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STRUCTURE AND MECHANICAL PROPERTIES OF Fe-Cr-C-Co STEELS

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ABSTRACT

As part of a continuing program concerning the microstructures and mechanical properties of steels in which particular attention is given to transformation substructures, the present work is concerned with martensite and bainite in Fe-Cr-C steels with and without cobalt. Although cobalt raises the M_s temperature it does not affect the extent of twinning for the same carbon level and so M_s temperature alone does not control transformation substructure. Thus cobalt is not effective in retaining dislocated martensite as carbon is increased and in this regard cobalt is not beneficial to toughness.

The M_s temperatures of the steels were relatively high and hence isothermal transformation yielded mixtures of bainites and tempered martensite depending on the temperature of transformation. The mechanical properties of the isothermally transformed steels were inferior to that of the tempered steels due to the interference of upper bainite or (tempered) martensite during the isothermal transformation. Thus, in the steels having high M_s temperatures, the twinned tempered martensitic structure had relatively better mechanical properties compared to the isothermally transformed steels. Attempts to produce desirable autotempered structures by continuous cooling (single heat treatments) were not successful and did not improve the mechanical properties since the structure consisted of a mixture of bainite and martensite.

INTRODUCTION

In recent years considerable interest has been directed towards the production of high-strength steels with appreciable toughness. Many processes have been successfully developed recently[1,2,3] but all of them involve mechanical treatment in addition to heat treatment. It would be very attractive to develop high strength and high toughness by heat treatment alone. High strength is easily obtained simply by quenching steels with increasing carbon contents, but as is well known, there is a corresponding decrease in toughness. This may be associated with the change from dislocated to twinned martensite. Low carbon (less than 0.25%) martensite consists mainly of laths[4,5,6] with a high dislocation density. In high carbon (more than 0.3%) martensites the structure consists mainly of plates rather than laths and many of the plates are internally twinned. The formation of twins in the high carbon steels are associated with a decrease in the M_s temperature of the steels. Based on experimental evidence,[5-8] it has been suggested that the M_s temperature of the steel could be the controlling parameter for twinning. If this is true, it should be possible to eliminate the formation of twins in the martensite by raising the M_s of the steel. It has been suggested[5,9] that the presence of twins could seriously affect the fracture toughness which, in turn, would imply that the M_s temperature is a key parameter in controlling the twinning and hence the fracture toughness. Since cobalt is known to raise M_s it may be possible to have both high carbon and untwinned martensite in cobalt bearing alloys, although a recent investigation in Fe-Ni-C steels showed cobalt was not effective in reducing twinning.[10]

In the present work two steels with the same carbon (0.35%C) and chromium (4% Cr) but one without cobalt and the other with 5.3% cobalt were chosen in addition to a low carbon steel (Table 1). The steels are referred to by their heat numbers.

A brief study of the mechanical properties of the tempered martensite and bainite was done to evaluate their relative merits and demerits. For example, it has been shown[10-14] conclusively that in a high carbon steel, the mechanical properties of the tempered twinned martensite are inferior to those of twin-free[15,16] bainites. However, contradictory observations have also been made.[17,18] In low carbon steels, tempered martensite, having no twins, seems to be superior to bainitic steels. Continuous cooling was also attempted in order to see if desirable structures and properties could be obtained in the treatment.

EXPERIMENTAL PROCEDURE

Heat Treatment

The ingots were placed in cast iron tubes and packed with cast iron chips to prevent decarburization and then homogenized at 2300°F for three days. Pieces were cut from the homogenized ingots, forged, and finally rolled to the required thickness.

The specimens were homogenized in an argon atmosphere at 1800°F for an hour and then quenched directly into water. They were immediately transferred to a liquid nitrogen dewar and stored there for about an hour to ensure complete transformation of any untransformed austenite. For tempering and isothermal transformations, low-temperature salt baths were used, operating in the range of 350°F to 1050°F. Tempering was done at four different temperatures for 4 hours followed by quenching in water. For isothermal transformations, the specimens were directly quenched into the salt bath operating at the required temperature and then held for the required period. The heat-treated specimens were sandblasted to remove any decarburized layer. For continuous cooling studies, the specimens were dropped out of the furnace after homogenization and then were allowed to cool in air.

Mechanical Testing

Tensile tests were performed in an Instron machine with a cross-head speed of 0.0423"/sec (0.1 cm/min). Impact testing was performed at room temperature using a substandard Charpy impact machine using a 16-ft-lb hammer. The impact values listed in the tables thus correspond to the 16-ft-lb hammer.

Electron Microscopy

Specimens for the electron microscope were about 30 to 40 mils thick and were heat-treated together with the tensile and impact specimens. The bulk specimens were then chemically thinned in H_2O_2 containing 2% HF at room temperature. The specimens were thinned chemically to about 4 mils thick and then electropolished. Disks of the size of the standard Siemens specimen holder were punched and then polished in a twin-jet polishing apparatus. Electropolishing was done using a chromic-acetic acid solution (75 gms CrO_3 + 400 ml acetic acid + 20 ml of distilled water). The voltage varied from 19-25 volts and the current varied from 12-16 milliamps. The polishing conditions, however, depended on the jet speed and the spacing between the jets. Normal polishing time was about three to six minutes depending on the thickness of the initial disk. The disks were then examined in a Siemens Elemiskop I microscope operating at 100 kV.

Electron Fractography

A two-stage plastic-carbon replica was employed for fracture studies. The fracture surfaces of the Charpy specimens were replicated with cellulose-acetate tape followed by shadowing with chromium chips at a 45° angle to the surface, and finally carbon was normally evaporated on the surface. The tape was then dissolved in acetone and the carbon film was dried and examined at 80 kV and at a magnification of 6000x.

RESULTS

Mechanical Properties of Tempered Martensite and Bainite

Figures 1-4 summarize the mechanical properties of the tempered steels. All the steels showed similar behavior on tempering as shown in Figs. 1, 2 and 3. When tempered at 400°F, the tensile and yield strengths decreased with an attendent increase in ductility and notch toughness. The softening rate decreased when tempered in the range of 600-800°F followed by a rapid softening on tempering at 1000°F. The notch toughness values showed a slight increase on tempering at 400°F then remained fairly constant up to 800°F tempering and then increased considerably at 1000°F. Seal and Honeycombe[19] also found an arrest in the mechanical properties on tempering a 9 Cr-0.21% C steel and they attributed this to the stabilization of cementite precipitates. However, Ronald and Bodsworth,[20] from their work on 5 Cr-0.2% C steel, indicated the possibilities of nucleation of Cr_7C_3 on tempering.

In general, the mechanical properties of isothermally decomposed steels were inferior to those of tempered martensite. Figure 4 summarizes the properties of both tempered and isothermally transformed steels. After continuous cooling, steel 12 had a higher strength and high toughness. Steel 24 had intermediate properties as compared to tempering or isothermal transformation treatments.

Morphology of Martensite

Electron microscopy showed that as quenched martensites of steel 12 and 26 were very similar and consisted of twinned plates and some dislocated laths. Figures 5 and 6 are representative of these structures. Thus a difference of +75°F between the M_s temperatures of steels 12 and 26 by adding 5% cobalt did not result in any significant change in the amount of twinning in the steels. Steel 24, which had 0.28% C, showed mainly dislocated laths and some twinned plates (Fig. 7).

Autotempering was observed in steel 26 and it was of interest to observe that the autotempered precipitates were not present in any of the twinned plates but were only resolved in the dislocated laths and untwinned plates. This strongly suggests that dislocated laths and untwinned plates form first near M_s and the twinned plates at lower temperatures, i.e. near M_f.

Tempered Martensite

On tempering at 400°F, most of the carbides were cementite, although in some regions, wavy ε-carbide was also observed. The latter could be identified by trace analysis since the traces were close to {001} and not {110} nor {112} typical of Fe_3C. The carbide morphology was considerably altered in the presence of twins. Twin boundary precipitation of cementite started to form when tempered at 400°F as indicated in Fig. 8. The carbide nucleated discontinuously along the twin boundaries (Fig. 8c) and then subsequently grew coarser on further tempering. The cementite precipitation in an untwinned plate was of Widmanstatten {110} type (Fig. 9a). Carbides other than Fe_3C (e.g. Cr_7C_3) were not detected.

Precipitation of carbides along plate boundaries and prior austenitic grain boundaries were observed at tempering temperatures above 600°F. Figure 9b shows carbide precipitation along plate boundaries and in the matrix when tempered at 800°F. Tempering at 1000°F resulted in coarsening of the precipitates but did not produce any recrystallization of ferrite.

Structure of Isothermally Transformed and Continuously Cooled Steels

Since the M_s temperatures of the steels are relatively high, isothermal transformations carried out just above the M_s temperature resulted in a mixture of lower and upper bainite (Fig. 10). Increasing the transformation temperatures increased the proportion of upper bainite and a decrease in the temperature decreased the proportion of upper bainite but increased the amount of tempered martensite. It was not possible to obtain 100% lower bainite in these steels. The carbides in the lower bainite were identified to be cementite by electron diffraction.

When continuously cooled, steel 12 showed a mixed structure of upper bainite, lower bainite and autotempered martensite. The width of bainitic ferrite laths in the continuously cooled steel was smaller than the ones formed isothermally. No martensite was detected in continuously cooled specimens of steel 26. This difference in structure probably accounts for the considerably higher strength of normalized steel 12 compared to steel 26 (Fig. 4).

Fractography Studies

Figure 11 is a fractograph of steel 12, as quenched, and shows cleavage rupture whereas Fig. 12 shows the same steel fractured after tempering at 1000°F. This failure is typically a dimpled rupture. Figure 13 is the fracture surface of steel 12 after being tempered at 600°F where the arrest in the yield strength had occurred. Since this steel did not show any predominantly intergranular failure, Fig. 13 indicates that the failure was not due to any grain boundary carbide precipitation.

DISCUSSION

Martensite Substructure and Effect of M_s on Twinning

In steel 26 autotempering was observed only in the dislocated lath martensite and not in the twinned martensite, suggesting that the twinned martensite was formed after the dislocated martensite and at lower temperatures. While this temperature dependence of the martensite substructure in the same steel is confirmed, the results of the effects of cobalt showed that although 5% cobalt raised M_s by 75°F there was no decrease in twinning. However, alloy 24 of similar M_s but lower carbon (Table 1) was mostly dislocated. This indicates that M_s itself is not the controlling parameter on twinning. Considering that it takes more than about 28% nickel to obtain twinned martensite in Fe-Ni alloys (M_s ~ 70°F) and 0.3% C in Fe-C alloys (M_s ~700°F), it is difficult to directly relate M_s temperature and twinning for steels in general. Alloying elements not only alter M_s but also other factors, such as the critical resolved shear stress for slip and twinning. Even if M_s is high the CRSS for slip may be larger than that for twinning so that twinned martensite is formed. This is probably the reason for the very large effect that carbon has on the substructure (and strength) of martensite. Further discussion of these factors has recently been made.

The present results confirm those of Das and Thomas[10] in that cobalt does not appear to be effective in reducing twinning and consequently from this viewpoint cobalt is not beneficial to toughness. Thermal-mechanical treatments such as ausforming are effective but in these cases carbides are formed prior to transformation to martensite so that

the martensite itself is then low carbon and dislocated. Thus, at the present time it appears impossible to produce twin free high carbon martensite, which was one of the aims of this project.

Structure and Mechanical Properties of Tempered Martensite

The observed resistance to softening cannot be attributed to twin boundary or plate boundary carbide precipitation since such precipitation occurs at all tempering temperature above 400°F.

Earlier workers[19-23] have shown that in Fe-Cr steels Cr_7C_3 forms at tempering temperatures above 500°C below which cementite is the stable carbide. Ronald and Bodsworth[20] have demonstrated that in Cr bearing steels having less than 2% Cr, Fe_3C-Cr_7C_3 transition occurs in situ and with increasing Cr contents of the steel, the tendency for the in situ transition decreases, and independent nucleation of Cr_7C_3 is favored.

The arrest in the mechanical properties in the 600 - 800°F tempering range for the present steels cannot be attributed to the resistance to coarsening of the cementite particles as has been suggested for Fe-9 Cr-0.21 C steel.[19] This would mean that the carbide particle size is unaltered in the above mentioned tempering range. On comparing Figs. 9a,b it is evident that this is not true since there is considerable coarsening when tempered at 800°F. The Widmanstatten cementite at 400°F is replaced by coarse partially spherodized carbides at 800°F.

Attempts were made to identify carbides other than iron carbides by electron diffraction and x-ray microprobe analysis but this was not successful except for overtempered steels (i.e. tempered 1000°F for 4 hrs) where Cr_7C_3 was found. Consequently, it has not been proved that the

arrest in softening upon tempering can be explained by independent precipitation of chromium carbide(s) as suggested by Ronald and Bodsworth.[20]

Effect of Twinning on Toughness

Earlier results[10,11] indicate that twinned martensite structures have inferior notch toughness when compared to twin free bainitic structures of equivalent strengths. The transformation twins in the as-quenched martensite alter the morphology of the subsequent carbide precipitation on tempering. In steels, one cannot evaluate the effect of twins on the toughness because the effect of carbide morphology comes into play on tempering. It is not clear whether the decreased toughness of the twinned structures compared to that of the twin free lower bainite is due to the twins in the martensite or due to carbide precipitation along the twins, or both.

CONCLUSIONS

1. For the same carbon content, an increase in M_s temperature does not decrease twinning and hence M_s is not the sole factor determining twinning. Thus, two steels having the same M_s temperature but different composition need not exhibit the same extent of twinning.
2. The morphology of martensite (laths or plates, twinned or untwinned) is predominantly affected by carbon rather than the substitutional alloying elements. Hence, it does not seem practicable to produce a twin-free high carbon martensite in the common structural steels.
3. Although M_s is no indication of twinning when comparing two different steels, in the same steel the temperatures at which martensite forms (M_s-M_f) determine the extent of twinning in the plates. Plates formed initially were relatively less twinned compared to the ones formed later at lower temperatures.
4. The observed arrest in softening during tempering is not accompanied by resolvable changes in precipitation. Thus it is not proved that small amounts of chromium carbide may have nucleated.
5. In steels having high M_s temperatures, isothermal transformations do not yield superior structures because of the formation of upper bainite. In such steels, tempered martensite has better mechanical properties (in spite of the twinned structure).
6. The width of the bainitic ferrite laths formed during continuous cooling is smaller than the ones formed by isothermal transformations.
7. Addition of 5% Co in the steels does not improve the mechanical properties of the steels.

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Table I. Chemical composition of alloys used in this investigation.

	Heat No.	Composition				M_s* temperature
		%Cr	%C	%Co	%Fe	°F
1	12	4	0.343	0	bal	660
2	26	4	0.351	5.3	bal	735
3	24	4	0.281	1.4	bal	725

FIGURE CAPTIONS

Fig. 1. Effect of tempering on the mechanical properties of steel 12.

Fig. 2. Effect of tempering on the mechanical properties of steel 26.

Fig. 3. Effect of tempering on the mechanical properties of steel 24.

Fig. 4. Yield strength vs. notch toughness plot of the heat treated steels. Plots marked "N" correspond to continuously cooled steels.

Fig. 5. Bright field image showing extensive twins in martensite of steel 12.

Fig. 6. Dark field micrograph of as-quenched martensite in steel 26 showing reversal of contrast of twins.

Fig. 7. Bright field micrograph showing dislocated martensite in steel 24.

Fig. 8. Steel 26, quenched and tempered at 400°F for 4 hrs. (a) Dark field image of (110) twin spot reversing contrast of the twins. (b) Bright field micrograph of extensive twins. The cementite precipitated along the twins are not clearly visible in the bright field image but the dark field micrograph of a cementite reflection (c) reverses the contrast of carbides at the twins.

Fig. 9. (a) Bright field image of steel 26, quenched and tempered at 400°F showing typical Widmanstatten type cementite precipitation and (b) dark field image of the same steel quenched and tempered at 800°F showing reversal of contrast of cementite at the lath boundaries and within the laths.

Fig. 10. Steel 26, isothermally transformed at 750°F for 24 hrs. (a) Bright field micrograph showing regions of upper bainite where cementite forms at the lath boundaries. (b) Bright field image showing lower bainite.

Fig. 11. Replica fractograph of martensite of steel 12 showing cleavage failure.

Fig. 12. Replica fractograph of steel 12 quenched and tempered at 1000°F showing dimple rupture.

Fig. 13. Replica fractograph of steel 12 quenched and tempered at 600°F showing dimple rupture.

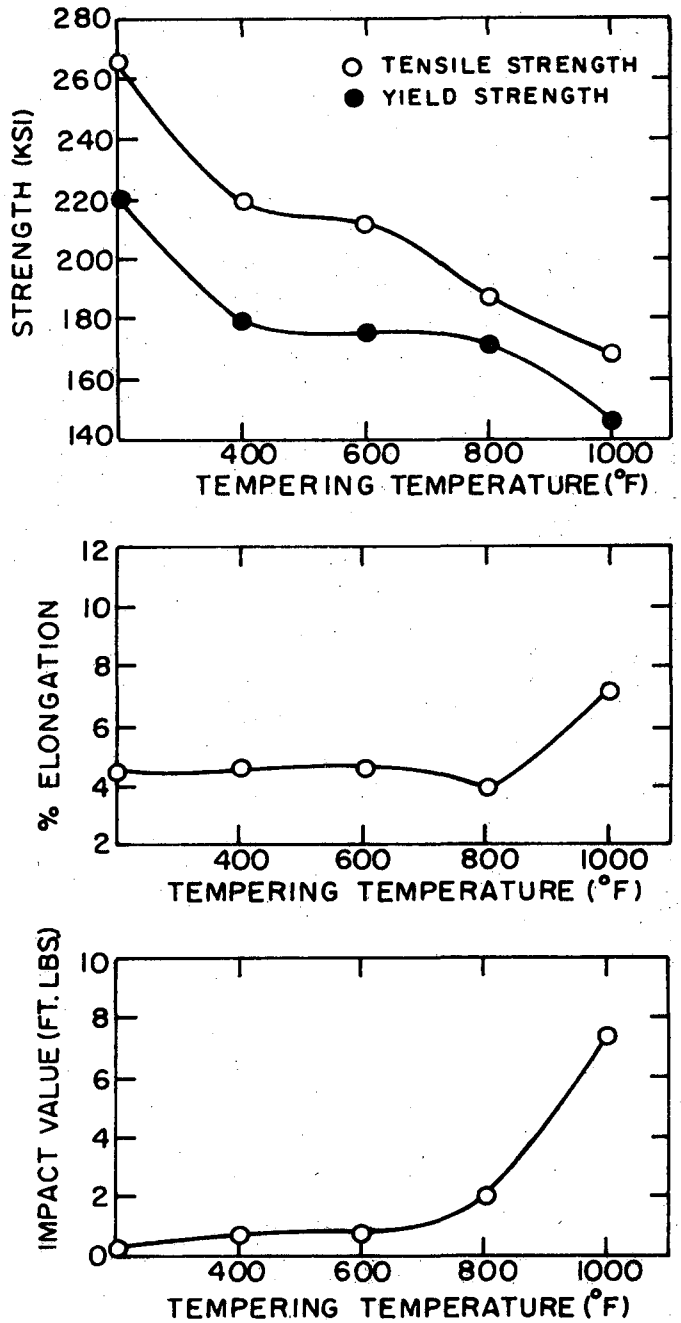

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Fig. 1

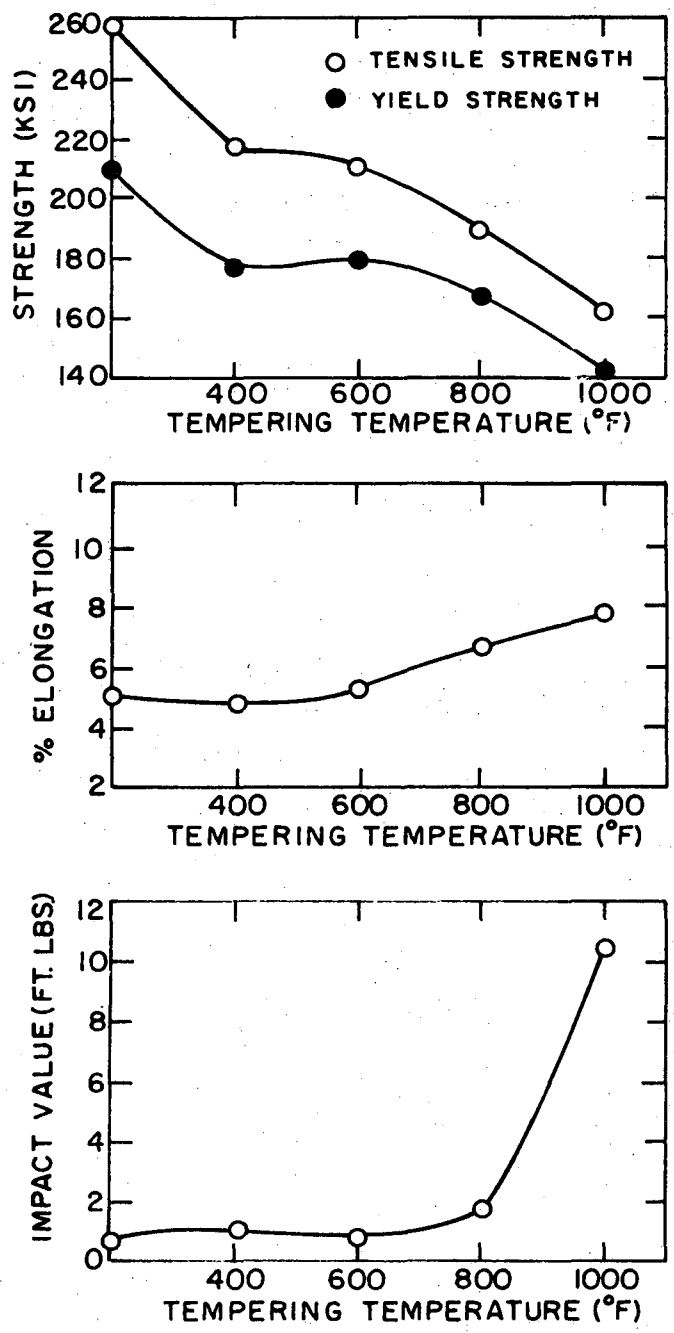

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Fig. 2

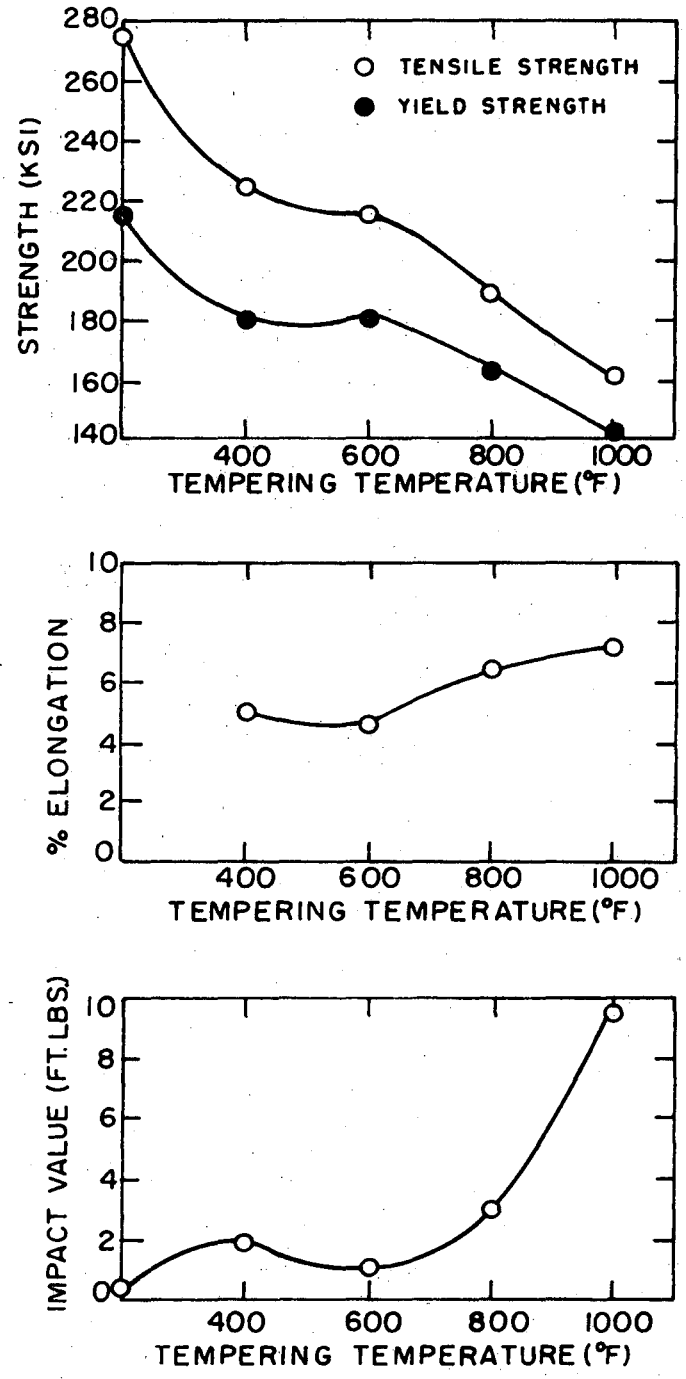

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Fig. 3

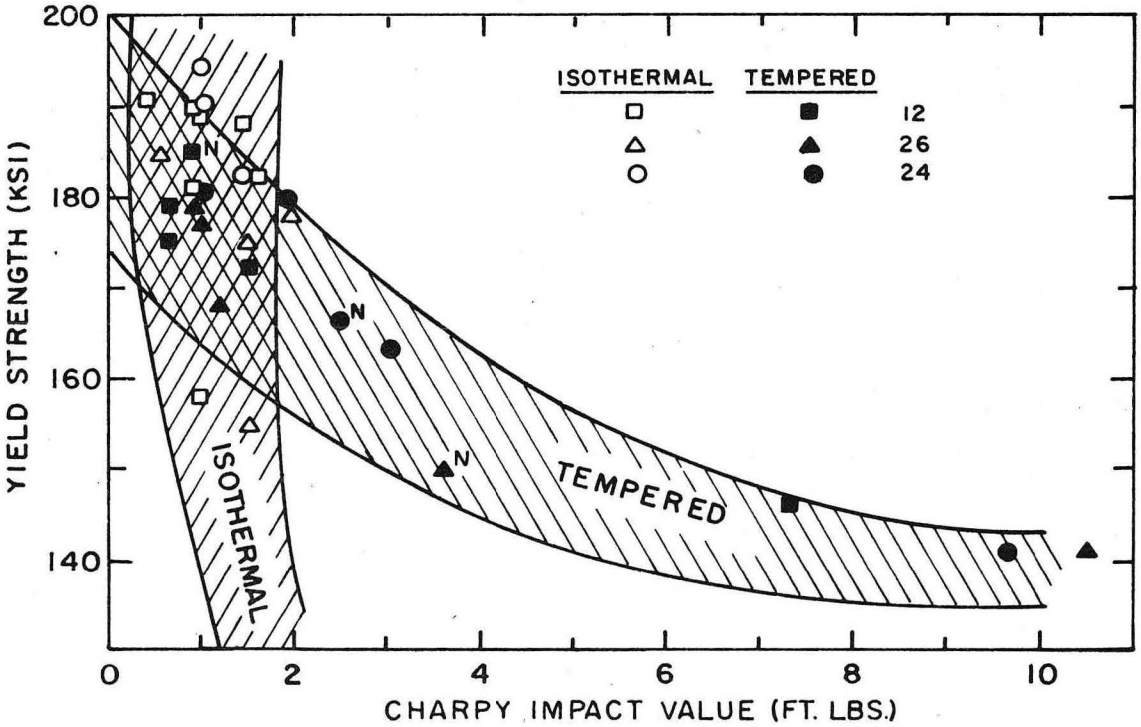

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Fig. 4

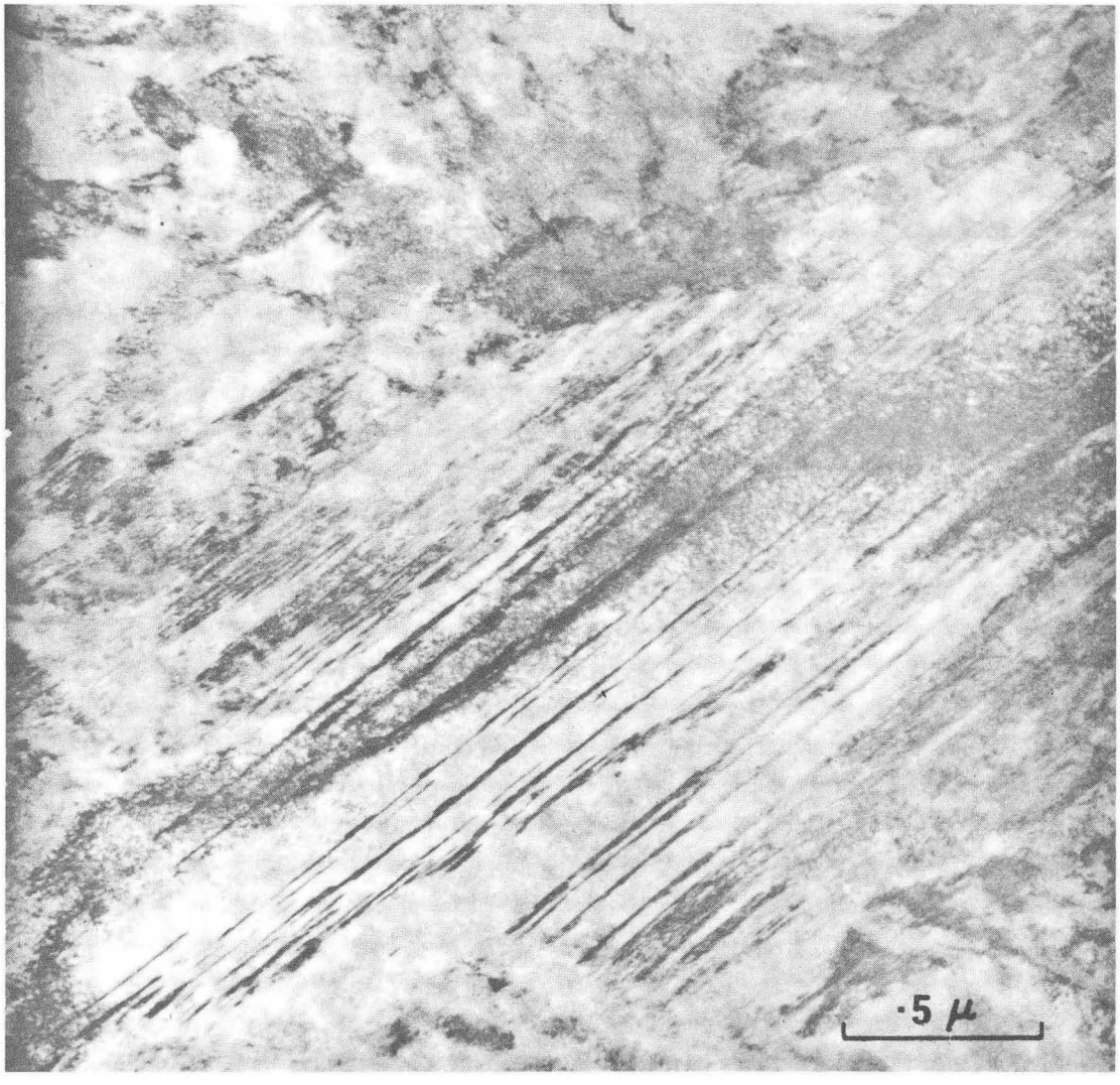

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Fig. 5

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Fig. 6

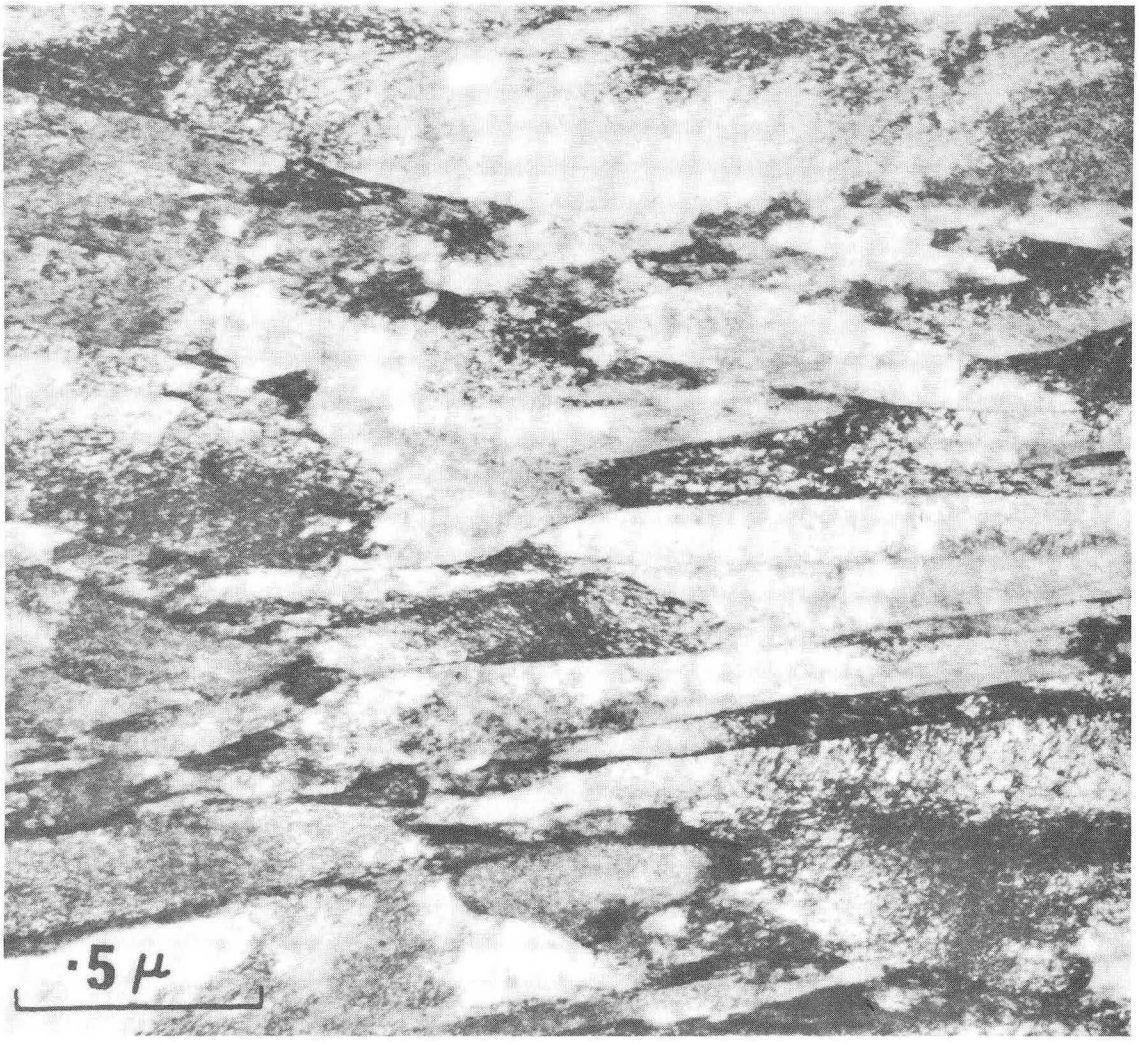

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Fig. 7

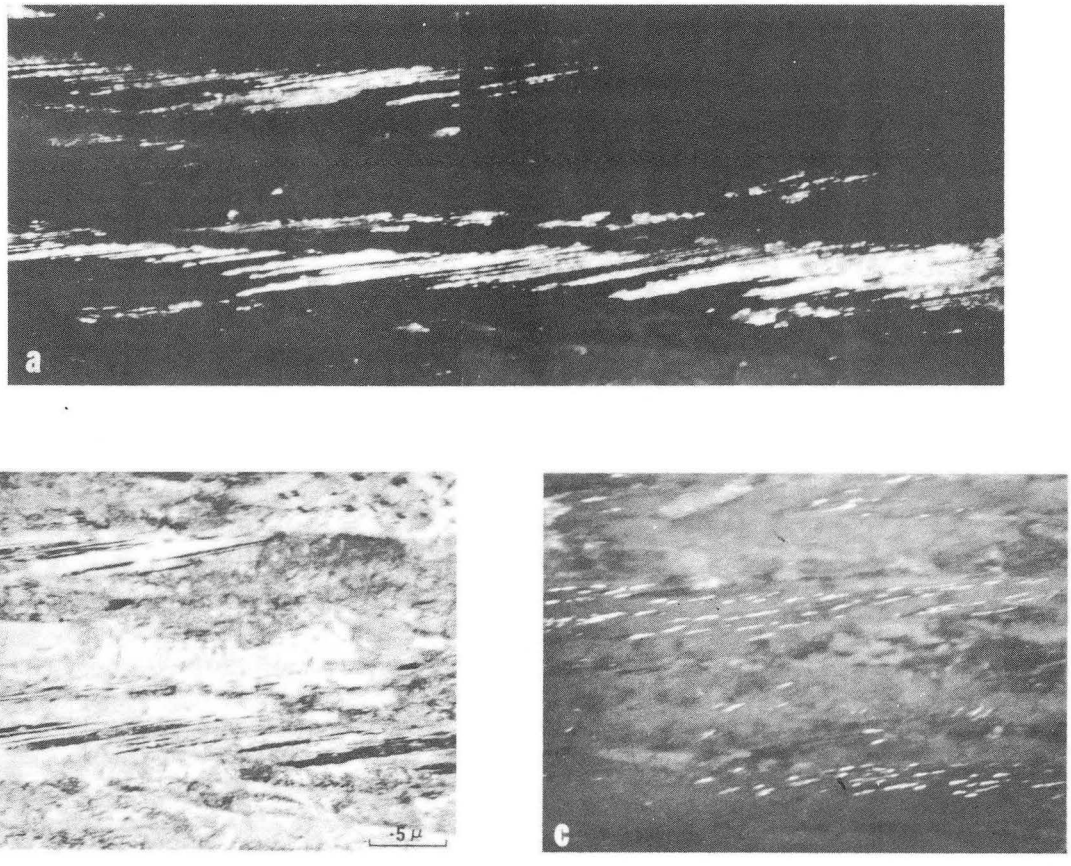

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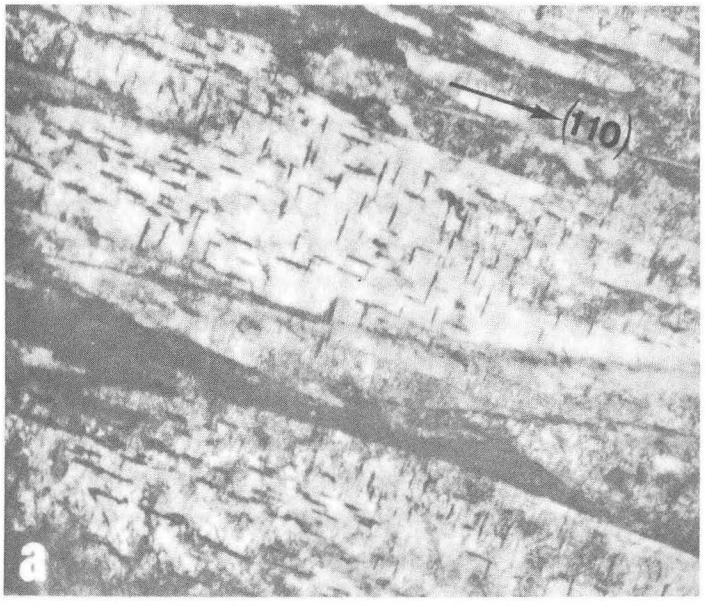
Fig. 8



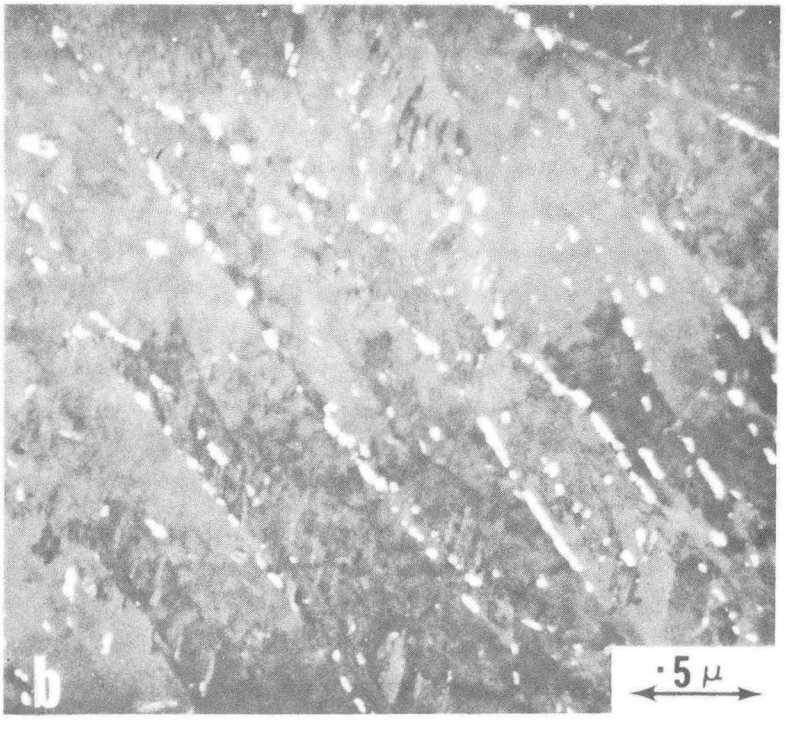


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Fig. 9

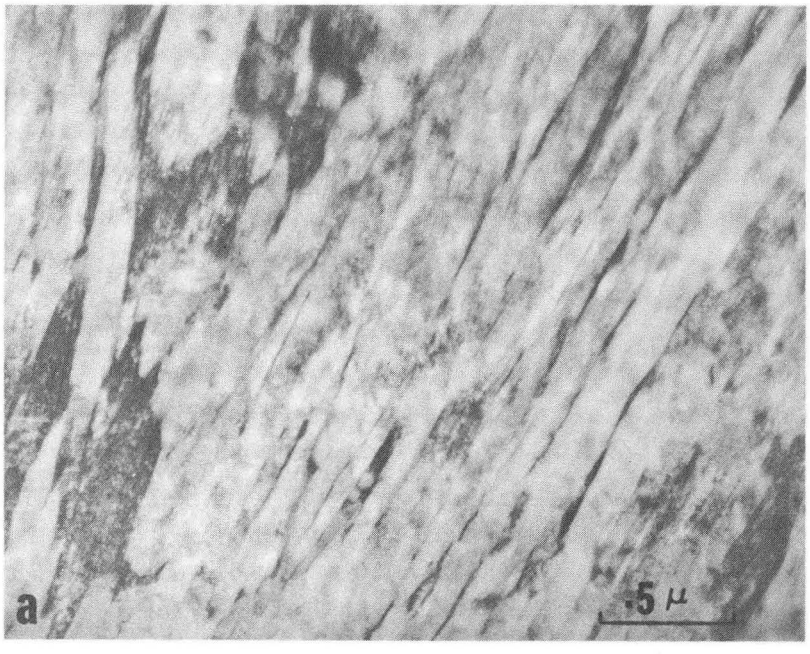

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Fig. 10

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