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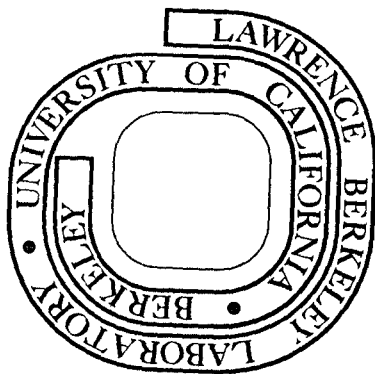
G. Thomas and J-Y Koo

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DISCLAIMER

Developments in Strong, Ductile Duplex Ferritic - Martensitic Steels[(*)]

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ABSTRACT

This paper is concerned with the morphology and structure-property relations in a range of duplex ferritic-martensitic (DFM) steels. It is shown that the properties depend, in a complex way, on all the parameters of the equation of mixtures viz. ferrite and martensite strengths and volume fractions. These parameters depend on alloy composition and heat treatments. Morphology is especially important in controlling ductility, hence the intial microstructure and the path by which the final ferrite-martensite mixtures is obtained is very important. Disolcation dynamics must be accounted for to explain the ductility and work-hardening behavior. Alloys have been designed by which the tensile properties are essentially independent of volume fraction of martensite, at least up to 0.4. In principle, the strength (and ductility) can increase, decrease or be constant with % martensite depending on the balance between the properties of ferrite and martensite. In all cases the properties of DFM steels are superior to those of "conventional" HSLA steels.

Introduction

The interest in duplex ferritic – martensitic (DFM) low carbon steels has grown enormously in the past two years and many of the underlying principles have already been documented, e.g., in the recent symposium on "Modern developments in HSLA formable steels.[1] While this interest has been generated largely by the fuel crisis and its impact on the need for weight savings in transportation systems, the potential applications of dual phase alloys are broad indeed. In fact they form a new class of strong, ductile steels for applications requiring tensile strengths of the order of 100,000 psi. Essentially these duplex steels can be regarded as composites of strong lath martensite (Ms) and ductile ferrite (α) in which the mechanical properties can be optimized by controlling the composite morphology, the volume fraction of martensite, the carbon content of martensite, and the ferrite substructure.[1-4] This is done by aging at the appropriate temperature (tie-line) in the two phase ($\alpha+\gamma$) field and then quenching to transform the austenite into martensite. The principles of our alloy design program have been described previously;[4] proper choice of alloying elements is required to allow a favorable morphology to be obtained.[4] Optimum results have been achieved with simple economical steels, e.g., Fe/Si/C.[2]

One of the advantages of this method of obtaining DFM steels is that a "composite" is obtained by a phase tranformation alone, and in this case good coherency between the phases present can be achieved.[3] Consequently problems such as delamination which occur in mechanically formed composites can be minimized, and is not observed in the steels we have studied.

In most of the work reported so far, the strength of these two phase alloys is given empirically by the law of mixtures, independent of mor-

phology, viz:

$$\sigma_c = \sigma_m V_m + \sigma_\alpha (1-Vm) \qquad\qquad \text{eq. 1,}$$

where σ_m and σ_α are the strengths of martensite and ferrite and V_m and $[1-V_m]$ are their respective volume fractions. In general, the ductility also follows this relationship, but in an inverse manner to that for strength. Some of the factors to be considered in the applicability of this equation to DFM steels have been discussed earlier.[1-4] The need also to consider dislocation dynamics has been apparent when considering the significance of ferrite in the ductility and work hardening characteristics.

In this paper we summarize recent work in our Duplex Steel Design program at Berkeley, with emphasis here on the physical metallurgy including the following aspects:

1. The influence of the path by which the (α+Ms) two phase mixture is obtained (i.e., $\gamma \rightarrow [\alpha+\gamma]$, or (Ms or pearlite)$\rightarrow [\alpha+\gamma]$ on morphology, microstructure and properties, especially ductility.

2. The role of small amounts of ternary and quaternary alloying elements on structure and properties.

3. The determination of the factors associated with ferrite substructure and morphology and their effect on strength and ductility.

4. An analysis of the applicability of the law of mixtures equation and the importance of each parameter (equation 1.)

5. Although small amounts of austenite, retained at interlath boundaries within the martensite packets, have been observed in all of the steels examined, its significance if any, on the properties is not known at this time and will not be discussed here.

Principles of DFM Alloy Design

The main principles of alloy design used in our research program have already been discussed in our prior papers[2,4] dealing with 1010, 1020, Fe/Si/C and Fe/Cr/C alloys. In addition we point out the following aspects concerning our choices of alloying and treatments.

A.   Alloying Elements

1.   The effectiveness of alloying elements other than Si such as Al, Mo in increasing the slope of the A_3 line so as to increase the flexibility of the two phase annealing process, in controlling volume fraction and compositions of the two phases.

2.   Si and Al combinations should be effective in "grain refining" the martensite dispersion and also should inhibit coarse carbide formation especially at ferrite-martensite interfaces. Si and Al both increase the activity of carbon in ferrite and so should improve ductility.

3.   Additions of elements to improve hardenability e.g., carbide formers B ., Mo, Cr may also increase flexibility of processing but may also cause carbide precipitation. This effect has been studied in the present work.

B.   Heat Treatments

The scheme of heat treatments is shown in Fig. 1. These schemes illustrate the paths by which the two phase ferrite-martensite final microstructures can be obtained. Obviously good combinations of strengths and ductility can be achieved by direct cooling (Fig. 1(a)), and this is a very attractive method from an economic processing view-point since it is essentially a normalizing treatment, (the effectiveness depends on intial

hardenability). However, details of this transformation path and resulting properties will not be discussed in this paper.

C. Alloys Investigated

    1. Prior work[2,4,5]

        Fe/0.5Mn/0.1C 1010 commercial grade

        Fe/0.5Mn/0.2C 1020 commercial grade

        Fe/0.5Cr/0.06C (vacuum melted)

        Fe/2Cr/0.07C

        Fe/4Cr/0.07C

        Fe/2Si/0.07C

        Fe/0.5Si/0.07C

    2. Current Work

        In the current work air melted and vacuum melted ternary and quaternary alloys containing Al[10] and/or carbide formers such as Nb and Mo[9] have been studied.

Experimental

Alloy preparation was done as described previously.[2] The commercial 1010 and 1020 steels, the Fe/Mo/C and Fe/Al/C steels were air melted. Otherwise all other alloys were vacuum melted. Standard tensile tests using round tensile bars of gage length $1\frac{1}{4}$ inch were performed. Optical and electron metallographic examinations were carried out in the usual way. Figure 1 shows the scheme of heat treatments employed. Details may be found in our previous papers.[2,4] In addition, charpy fracture tests and fractographic analyses in the scanning electron microscope are being carried out.

also been made to obtain local X-ray chemical analysis using STEM techniques, and lattice imaging[3] to estimate compositions of light elements (e.g., C.N.).

Results and Discussion

1. Constituent Morphology: Transformation Path

    a) Ductility

Good ductility appears to be associated with the connectivity of ferrite (or martensite), especially interconnected martensite along the prior austenite grain boundaries. Thus the transformation path by which the final ferrite (α) + martensite (Ms) is attained is very important. Also, the influence of alloying elements on the kinetics nad morphology of the "step quenching" [$\gamma \rightarrow (\alpha+\gamma) \rightarrow \alpha+Ms$] or "intermediate quenching" --
[α + pearlite (or Ms)$\rightarrow$ ($\alpha+\gamma$)$\rightarrow$ ($\alpha+Ms$)] transformation paths must be considered. Figure 2 shows sketches of the duplex microstructures obtained as a result of the different transformation paths indicated. The detailed microstructural characteristics will depend upon the specific alloying elements present. Examples are illustrated in the optical micrographs shown in Figs. 3 (a) and (b) taken from the duplex structures developed in 1010 steel subjected to the intermediate quenching (Fig. 3(a)) and step quenching (Fig. 3 (b)).[5] The two microstructures differ in their respective macroscopic morphologies in that the latter shows a much coarser structure and a higher degree of connectivitiy of the martensite islands in the ferritic matrix. This geometric difference will influence the homogeneity of plastic flow in the ferrite region upon deformation. As a result, significant changes in the mechanical properties of the duplex structures, are expected. Such results are shown in Figs. 4 and 5.

It is important to emphasize here that the other microstructural fea-

tures, e.g., precipitates and substructure, must be carefully identified
and characterized if valid correlations between the microstructures and
properties are to be established. The presence of any fine precipitates in
the ferrite, for instance, can affect the mechanical properties of duplex
steels, as will be discussed later. In the present example for 1010 duplex
structures (Fig. 3 (a) and (b)) the only structural difference that was ob-
served was the size and shape of the constituent phases. Transmission elec-
tron microscopy showed no significant substructural differences.[5] Both
uniform and total elongations at the same volume fraction of martensite
of the intermediately quenched structure are superior to those of the step
quenched structure over a wide range of martensite volume fractions examined.
From a continuum mechanics viewpoint this is to be expected, since the
coarse and the more connected martensite geometry in the ferrite (Fig. 3 (b))
causes more severe inhomogeneous deformation and restricts initial plastic
flow to a smaller fraction of the total volume of the ferrite matrix. Also
void growth will occur at a faster rate when martensite is more interconnec-
ted, but with less plastic strain. As a result the over-all ductility
measured by tensile elongation and reduction in area will be lower. A
similiar trend, but a more drastic decrease in ductility was found for
the duplex Fe.2Si/0.1C steel subjected to $\gamma \rightarrow (\alpha + \gamma)$ transformation path
compared to that of the $(\alpha + \text{pearlite}) \rightarrow (\alpha + \gamma)$ treatment.[6]

b) Strength

Strength seems to be less sensitive to morphology than ductility,
and depends to a good approximation on the "law" of two phase mixtures,
given in eq., 1. Figure 5 shows the linear increase in strength as a func-
tion of volume fraction martensite. It is noted that the slopes of the
straight lines are slightly different from each other in magnitude, de-

spite the fact that σ_m is the same for both structures at the same volume

fraction, and therefore the slopes should be identical according to the mix-

ture rule. This discrepancy in fact suggests that the mixture rule, which

is based on continuum mechanics, should be applied to the duplex steels in

conjunction with dislocation theory (the micromechanical viewpoint) since

the latter emphasizes the characteristic slip distance available in the

ferrite. The slip distance will in turn be determined by the substructure

and macroscopic geometry of the constituent phases.[7]

Nonetheless, the mixture law provides an important guideline which can

predict with faily good accuracy the strength level of duplex steels at the

various volume fractions of martensite, provided a minimum of two data points

are known. However, deviations can occur in the above relationship of the

law of mixtures when third phase precipitates especially in ferrite are

present. These deviations are described in the following:

2. Ferrite Characteristics

It is generally agreed that the good formability of duplex ferrite-mar-

tensite steels is determined mainly by the ferrite constituent which is normally

highly ductile. Ferrite is also plastic because of the "fresh" dislocations

created by the transformation stresses resulting from the quench from the

$(\alpha+\gamma)$ region. It is important to know therefore, how and to what extent the

mechanical properties of duplex steels will be affected in the presence of

fine precipitates in the ferrite regions. This situation is most likely to

occur in the commercially developed duplex steels, e.g., duplex treated

Van 80, which contain strong carbide or nitride forming elements. Thus

to investigate this aspect, we have studied the structure and property

relations of simpler alloys containing carbide formers, and

the results of the tensile properties are summarized in Table 1.

Table 1 – Tensile Property Data

(at ambient temperature: untempered)

Alloy A	Heat Treatment Intermediate quench	σy Ksi(mPa)	σ uts Ksi(mPa)	Unif. Elong %	Total Elong %	R.A. %
Fe/Al/C Series[a]	20% martensite	73(504)	111(765)	11.7	21.8	72
	40% martensite	74(511)	109(749)	11.1	22.2	74
Alloy B	20% martensite	88(606)	121(834)	12.9	19.7	46
Fe/Si/C + Nb[b]	40% martensite	81(558)	130(896)	13.9	19.5	33

(a) Unpublished work: M.S. Thesis T. O'Neil[10]
(b) Unpublished work: M.S. Thesis R.K. Costello[9]

Alloy B

As Table 1 shows, the yield strength decreases with increasing volume fraction and this represents an anomaly in the usual "law of mixtures" behavior. Detailed analysis by electron microscopy shows that the reason in this case is due to precipitates in the ferrite. The precipitating phase in this system is a carbide, perhaps ε or M_3C[9]. The higher yield strength of this alloy with 20% martensite compared to that with 40% martensite is to be expected due to a greater density of carbide in the ferrite region in the former case. This is so because the yield strength of duplex steels with a continuous soft phase ferrite is primarily determined by the flow strength of ferrite, independently of the strength of martensite.

As can be seen from Fig. 6, one effect of increasing the martensitic volume fraction, by raising the holding temperature in the ($\alpha+\gamma$) field, is that the carbon content in ferrite decreases. Depending on the alloy content it is possible that the concentration (and subsequent supersaturation) of carbon in ferrite can be doubled or tripled when the percentage marten-

site is lowered (fig. 6 (b)). Consequently more carbides will be present as the % martensite decreases.

Clearly the amount, type, and distribution of fine precipitates in the ferrite phases of the duplex structure will have a significant influence on the strength and ductility of ferrite and thus of the composite duplex structure. Furthermore the influence of precipitation depends upon the volume fraction of the ferrite and martensite phases. Thus whilst the percentage of martensite increases the strength of martensite can decrease, so that the overall effect can be to produce a negative slope in the "mixtures" equation (e.g., 1), depending on the strength of ferrite , as is found in the data of Table 1.

From Figure 6 a simple calculation based on the mixture law (eq. 1) for the tensile strength, $\sigma = \sigma_m V_m + \sigma_\alpha (1-V_m)$ (eq. 1), shows that as V_m is increased by a factor of 2 and since σ_m is directly proportional to %C, (as is quite well established for dislocated martensites[11]), the product $\sigma_m V_M$ is about the same at 20% and 40% martensite, since the carbon content in martensite is about halved as the % of martensite is doubled. Thus for σ to be constant the value of the strength of ferrite σ_α must increase by about 30%. It is quite reasonable to expect such an increase due to the observed dispersion of precipitates. Likewise, σ can increase or decrease (Table 1) depending on the dispersion strengthing of ferrite and the change in the strength of martensite as % martensite is changed.

Thus we emphasise that solute dispersion especially carbon and nitrogen and resulting precipitates in ferrite is as important on the mechanical properties as are the strength and volume fraction of martensite.

Alloy A

In the case of this duplex alloy, the 20% increase in volume fraction of martensite from 20% to 40% (total) has no substantial effect on either strength or ductility (Table 1). Detailed examination of specimens by TEM and STEM has shown that this unusual behavior is due to a fine dispersion of precipitates, which are formed in the course of duplex heat treatment. (More details will be published separately). The density of these precipitates was greater in the ferrite than martensite presumably because ferrite has a higher solubility for Al. In addition, the precipitate density is expected to be higher in the ferrite of the alloy with 20% martensite than that in the 40% martensite alloy since in the former case there is greater interstitial solubility according to the phase diagram. This is again illustrated by Fig. 6 and the explanation for this "anomalous" property behavior is similiar to that given above for alloy B.

The presence of such precipitates in the ferrite area will increase the flow strength of ferrite, and simultaneously lower ductility. Therefore, in Table 1, the strength increment expected through the increase in volume fraction of martensite by 20% will be balanced with a loss in strength of ferrite due to the reduced density of precipitates in the alloy A con-taining 40% martensite. A similiar reasoning holds for the ductility. Thus, the overall effect of precipitation on the tensile properties of these du-plex steels is that the properties are essentially invariant in the range of volume fraction martensite that has been investigated. These findings are important in the practical sense that the reproducibility of such properties will be excellent with a wide flexibility of heat treatment available. A summary of the tensile data is given in fig. 8. The corre-lation of microstructure and properties thus requires detecting the exis-

tence of phases other than ferrite and martensite, particularly in steels containing strong carbide (or nitride) forming elements. Thus detailed electron microscopy is essential in order to characterize such effects.

A recent development in high resolution metallography is the facility for carrying out chemical analysis in-situ in the electron microscope using modern STEM instruments. Preliminary investigations of alloy A indicate there is considerable partitioning of aluminum between ferrite and martensite (i.e. in the original ferrite-austenite during isothermal holding), as shown in fig 7. These X-ray data show the higher Al content in ferrite and, as expected, corresponds to the preferential formation of aluminum containing precipitates in this phase. Whilst carbon cannot be detected by such methods our previous work using lattice imaging[3] showed that the carbon contents can be estimated this way. More work will be done using this technique.

3. Role of Alloying Elements

The results we have obtained so far from on-going research program allows the following summary to be made concerning the role of some important alloying elements on the duplex structure-property relations.

1. Si   (a) Increases the activity of carbon and hence promotes ductility of ferrite.

(b) Inhibits carbide formation, particularly Fe_3C at the ferrite - martensite interface.

(c) May also contribute to solid solution strengthening.

(d) Increases the slope of the A_3 line, thus allowing more flexibility in heat treatment.

(e) Raises transformation temperatures.

(f) Refines the microstructure.

2. Al (a) The items a), b), d) e), and f), listed above also hold

for Al.

(b) Al forms AIN in ferrite in the presence of nitrogen.

3. Nb (a) May form carbides depending on the heat treatment process.

(b) Refines duplex microstructures

(c) Increase the slope of the A_3 line.

4. Cr (a) Increases hardenability

(b) Increases the connectivity of martensite.

5. C (a) Good ductility and toughness requires initial carbon

content about 0.1 wt.% or less so that the carbon content of the

final ferrite and martensite phases can be controlled. For strong

tough martensite this value is ~0.4 %C depending on total alloy

content.

(b) The higher the carbon content, the more stringent control

is needed. This can be seen from fig. 6.

6. Mo (a) Increases the slope of the A_3 line, allowing for more flex-

ibility in heat treatment.

(b) Increases hardenability.

(c) Produces carbide precipitation in ferrite.

4. Microstructure Control

The important microstructural features appear to be:

(a) Ferrite: For high ductility the ferrite should contain enough

mobile dislocations and should therefore be "clean" and free from

extensive pinning. Thus the carbon content and distribution are key

factors (depend on alloy content, treatment). Part of the benefit of

a fast quench is that fresh dislocations will be generated in ferr-

ite due to the $\gamma \rightarrow$ Ms transformation and the segreatation of inter-

stitial elements to these dislocations should be less severe. (The intermediate quench is also beneficial for these reasons).

(b) Martensite: The tensile strength is determined mainly by the % martensite and the fracture toughness of martensite. For this reason, the carbon content and hence transformation substructure must be controlled. [2,4] In martensitic steels the toughness drops with increasing % carbon as transformation substructure changes from dislocated packet lath martensite to twin plates (at $>$ 0.4% C) -- (ref. 12,13). In duplex steels the carbon content at which this occurs can be higher because transformation strains can be accomodated by slip in the surrounding ferrite. However, to ensure good toughness, packet dislocated (lath) martensite is needed and this means the carbon content in the martensite phase should probably not exceed 0.4% in duplex steels, considering that other solutes are also usually present.

5. The "Law" of Mixtures

Although tensile strength and ductility appear to be inversely related through the mixtures relationship (equation 1), the properties for particular steels and heat treatments will depend on all of the parameters σ_α, σ_m and V_m through the microstructure. As shown in this paper, these parameters can all change simultaneously. Generally speaking then, as V_m increases, σ_m decreases (due to lower % C), but σ_α can increase because of precipitation in ferrite. In principle therefore the tensile strength and ductility can increase, decrease or be constant with % martensite depending on the balancing effects of σ_α & σ_m. As Table 1 shows, the ductility will behave in

an inverse manner compared to strength.

This "law" does not adequately describe the details of the yielding nor
work - hardening behavior for which one must take into account dislocation
behavior and the dispersion strengthening effect of the martensite[11] on
plastic flow in the ferrite.[4,7]

This aspect is particularly important in considering the significant
effect of morphology on ductility. As discussed in section one of this paper,
and in previous work[5] the morphology of the ferrite - martensite mixture
(or other transformation products) depends on the initial microstructure prior
to the duplex heat treatment and the transformation path by which the duplex
structure is attained (fig. 2),- and must be accounted for in terms of the
dislocation behavior (yielding, multiplication).

Summary

The on-going resarch program has been described with particular emphasis
on the effects of macroscopic geometry and microstructural features on the
tensile properties of various duplex steels. A summary of some tensile prop-
erties is given in fig. 8. Some important conclusions from these studies
are summarized in the following:

1. Excellent combinations of strength and ductility are obtained in
duplex ferrite-martensite steels by controlling the duplex microstructures
(composition and transformation conditions). The best results to date
are still those obtained with Al/2Si/0.07C reported earlier[See fig. 5, of ref.2]
where desired combinations of properties were optimized by controlling
% martensite.[2]

2. The transformation paths by which duplex ferrite - martensite
structures can be obtained are of paramount importance on the prop-
erties. The choice of the specific path should be determined by the

hardenability, chemical composition, and the final microstructural morphology that is desired.

3. The step quenching [$\gamma \rightarrow (\alpha+\gamma) \rightarrow (\alpha+ \text{martensite})$] treatment brings about a coarser and more connected martensite geometry compared to that obtained after intermediate quenching. This results in poorer ductility.

4. The presence of fine precipitates in the ferrite phase formed during the duplex structures has the following effects:

    a) The strength of ferrite increases but is accompanied by simultaneous loss in ductility. Thus, "clean" ferrite and mobile dislocations are essential if dutility is of primary concern.

    b.) The "law" of two phase mixtures is modified from the "normal" behavior

    c) Therefore, detailed substructure and microchemical characterization is absolutely necessary in order to understand each alloy being investigated.

5. Summary plots of our mechanical property data are shown in fig. 8. In all cases the duplex ferrite - martensitic steels have superior tensile properties compared to "conventional" HSLA steels.

We wish to thank Republic Steel Corporation and Daido Steel Corporation, (Nagoya, Japan) for providing some of the steels used in these investigations.

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FIGURES

Fig. 1. Schematic diagram utilizing the Fe-C system to show heat treatments used to obtain ferrite-martensite duplex microstructures.

Fig. 2. Schematic illustration of microstructures expected to result from the transformation paths indicated (see also Fig. 1). Light regions represent ferrite and shaded regions represent martensite (or other austenitic decomposition products).

Fig. 3. Light micrographic examples of microstructures formed as a result of (a) intermediate quenching and (b) step quenching in 1010 steel. (Untempered) (See Fig. 2).

Fig. 4. Variation of tensile elongation as a function of volume fraction of martensite for the two microstructures shown in Fig. 3: 1010 steel.

Fig. 5. Variation of tensile strength as a function of volume fraction of martensite for the two microstructures shown in Fig. 3: 1010 steel.

Fig. 6. Phase diagrams of Fe-rich portion of the Fe-C binary system (upper diagram), and the Fe-C + ferrite stabilizer (lower diagram) showing the variations of the A_3 and ferrite solvus lines as ferrite stabilizing elements (e.g., Si. Al) are added to the Fe-C system.

Fig. 7. X-ray STEM microanalysis data showing the concentration profile of Al in the duplex ferrite-martensite structure of alloy A. (Courtesy M. Raghavan).

Fig. 8. Summary of current and previous results obtained at Berkeley showing the strength -elongation data for a range of DFM steels, treated by the intermediate quenching method (see fig. 1). The symbols are data from the current program and are compared to conventional HSLA steels (shaded areas).
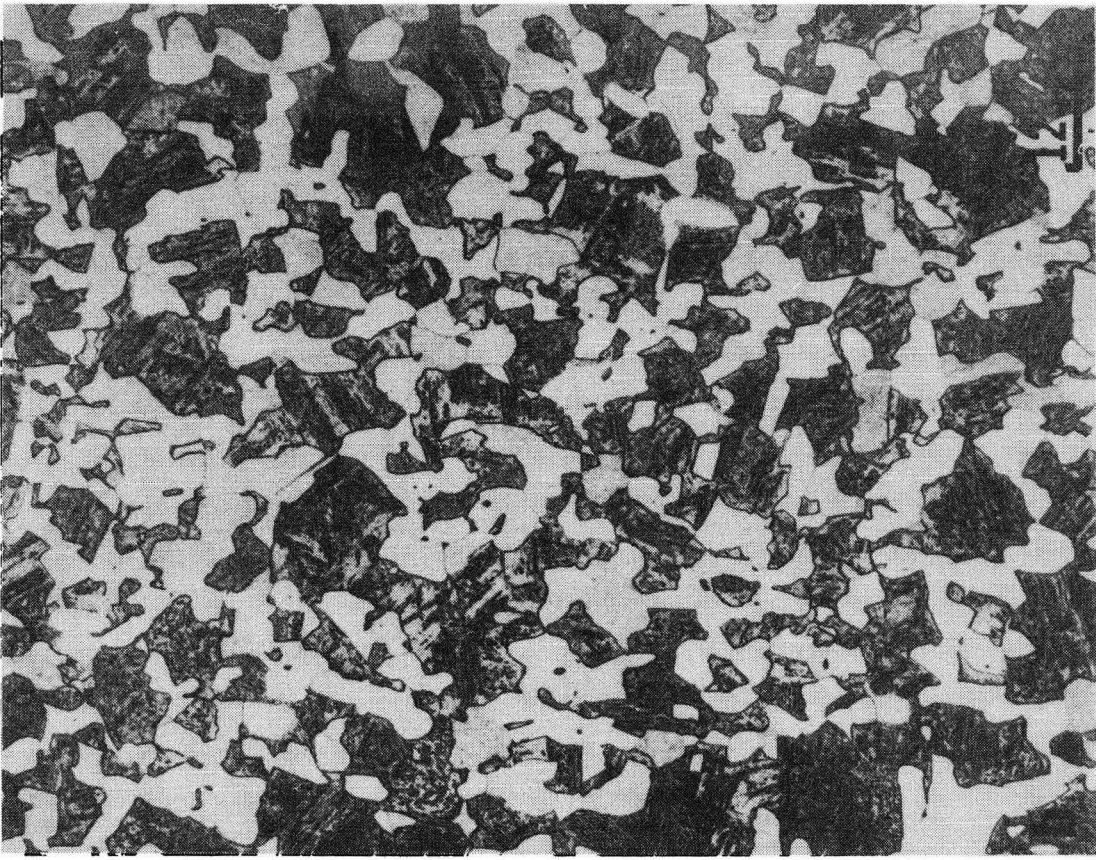
Fe rich portion of
Fe-C phase diagram

Experimental Heat Treatment

(a) continuous cooling

(b) intermediate quenching
or intermediate air cooling

(c) step-quenching

$\gamma \rightarrow \alpha + Ms$ or
$\gamma \rightarrow \alpha + pearlite$

$\gamma \rightarrow Ms \rightarrow \alpha + \gamma \rightarrow \alpha + Ms$

$\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + Ms$

XBL791-5511

Figure 1

Figure 2

XBL 792-5685

XBB 791-979

Fig. 3(b)

Fig. 3(a)

Figure 4

XBL 791-5509

Figure 5

Fe-rich portion of the Fe-C system

Fe-C system with ferrite stabilizer

Figure 6

Figure 7

XBL 792-5686

XBL7812-6281A

Figure 8