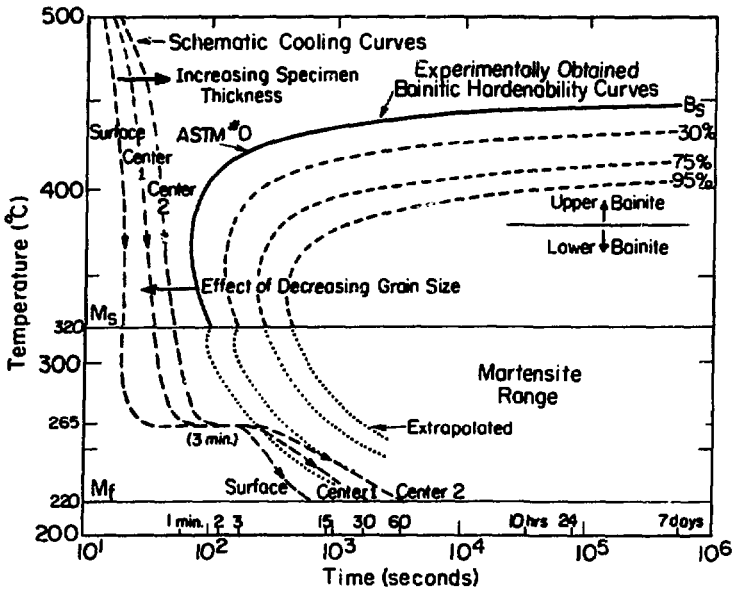
Heat-treatment	T _{q1}	t ₁	T ₂	t _{q2}	t ₃
C7	265	3	10	265	3
G6	265	3	60	265	3
G5	265	3	30	200	1-1/2
D5	360	15	30	265	3



(b)

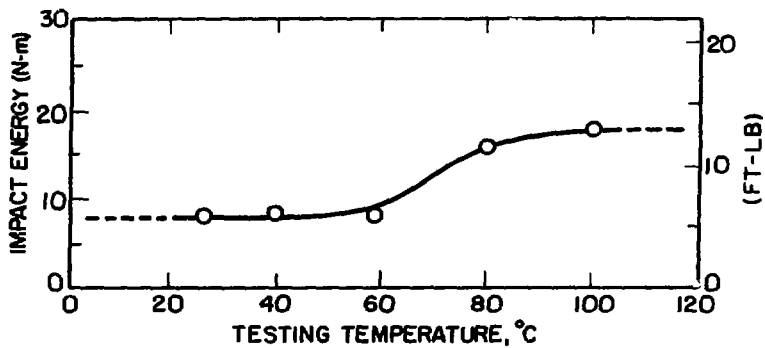
XBL754-6177

Fig. 1



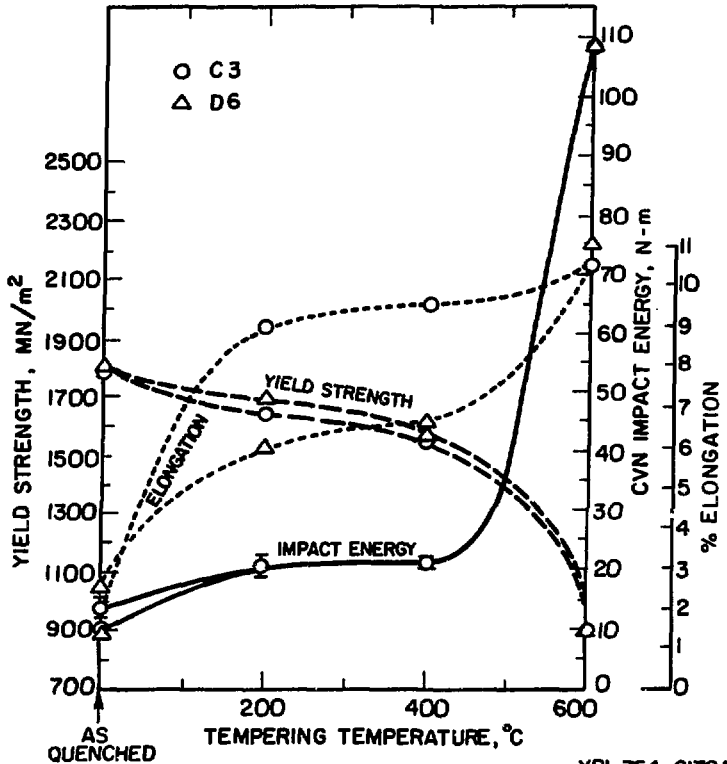
XBL 7511-7577

Fig. 2



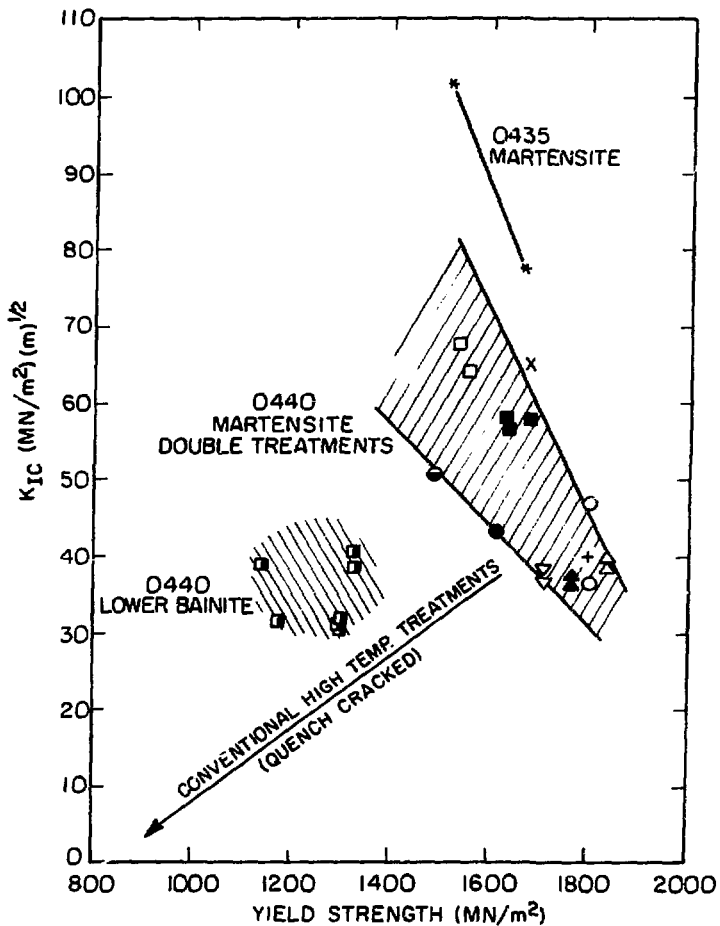
XBL 747-6798A

Fig. 3



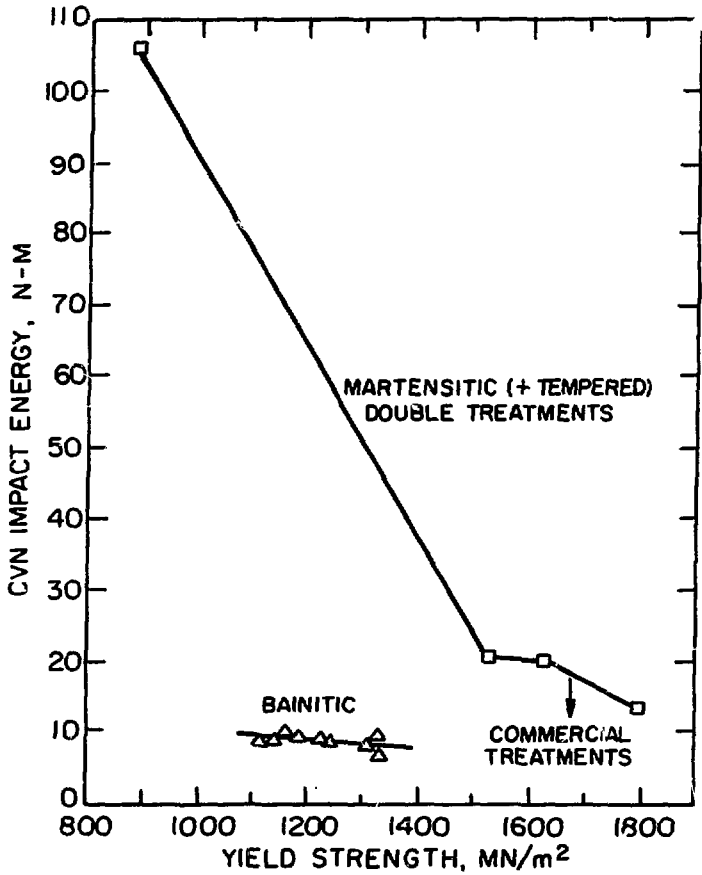
XBL 754-6178A

Fig. 4



XBL 754-6180A

Fig. 5



XBL 754-6181A

Fig. 6

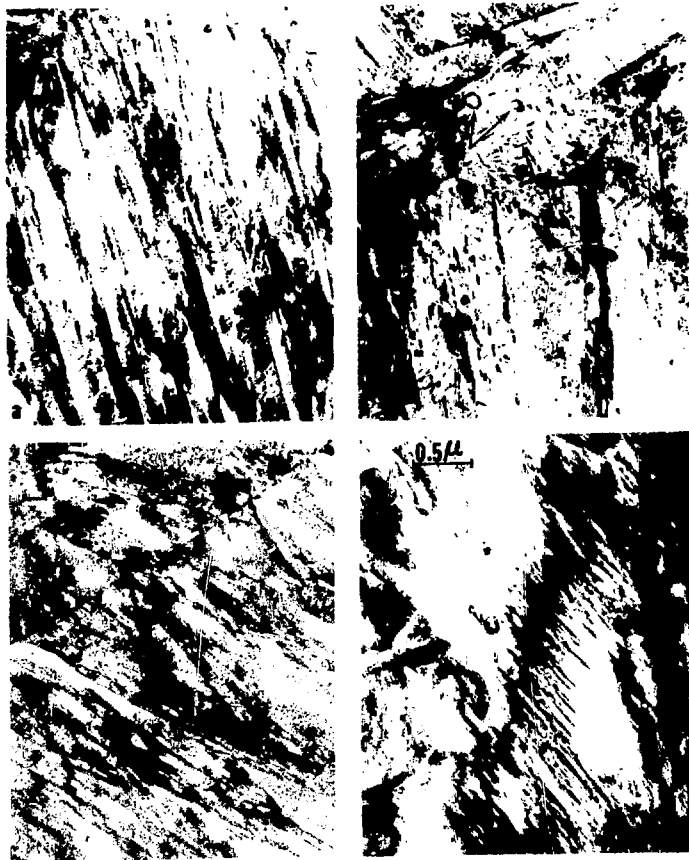


Fig. 7

XBB 755-3484

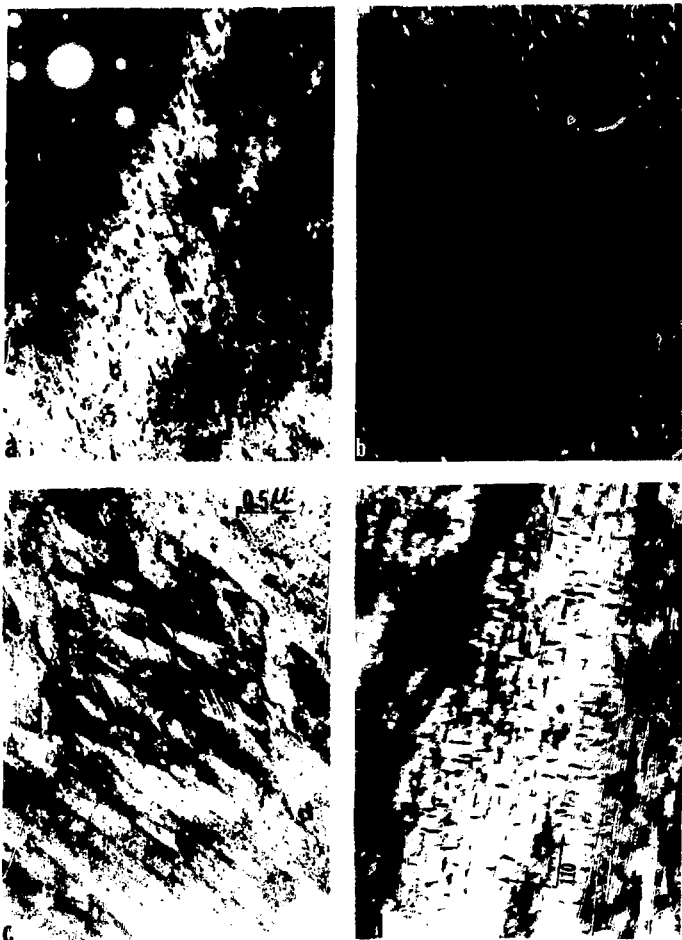
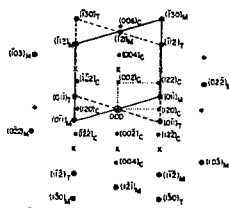
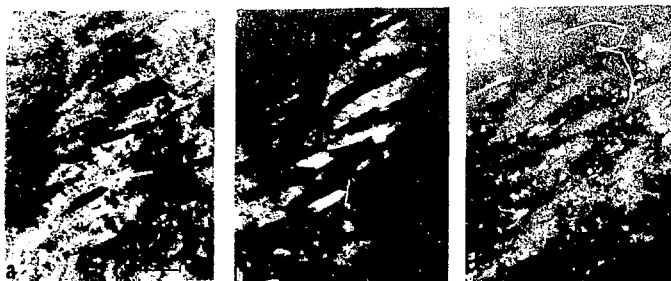


Fig. 8

XBB 755-487



e

Fig. 9

XBB 755-3482



Fig. 10

XBB 755-3488

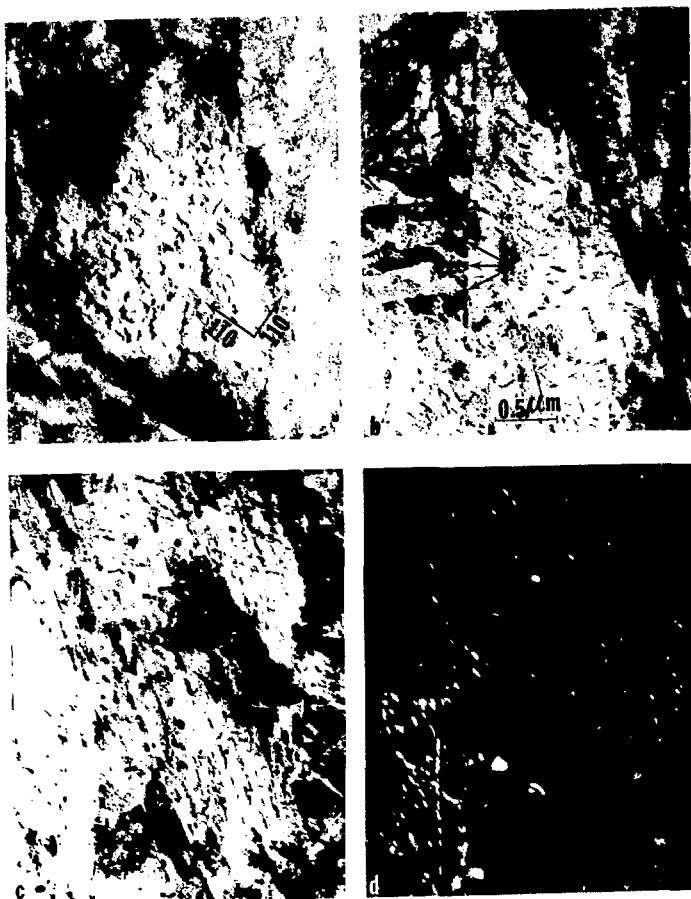


Fig. 11

XBB 755-8799



Fig. 12

XBB 755-8801

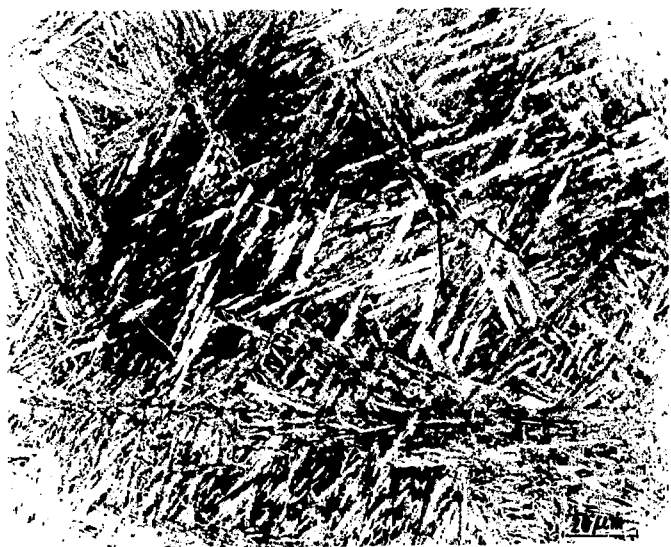


Fig. 13

XBB 755-8802

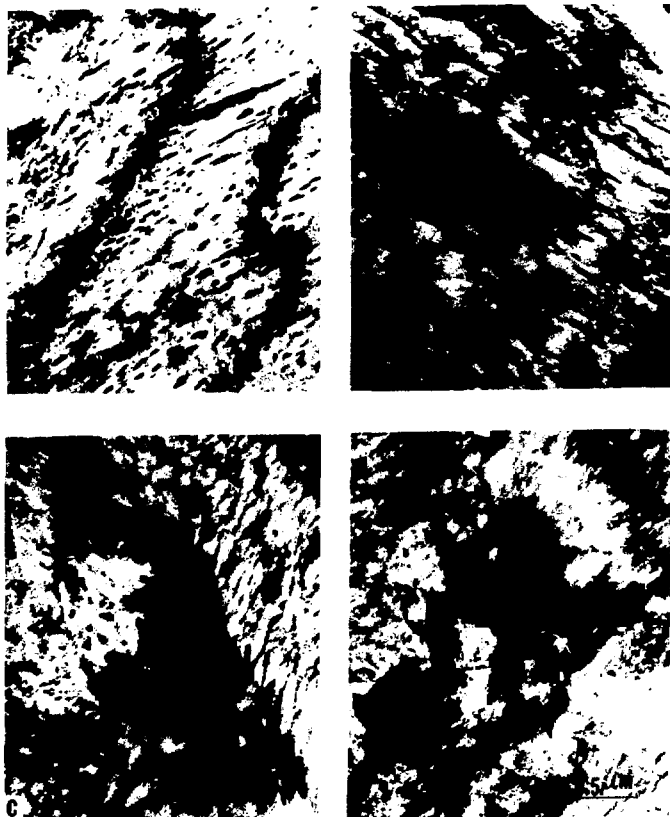


Fig. 14

XBB 755-8800

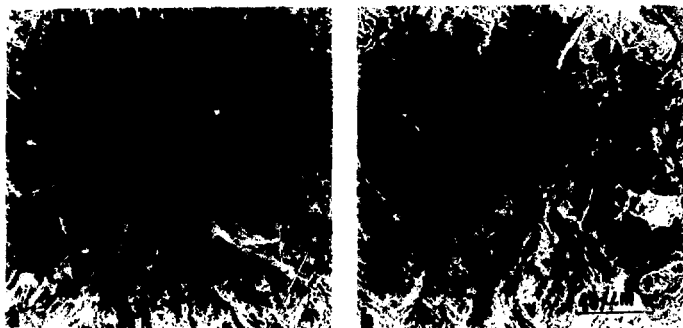


Fig. 15

XBB 755-8803