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by

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ABSTRACT

The research reported here addresses the microstructural modification of ferritic Fe-Mn alloys to improve low temperature properties. The alloys Fe-12Mn-0.2Ti and Fe-8Mn-0.2Ti were specifically studied. In the as-quenched condition the alloys have ductile-brittle transition temperatures near -50°C and room temperature respectively. The brittleness of Fe-12Mn is due to the intrusion of an intergranular fracture mode; that of Fe-8Mn is due to quasi-cleavage. The transition temperature of the 12Mn alloy may be suppressed by annealing in the two-phase ($\alpha + \gamma$) range to introduce a distribution of austenite or by grain refinement through deformation processing. In the latter case an excellent combination of strength and toughness is obtained at liquid nitrogen temperature. The 12Mn alloy may not be thermally processed to fine grain size because of the malevolent influence of the ε-martensite phase present in the as-quenched structure. No such phase is present in the 8Mn alloy. This alloy may be thermally processed to ultrafine grain size with a concommitant marked improvement in low temperature mechanical properties.

I. INTRODUCTION

The increasing use of cryogenics in advanced engineering systems for the production, transport, and storage of useful energy creates a potential demand for inexpensive structural alloys with good low-temperature properties.[1] The principal structural steels in current use at LNG temperatures and below contain a significant nickel alloy addition, and are hence inherently expensive. A significant economic benefit could be obtained if it were possible to replace the nickel present in these alloys with a moderate concentration of relatively inexpensive alloy additions without sacrificing properties or incuring prohibitive processing costs.

The research reported here addressed the development of nickel-free ferritic Fe-Mn alloys for cryogenic use. These alloys are competitive in strength with the Fe-Ni alloys, but have very high ductile-brittle transition temperatures in the as-quenched condition, as a consequence of which they have not been regarded as promising cryogenic materials. However, as reported below, the microstructure of Fe-12Mn-0.2Ti and Fe-8Mn-0.2Ti alloys can be controlled through suitable processing to suppress the transition temperature to below LNG temperature. The resulting alloys have excellent combinations of strength and toughness at low temperature. While the processing techniques used in this particular research project are too complex for immediate commercial exploitation the results document the potential of ferritic Fe-Mn alloys for low-temperature use.

II. EXPERIMENTAL

Ingots of nominal composition Fe-12Mn-0.2Ti (by weight) and Fe-8Mn-0.2Ti were melted under an argon gas atmosphere, homogenized at 1200°C for 24 hours under vacuum, and then upset cross-forged to 25 mm plate at 1100°C. The plates were then solution treated at 900°C for two hours under argon gas and brine quenched. The plates were then given the thermal or mechanical treatment described in the following. Cold working of the 12Mn alloy was accomplished by multi-pass rolling a plate of 25 mm initial thickness at room temperature to achieve a 50% reduction in thickness.

The microstructures of the processed alloys were examined through optical and transmission electron microscopy. The quantitative phase analyses were obtained through X-ray diffraction. Some degree of preferred orientation was found in the specimens. The data reported here are from transverse sections and should be regarded as approximate.

The fracture toughness and Charpy impact tests reported below were conducted according to ASTM standards. Compact tension specimens were used for the fracture toughness tests. The tensile tests employed subsize cylindrical specimens of 12 mm gage length and 3 mm diameter.

III. RESULTS AND DISCUSSION

A. Fe-12Mn-0.2Ti

(1) As-Quenched Condition (AS)

During solution treatment of 2 hours at 900°C the 12Mn alloy develops an austenite (γ) grain size of $\sim$70 μm. On subsequent quenching the alloy transforms to a body centered cubic martensite (α') with a small admixture of hexagonal ε-martensite. A typical transformation substructure is shown in Fig. 1. The ε-phase occurs in the form of thin plates which bound thicker α' laths divided into a row of block-like dislocated crystallites.[1,2]

The low temperature mechanical properties of the 12Mn alloy in the as-quenched (AS) condition are listed in Table I. While the yield strength of this alloy is competitive with that of Fe-Ni cryogenic steels its fracture toughness is low. The data presented in Fig. 2 show that the ductile-brittle transition occurs in the AS condition at ∿-50°C. The source of the embrittlement is the onset of catastrophic intergranular fracture, as illustrated by the scanning electron fractographs presented in Fig. 3.

The source of the intergranular embrittlement of Fe-12Mn is subtle and is currently under investigation.

(2) The Tempered Condition

Given the similarity in phase transformation behavior between the Fe-Ni[3] and Fe-Mn systems the best tempering response of Fe-12Mn-0.2Ti is expected when the alloy is tempered at a relatively low temperature within the two-phase ($\alpha + \gamma$) region. This tempering treatment causes three significant changes in the microstructure. First, the dislocated α' martensite is annealed with the removal of part of its high dislocation density and the recovery of much of the remainder into a cell structure. Second, austenite forms in the boundaries of the martensite laths causing an apparent refinement of the structure. Third, if the tempering temperature is relatively low much of this reverted austenite is retained on subsequent cooling to room temperature, creating a three phase ($\alpha + \varepsilon + \gamma$) tempered microstructure.

Of these microstructural changes the one of most immediate interest is the introduction of retained austenite. In research on the Fe-Ni system[3-5] an improvement in low temperature properties has invariably been formed in association with the retention of stable austenite in grain and lath boundaries. Surprisingly this effect has not been specifically exploited in previous research on ferritic Fe-Mn alloys.[6]

In Fig. 4 are plotted the relative amounts of the α, ε, and γ phases found after tempering Fe-12Mn-0.2Ti for four hours at the temperature shown on the abscissa and cooling in liquid nitrogen (-196°C). The corresponding Charpy impact energy (CVN) at -196°C is also shown. This data suggests that, as in Fe-Ni alloys, the presence of the γ phase has a beneficial effect on low temperature toughness. On the other hand the impact energy falls concurrently with the rapid increase of the ε phase at higher tempering temperatures. While this drop in toughness with the ε content may reflect an ε-embrittlement it is more likely associated with the lower stability of the austenite introduced at higher temperatures and with the decreasing amount of γ present in the final structure.

The data shown in Fig. 4 suggest an optimum tempering temperature near 500°C. The low temperature mechanical properties of Fe-12Mn-0.2Ti tempered for 10 hours at 500°C were determined and are presented in Table I and in Fig. 2. The tempered microstructure is shown in Fig. 5(a). The tempering treatment yields a simultaneous increase in the strength, tensile ductility, and fracture toughness of the alloy. The transition temperature decreases and the Charpy shelf energy rises.

Despite the beneficial effect of the tempering treatment, however, the cryogenic toughness of the 12Mn alloy remains below that of available cryogenic steels of comparable strength. At least part of the reason is that this tempering treatment does not fully suppress intergranular fracture, as is revealed in the scanning electron fractograph in Fig. 6.

(3) Grain Refinement

By analogy to the Fe-Ni system one would anticipate a further improvement in the low temperature properties of Fe-12Mn if the alloy were fine-grained. However, the thermal cycling technique[7,8] which was successfully used to refine the grain size of 9Ni and 12Ni steels is inapplicable in this case. The problem is associated with the presence of the ε phase in the as-quenched structure. On heating the ε phase reverts to create sheet-like γ grains which either retain or revert to ε on subsequent cooling. Aspects of this process are recognizable in the electron micrograph in Fig. 5(a). The sheet-like phase bounding α laths is regenerated on thermal cycling and no effective grain refinement is achieved.

The 12Mn alloy may, however, be grain refined using deformation processing similar to that known to be effective for Fe-Ni alloys.[9,10] If the 12Mn alloy is severely cold-wroked two microstructural changes occur which significantly affect the response of the alloy to subsequent tempering. First the metastable ε phase transforms to α' martensite, hence removing the preferential source for sheet-like austenite formation in the lath boundaries. Second, the martensite grains are severely deformed providing numerous heterogeneous sites for the fine-scale nucleation of austenite. These changes have the consequence that a treatment consisting of $\sim$50% cold work at room temperature followed by tempering in the $\alpha + \gamma$ range yields an extremely fine grain size and homogeneous grain distribution in Fe-12Mn (Fig. 5(b)).

The effect of cold work on phase retention after tempering and on the Charpy impact energy at -196°C are illustrated in Fig. 7. While the amount of retained austenite is considerably larger than in the simple tempering case the fraction of ε is decreased. This is primarily because of the increased stability of γ due to structural refinement. The impact toughness at -196°C corresponds closely to the volume fraction of γ; it shows no apparent sensitivity to the ε-fraction.

Low temperature mechanical properties for a chosen processing condition are presented in Table I, and the ductile-brittle transition curve is included in Fig. 2. A further improvement in mechanical properties is evident. The processed alloy has very high strength at -196°C while retaining good fracture toughness.

B. Fe-8Mn-0.2Ti

The Fe-12Mn alloy discussed in the previous section differs in behavior from the Fe-Ni alloys discussed in the previous paper[8] in two striking ways: First, the 12Mn alloy fractures in an intergranular mode when tested below its transition temperature in the as-quenched condition, while the Fe-Ni alloys fail in a quasi-cleavage mode. Second, the 12Mn alloy contains an admixture of ε-phase in the as-quenched condition which prevents grain refinement through the thermal cycling procedure used for the nickel alloys.

Interestingly, both these differences disappear when the Mn content of the alloy is decreased to below ∿10Mn. An Fe-8Mn-0.2Ti alloy fractures in a cleavage mode when tested below its transition temperature in the as quenched condition (Fig. 3) and, being free of ε-phase, has a dislocated martensite microstructure rather like that of the 9Ni and 12Ni alloys.[8] The 8Mn alloy is, however, inferior to the 9Ni and 12Ni alloys in that it has a higher transition temperature (∿30°C) in the as quenched condition.

Given the absence of ε-martensite in Fe-8Mn-0.2Ti a thermal cycling treatment virtually identical to that used for 12Ni steel was employed to refine the grain size ((750°C/2 hr. + 650°C/2 hrs.)/2 cycles). This treatment yields an apparent final grain size in the 1-5 μm range. The resulting microstructure is shown in Fig. 8. The grain-refined alloy is essentially 100% ferritic; neither the γ nor the ε phase is detected by X-ray analysis.

Preliminary mechanical property data for the grain-refined 8Mn alloy is presented in Table II. The grain refinement results in a significant improvement in tensile ductility and a substantial decrease in the impact transition temperature, to below -100°C, without loss of strength.

The impact transition temperature was decreased to ∿-150°C by adding a tempering treatment of 4 hours at 600°C which introduces ∿13% retained austenite into the grain-refined structure. This treatment does, however, cause a slight decrease in alloy strength.

If the decrease in transition temperature suggested by impact tests on the Fe-8Mn-0.2Ti alloy represents a true decrease in the fracture toughness (K_{IC}) transition temperature then the alloy is suitable for use to below LNG temperature in the grain-refined and tempered condition. In light of previous experience with Fe-Ni[5,8,11] alloys, however, the qualtitative results must be viewed with some caution until suitable fracture toughness tests have been completed.

IV. CONCLUSIONS

1. A nickel-free ferritic alloy of composition Fe-12Mn-0.2Ti can be processed to have a good combination of strength and toughness at -196°C through a combination of cold working and two-phase tempering. The good low temperature properties are associated with a fine alloy grain size and a suitable distribution of retained austenite.

2. The low temperature impact toughness of Fe-12Mn-0.2Ti is strongly influenced by the austenite phase retained after tempering. In contrast, the impact toughness appears to be relatively insensitive to the presence of ε-martensite.

3. The alloy Fe-8Mn-0.2Ti can be grain refined through a thermal cycling treatment similar to that used for Fe-Ni steels with a concommitant marked improvement in low-temperature mechanical properties.

ACKNOWLEDGMENT

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Table I. Mechanical Properties of Fe-12Mn-0.2Ti Steel at -196°C

Treatment	Yield Stress (MPa)	Ultimate Stress (MPa)	Uniform Elong. (%)	Total Elong. (%)	Reduction in Area (%)	K_{IC} (MPa$\sqrt{m}$)
AS	883	1351	11	25	54	59
500°C/10 hr.	952	1358	18	33	62	77
C.W. (50%)+600°C/4h.	1179	1503	26	38	66	100

Table II. Mechanical Properties of Fe-8Mn-0.2Ti Steel at -196°C

Treatment	Yield Stress (MPa)	Ultimate Stress (MPa)	Uniform Elong. (%)	Total Elong. (%)	Reduction in Area (%)	Transition Temperature* (°C)
AS	965	1044	4	4	6	30
(750°C/2hr.+650°C/2hr.)/2 cycles	967	1054	7	26	70	-100
Above + 600°C/4hr.	846	1080	18	32	64	-150

*Measured by Charpy impact test. Half-shelf energy criterion was used.

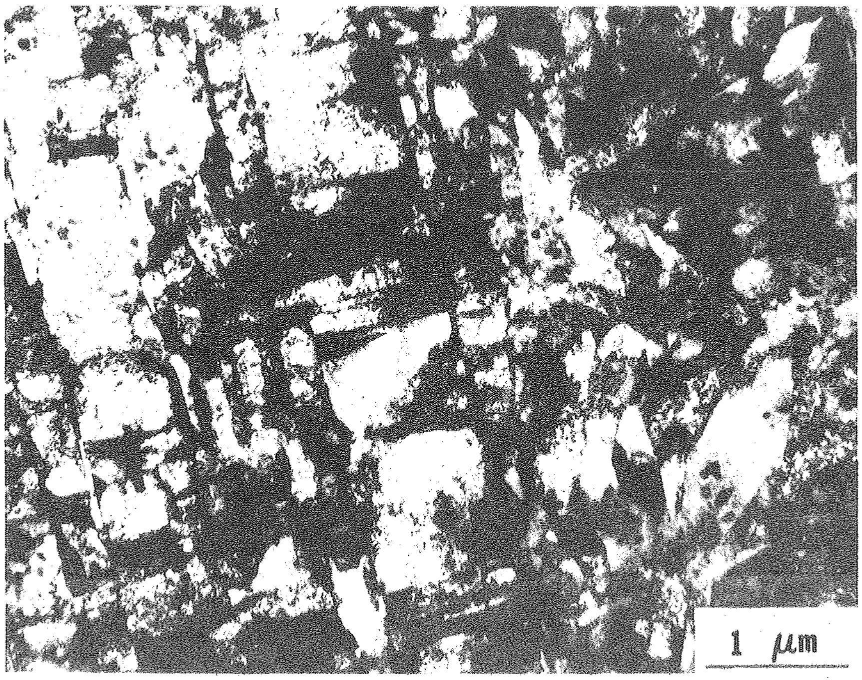


Fig. 1. Fe-12Mn-0.2Ti. Transmission electron micrographs of the as-quenched structure (AS) solution-treated for 2 hours at 900°C followed by brine-quenching.

(a) An area showing the substructure of dislocated martensite. Note the block-like laths bound by ε' phase. (XBB 762-1738)

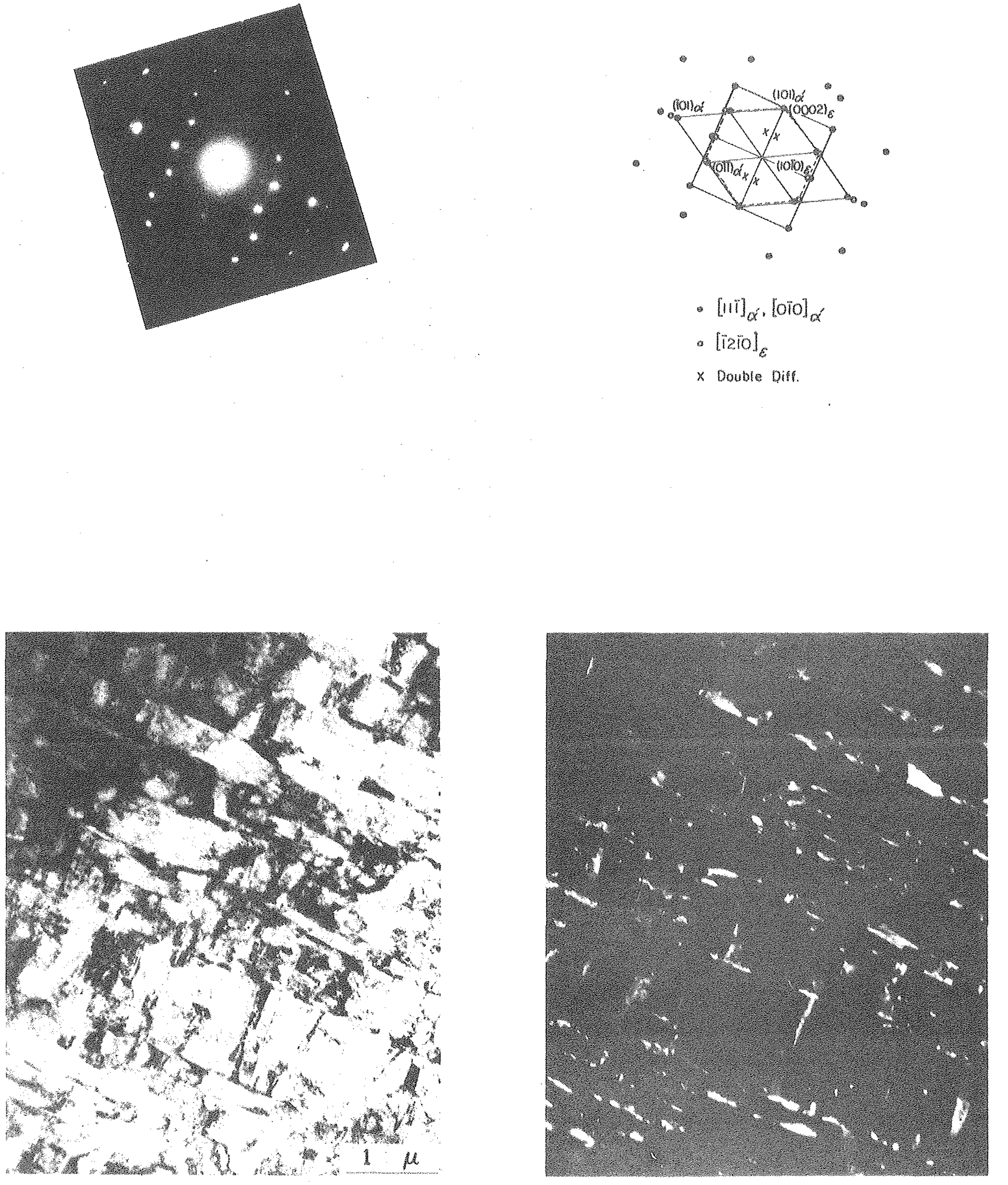


Fig. 1. (b) ε phase analysis by bright-field, dark-field and diffraction pattern. (XBB 7510-7954)

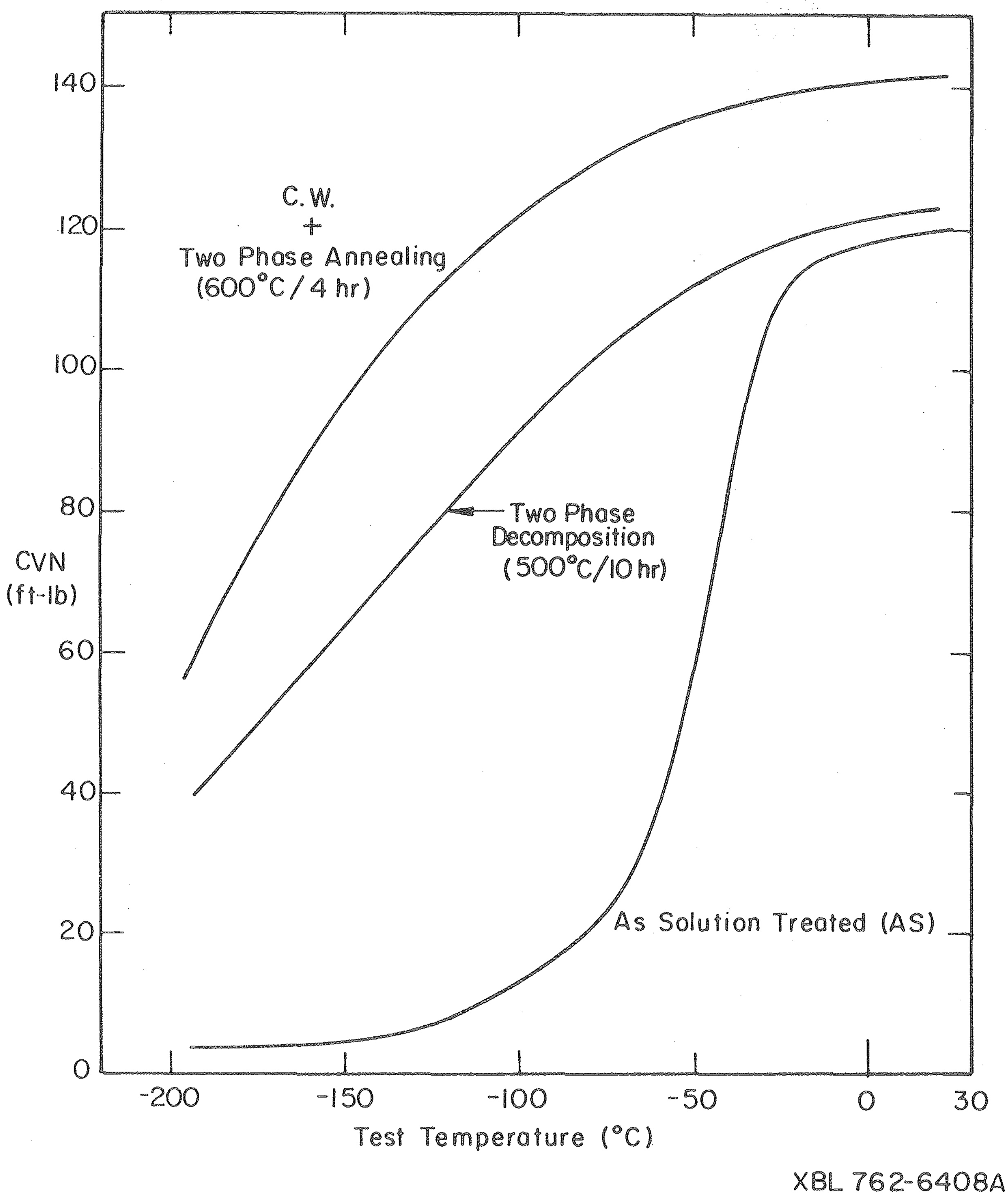


Fig. 2. Fe-12Mn-0.2Ti. Ductile-to-brittle transition curves for each treatment obtained by measuring the Charpy impact energy at different temperatures.

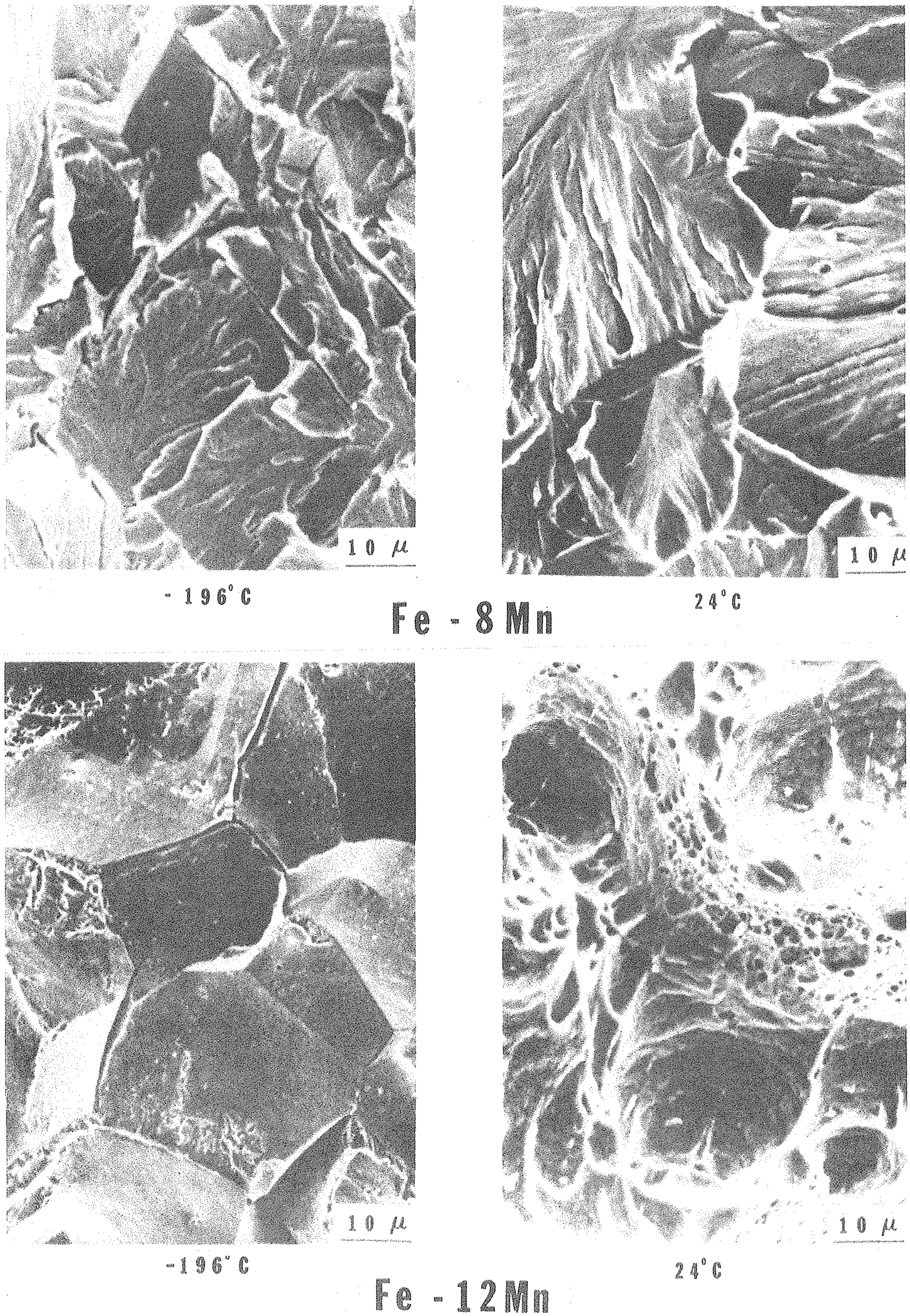


Fig. 3. Scanning electron micrographs taken from the fracture surfaces of Charpy samples tested at different temperatures in the as-

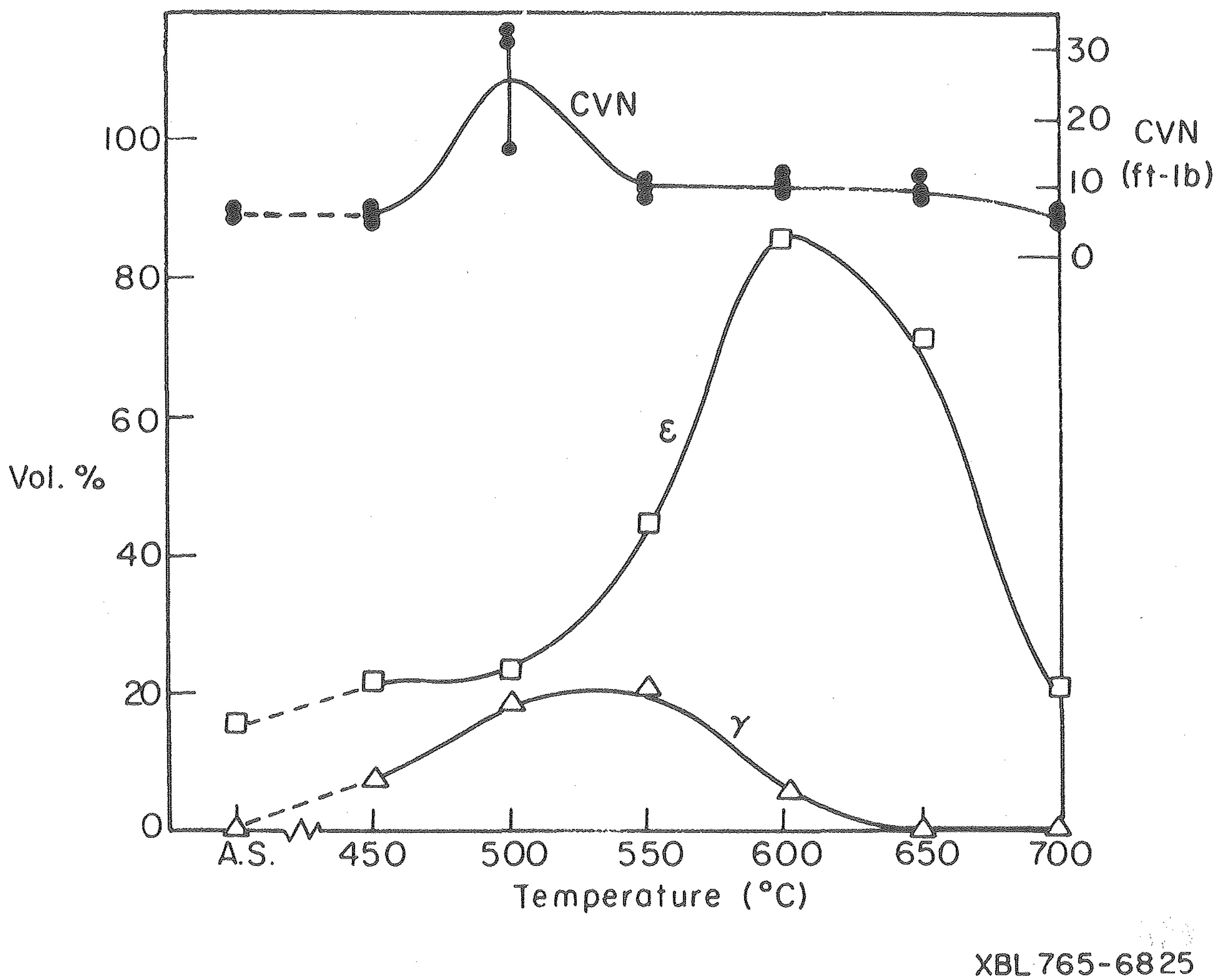


Fig. 4. Fe-12Mn-0.2Ti. Charpy V-notched impact energy (CVN) measured at -196°C and the amount of retained phases, γ and ε, after 4 hours tempering at different temperatures.

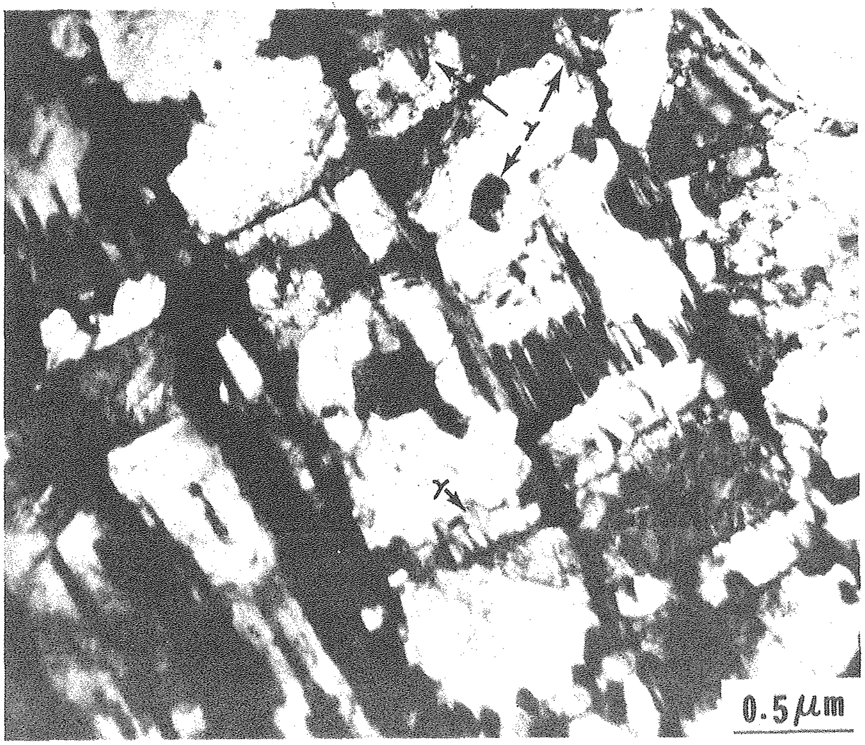


Fig. 5. Fe-12Mn-0.2Ti.

(a) Transmission electron micrograph of a tempered (at 500°C for 10 hours) structure without previous cold working. (XBB 762-1740)

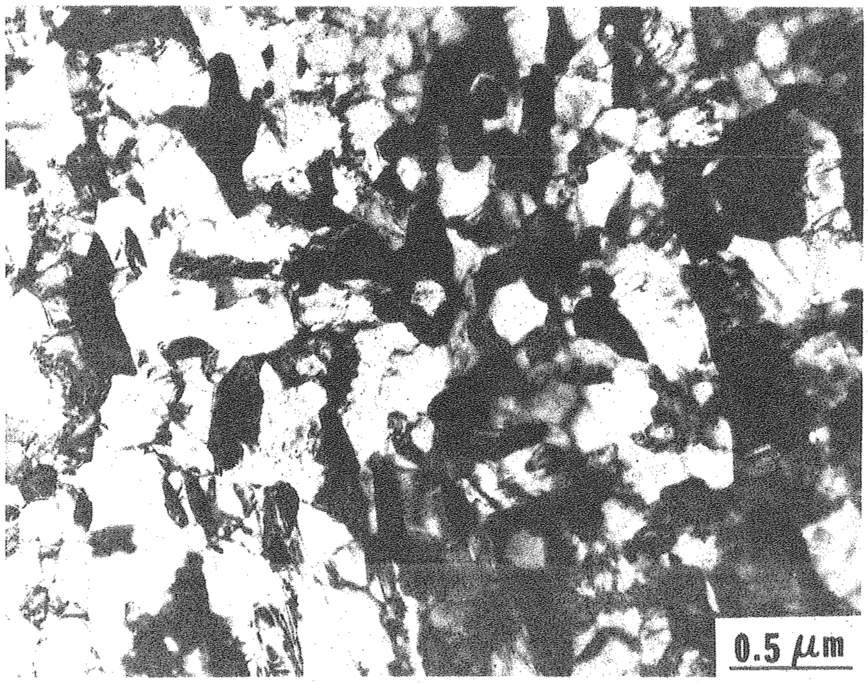
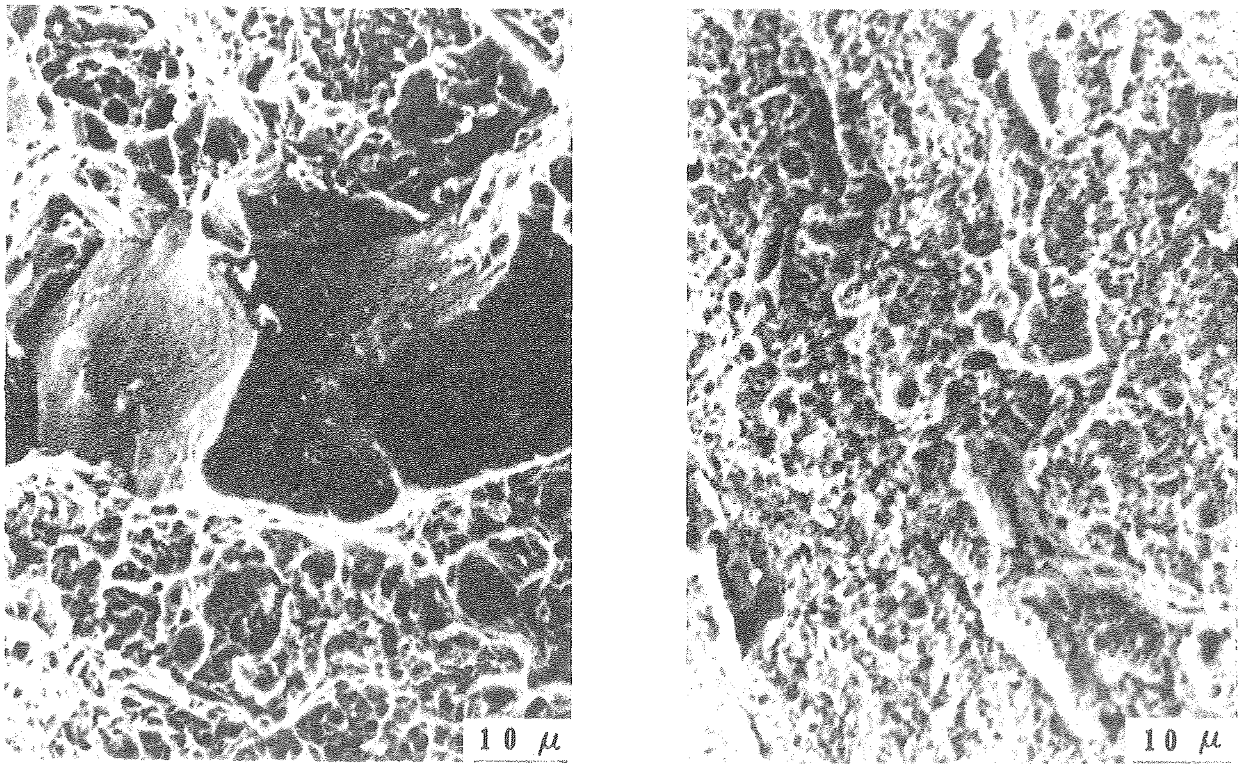


Fig. 5. (b) Transmission electron micrograph of a tempered (at 500°C for 10 hours) structure after 50% reduction at room temperature. (XBB 762-1735)



Temp.　　　　C.W. & An.

All -196°C

Fig. 6. Fe-12Mn-0.2Ti.

(a) Scanning electron micrograph of a Charpy specimen broken at -196°C. The specimen was tempered for 10 hours at 500°C.

(b) Scanning electron micrograph of a Charpy specimen broken at -196°C. The specimen was cold-worked 50% and tempered at 600°C for 4 hours. (XBB 7510-7530)

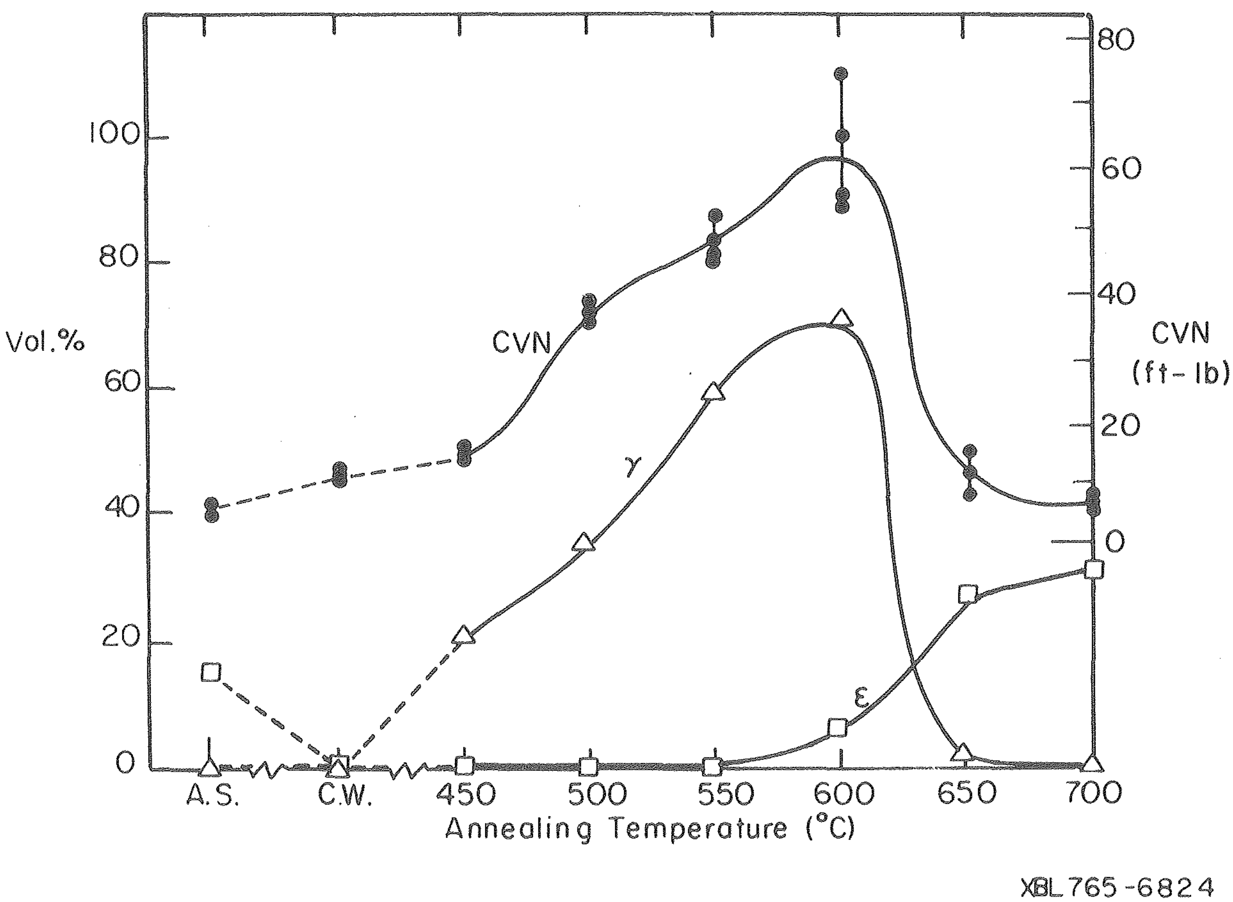
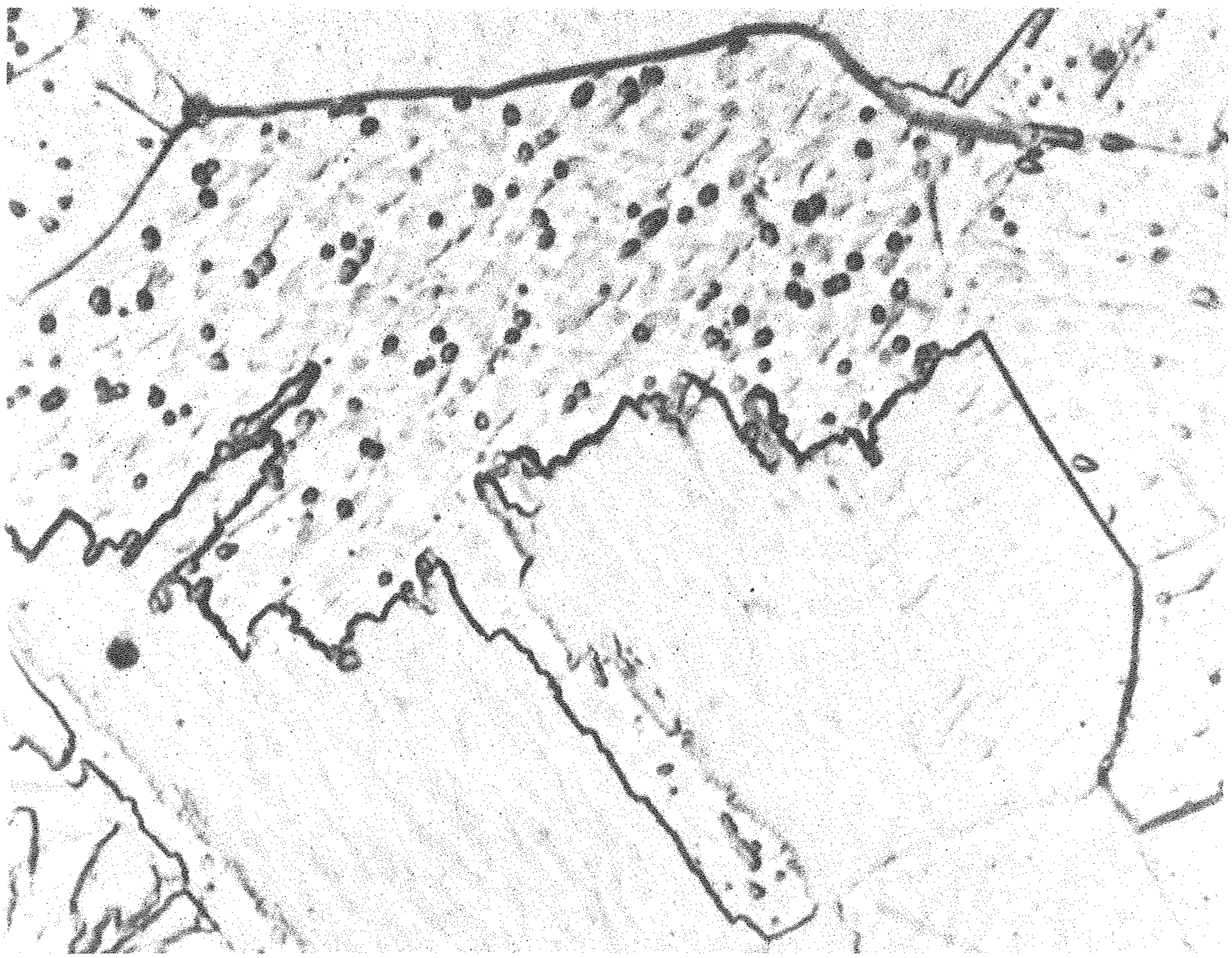


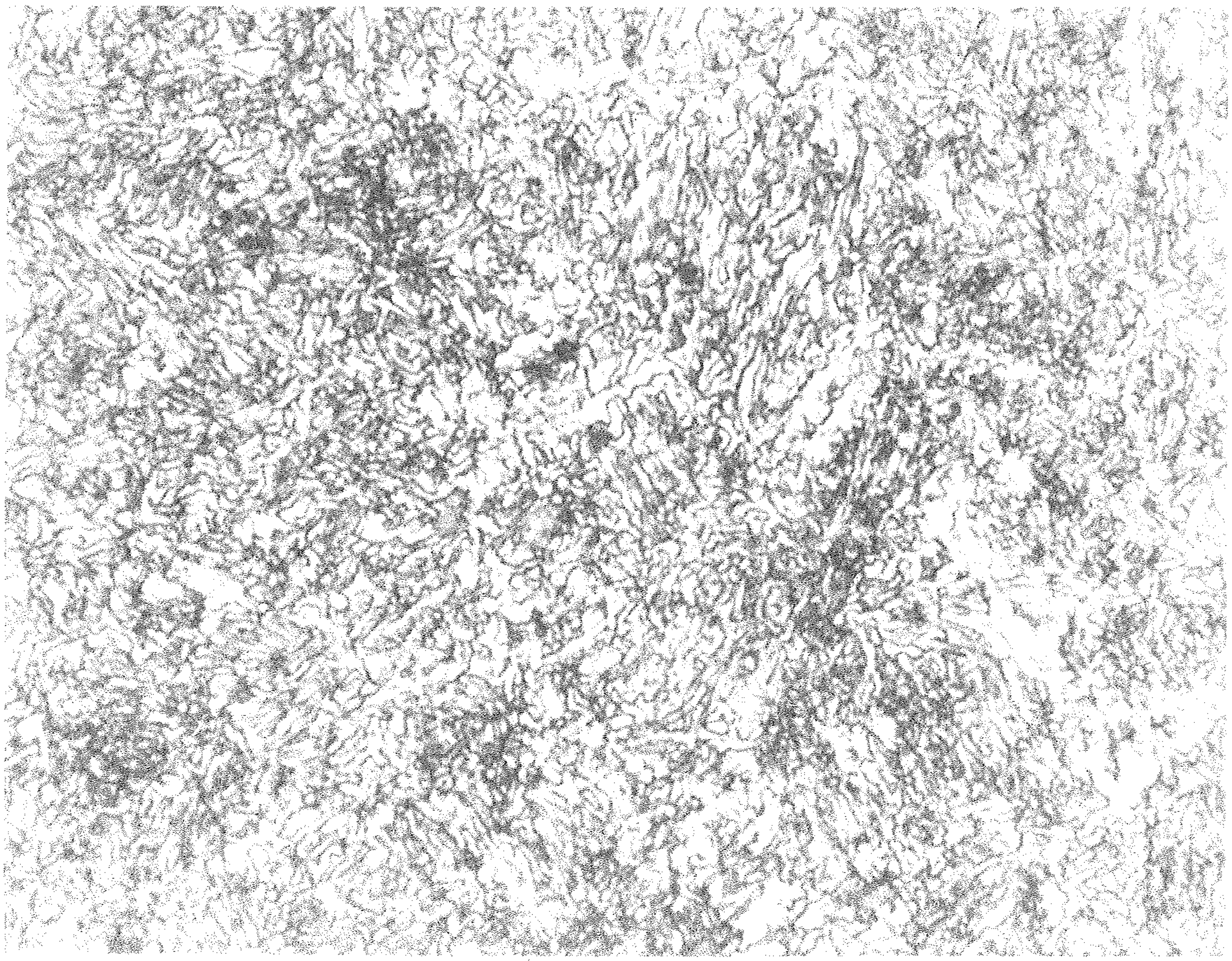
Fig. 7. Fe-12Mn-0.2Ti. Charpy V-notched impact energy (CVN) measured at -196°C and the amount of retained phases, γ and ε, after 50% reduction at room temperature followed by 4 hours tempering at different temperatures.



A.S.

Fig. 8. Fe-8Mn-0.2Ti.

(a) Optical micrograph of an as-quenched structure. (XBB 762-1741)



2 B

Fig. 8. (b) Optical micrograph of a grain-refined structure. The heat-treatment consisted of (750°C/2 hr./WQ + 650°C/2 hr./WQ) repeated twice. (XBB 762-1741)

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