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CRYOGENIC TOUGHNESS THROUGH MICROSTRUCTURE CONTROL IN A FERRITIC Fe-Ni-Ti ALLOY

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by

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ABSTRACT

This paper discusses the selection of composition and processing of a ferritic Fe-Ni-Ti alloy having a favorable combination of strength and toughness at cryogenic temperature. Criteria on alloy compositon lead to the choice of low interstitial Fe-12Ni-0.25Ti. The alloy naturally has a favorable microstructure, but cryogenic toughness must be imparted through grain refinement. Several alternate procedures are identified. Four of these are discussed in detail, along with the resulting tensile properties at 77°K, Charpy impact energies at 77°K and 5°K, and behavior in fracture toughness tests at 77°K. Alloys are obtained having yield strengths to 150 KSI with impact toughness to 5°K.

I. Introduction

As is well known, materials having a body-centered cubic crystal structure show an appreciable increase in strength when tested at low temperature. This "thermal component" of the yield strength of BCC alloys makes ferritic steels particularly attractive for cryogenic use; one may easily design alloys which become very strong at cryogenic service temperatures. However, as the strength of a ferritic alloy increases on cooling the alloy also tends to become brittle, often through a dramatic loss of toughness over a rather narrow temperature range which defines the "ductile-brittle transition temperature" (T_B). Low temperature embrittlement then severely restricts the engineering use of the alloy in cryogenic systems.

If metallurgical techniques can be employed to overcome low-temperature embrittlement in ferritic steels or to suppress T_B to well below service temperatures, it becomes possible to design steels having exceptional combinations of cryogenic strength and toughness. This paper reports how embrittlement has been suppressed in a laboratory steel (nominally Fe-12Ni-0.25Ti) through metallurgical control of the alloy microstructure. The resulting mechanical properties at cryogenic temperature are superior to any which, to our knowledge, have previously been obtained.

II. Alloy Selection

Initial alloy design criteria were chosen to insure a beneficial combination of strength and ductility at low temperature. These may be summarized as follows:

(1) To insure ductility the alloy must be structured so that internal stress concentrations are relieved and internal flaws blunted before they lead to failure. This requires deformation of individual grains and reasonable accomodation of deformation at grain boundaries. Free deformation of the individual grains requires that these grains be provided with potentially mobile dislocations. The dislocations may come from a dense initial dislocation distribution or from a dense distribution of active dislocations. To insure the mobility of these dislocations either the lattice concentration of free interstitials must be very low or the low temperature dislocation-interstitial interaction must be suppressed. The accomodation of deformation in adjacent grains is facilitated by fine grain size and requires that there be no significant brittle precipitation or film in the grain boundaries. Under appropriate conditions a ductile grain boundary phase may be beneficial.

(2) To achieve high strength consistent with ductility available dislocations must be efficiently pinned until the applied stress becomes large, in a way which does not sacrifice mobility once plastic deformation begins. One may devise solution-hardened, dislocation-hardened, or precipitation-hardened microstructures which will, at least in rough theory, function in this way. If the composition of a ferritic steel is properly chosen, it naturally forms a dense dislocation network on quenching to martensite. Precipitation hardening techniques may be used to supplement the hardening effect of this dislocation network. Since the nature and distribution of precipitate phases may be specified through a proper choice of composition and processing and since the precipitate distribution remains roughly constant during deformation, the

precipitation hardening mechanism has an inherent controllability which makes it appealing in alloy design. The precipitates employed must, of course, form in the interior of the grains and must act without poisoning or embrittling the grain boundaries.

Given these criteria, a low interstitial alloy of nominal composition Fe-12Ni-0.25Ti was chosen for this research. The advantages of a composition in this range are several. Low interstitial alloys of intermediate nickel content naturally form, on quenching, a highly dislocated martensite (ferritic) of good inherent ductility. Moreover, the phase diagram in this composition range contains a broad two-phase ferrite-austenite region at intermediate temperature (fig. 1), allowing use of a variety of processing and grain refining techniques. The nickel-titanium couple in iron is known to be a chemically effective agent for reducing the free interstitial content and suppressing the embrittling effect of free interstitials. An Ni_3Ti precipitate may be formed in the ferrite phase to restore the alloy strength lost on elimination of interstitial solutes.

III. Process Selection

While an Fe-12Ni-0.25 alloy is inherently strong at cryogenic temperature (with a yield strength near 140 KSI at 77°K) it is not inherently tough. The alloy must be made tough through proper processing. The processing sequences used in this research were designed to impart toughness through establishing fine-grained microstructure of non-aligned grains.

The grain-refinement techniques useful in alloys of intermediate nickel content may be roughly divided into two types, depending on whether the grain refinement is accomplished at temperatures in the austenite (γ) or two phase ($\alpha + \gamma$) range (figure 1). The microstructures one may achieve are shown schematically in figure 2.

If an Fe-12Ni-0.25Ti alloy is heated continuously from the ferrite (α) to austenite (γ) stability field the $\alpha \rightarrow \gamma$ transformation occurs primarily through a shear transformation mechanism[1] which initiates at a temperature near 660°C and is substantially complete at 715°C. If the alloy is then quenched to room temperature, the structure reverts to α through a martensite transformation. A single cycle of this sort leads to appreciable grain refinement of an annealed alloy; in a typical experiment alloy grain size was reduced from an initial 40μm (ASTM #6) to ∿15μm (ASTM #9). The driving force for grain refinement is believed to be the strain accumulated during the $\alpha \rightarrow \gamma$ shear transformation. The morphology of the reaction is (a) → (b) in figure 2; the final microstructure is chemically homogeneous and consists of generally non-aligned grains having a blocky, lathe martensite substructure.

If this simple γ-cycle is repeated, the grain structure is refined further. Succeeding cycles are, however, less efficient in grain refinement, and the grain size appears to stabilize at ∿10μm (ASTM #11) after 3-4 cycles.

The efficiency of the grain refinement may be increased by adding a moderate cold-work step between thermal cycles. Moderate cold-work does not significantly reduce the ultimate grain size, which remains near 10μm.

However with cold work this grain size is obtained after only two thermal cycles, and there may also be beneficial effects on the grain substructure.

If the alloy is annealed within the two-phase ($\alpha + \gamma$) region, the transformation proceeds through a nucleation and growth mechanism with nucleating preferentially in the grain boundaries and along the martensite lathe boundaries of the initial α structure. The morphology of the reaction depends on temperature.

If the annealing is carried out well inside the two-phase region, at a temperature above $\sim 600^{o}C$, both grain and lathe boundaries act as efficient nucleation sites. The structure decomposes into a layered structure similar to that shown schematically in figure 2(c), in which α and γ platelets alternate. On subsequent quenching to room temperature the γ platelets shear transform to α, leaving a final microstructure like that shown in figure 2(c) in which alternate plates differ in chemical composition: those which were γ during two-phase decomposition are relatively rich in Ni; those which were α are relatively depleted in Ni and may contain rod-like Ni_3Ti precipitates which coarsened during the anneal.

From superficial appearance one might state that structure 2(c) has been grain refined with respect to 2(a). From the perspective of alloy toughness, however, no significant refinement has occured. The interplatelet boundaries in structure 2(c) form preferential paths for crack propagation whose linear dimension is comparable with the grain size of the initial structure. In fact, a structure like 2(c) invariably leads to a deterioration in toughness.

To utilize substantial two-phase decomposition in grain refinement, one must add in a process which breaks up the platelet orientation. Two successful techniques are known. The first, due to Miller[2], employs severe cold work prior to the two-phase anneal. If the prior deformation is sufficient to supply internal nucleation sites (severly deformed regions, nodes in the dislocation network, dislocation substructure boundaries) then a shower of small γ grains may form on two-phase anneal and a highly refined structure (2(f)) may result. The second technique was developed in our own research and is described in ref. 1. In this process two-phase anneals are alternated with anneals in the γ field, as shown schematically in figure 1. A four step thermal process suffices to give a well-refined structure in which platelet orientation is almost completely destroyed. The structure resembles that shown in figure 2(e).

These two-phase processing techniques achieve an extremely fine grain size. On the other hand, they yield an alloy which is chemically heterogeneous on a fine scale, consisting of grains which, though all of the α-phase, have differing Ni concentrations. This heterogeneity must be kept in mind as it may lead to an increased susceptibility to corrosive environments.

A rather different type of grain refinement occurs if the initial structure is annealed in the low-temperature portion of the two-phase region (below about 600°C). In this case austenite nucleation is largely confined to grain boundaries. The new grains grow only slightly during anneal, and give the microstructure a final appearance like that

shown in figure 2(d) in which the grain boundaries are "beaded" by fine grains of diameter <1μm. If the alloy is rapidly quenched to room temperature, these fine grains may not revert to ferrite, but may rather remain as a fine grain boundary distribution of retained austenite. This retained austenite appears to have a beneficial effect on the cryogenic impact toughness of Fe-Ni steels, including the commercial 9Ni[3] and 6Ni[4] alloys as well as the Fe-12Ni-0.25Ti research alloy[5].

There are hence several alternate grain refinement processes which may be used to impart cryogenic toughness to an annealed and quenched Fe-12Ni-0.25Ti alloy. In the following we compare the effect of four of these treatments on the microstructure and cryogenic toughness. In this research we concentrate on processes which lead to an alloy which is essentially ferritic; the effect of adding a retained austenite phase will be treated subsequently.[5]

IV. Materials Preparation and Processing

A low carbon alloy of nominal composition Fe-12Ni-0.25Ti was obtained from pure starting materials (99.9% purity) by induction melting in an inert gas atmosphere. Twenty pound ingots of 2.75 in. (7.0 cm.) diameter were prepared by slow casting in a rotating copper chill mold. The composition of a typical ingot was determined to be (in weight percent) 12.07Ni, 0.26Ti, 0.001C, 0.014N, 0.003P, 0.0045 S, with the balance Fe. The ingots were homogenized under vacuum at 1050°C for 120 hours, cross-forged at ∿1100°C to thick plates, then air cooled to room temperature. The plates were then annealed at 900°C for two hours to remove most of the prior deformation strain and air cooled to room temperature. This final anneal was included to establish a standard

initial state for research purposes; prior work[6] has shown that the alloys have somewhat better cryogenic mechanical properties when grain refined directly from the as-forged condition.

The microstructure of the annealed starting material is shown in figure 3. The apparent grain size is 40-60 μm (ASTM #5-6).

To refine this grain size, we selected four alternate treatments, labelled A-D. Treatment A is a simple γ-cycle, involving a two hour anneal at 730°C followed by a quench to room temperature. In treatment B this γ-cycle is repeated four times. In treatment C the alloy is given a γ-cycle as in treatment A, then cold-worked ∿30%, then given a second identical γ-cycle. Treatment D is the alternate cycle refining process described in reference (1) and diagramed in figure (1). It consists of the $\gamma/\alpha + \gamma$ cycle: 730°C (2 hrs.), quench, 650°C (2 hrs.), quench, which is repeated two times.

The microstructures resulting from treatments A-D are shown in figure 4. Treatment A refines the apparent grain size to ∿15μm (ASTM #9). Treatments B and C both lead to apparent grain size near 10μm (ASTM #11). Treatment D yields a fine-grained microstructure of platelets ∿1-4μm long and a fraction of a micron in the short dimension (ASTM #15-18).

V. Effect of Processing on Mechanical Properties.

Specimens for mechanical testing at cryogenic temperature were taken from the starting material prepared as described in section IV. The annealed plates were cut into pieces 2.75" (7.0 cm) long. Each piece was then individually treated according to one of the procedures

described above. After processing, one fracture toughness specimen and two Charpy impact specimens were machined from each piece along the longitudinal direction of forging, ensuring the same treatment for both tests. Tensile specimens (transverse direction) were obtained from the far end of the broken fracture toughness specimens.

(a) Cryogenic Tensile Properties

Tensile tests were conducted at liquid nitrogen temperature using an Instron machine equipped with a cryostat. Subsize specimens of 0.5" (1.27 cm) guage length and 0.125" (0.32 cm) diameter were tested at a crosshead speed of 0.02 in./minute (0.05 cm/minute). The deviation in yield strength between tests on similarly treated samples was ∿5 KSI (35 Newton/m^2).

The results of the tensile tests are shown in Table I. The yield strength at 77°K is relatively insensitive to microstructure for the γ treated samples (A-C) and is in the range 134-140 KSI (∿9.5 X 10^8 Newton/m^2). The tensile ductility of these alloys is good, as reflected in their high tensile elongation and reduction in area before fracture. The two phase processed alloy (D) shows a slightly higher yield strength, ∿150 KSI (10.8 X 10^8 Newton/m^2) and a corresponding decrease in elongation and reduction in area. These changes may be due to the finer grain size of this alloy, or may (as we suspect) be principally due to coarsening of Ni_3Ti precipitates during the two-phase anneal.

(b) Cryogenic Impact Properties

Charpy V-notch impact tests were conducted at liquid nitrogen temperature (77°K) using ASTM standard techniques[7]. Since it is well

known that the Charpy impact test tends to underestimate the effective transition temperature, impact tests were also conducted near liquid helium temperature (5-6°K) using a method recently developed in this laboratory[8].

The test results are shown in Table II. The annealed alloy (I) showed an impact energy below 15 ft. lbs. (20 Joules) at 77°K, and hence was presumed brittle at 5°K. The alloy processed through a single γ-cycle (A) showed excellent toughness at 77°K. However, at 5°K we observed a striking variation in impact values from sample to sample. Our results scattered from about 25 ft. lbs. (34 Joules) to 148 ft. lbs. (201 Joules). The cause of this large scatter is uncertain. Possible sources include changes in the trace impurity content from ingot to ingot, failure to obtain complete alloy homogenization, and slight variations in sample treatment.

The frequent loss of toughness at low temperature in samples having treatment A may be overcome through further research. However, the results obtained with treatments B-D show that this transition behavior can be eliminated through the use of grain refinement treatments; all of these samples showed outstanding toughness to 5°K.

Comparing the shelf energies associated with the various heat treatments, the ranking of alloys is C>B>D. The two-phase processed alloy (D) had a shelf energy only 50% that of the cold-worked alloy (C). A literal interpretation of the Charpy test results suggests the conclusion that treatment C gives a decided advantage in cryogenic toughness. Such a conclusion is, however, premature, as the results of cryogenic fracture toughness tests show.

(c) Cryogenic Fracture Toughness

Fracture toughness tests were conducted at 77°K on an MTS machine equipped with a liquid nitrogen cryostat. Compact tension (WOL) specimens were prepared and fatigue pre-cracked according to ASTM specifications.[9] The specimens for treatments A, B, and D were 0.7" (1.78 cm.) in thickness; due to dimensional changes in cold-work, the specimens for treatment C were 0.625" (1.56 cm.). Two specimens of each treatment were tested.

The results of the tests are shown schematically in figure 5, along with photographs of the fracture surfaces obtained. All specimens were well away from plane strain conditions. In lieu of K_{1c} values, K_Q values were computed from the load-crack opening displacement (COD) curves. The results were: $K_Q \sim 130$ KSI$\sqrt{in}$ for treatments A and B, and $K_Q \sim 140$ KSI $\sqrt{in}$ for C and D. It is not clear whether the higher K_Q value for treatment C is due to better ductility or to the smaller thickness of the test sample.

Samples of A, B, and C all showed unstable crack propagation, as marked by the step in the curves of figure 5 and as is evident from the fracture surfaces. The ductility prior to crack instability increased in the sequence A-C, though again the results for C are compromised by the smaller specimen thickness. Treatment A shows a scatter in fracture toughness behavior at 77°K similar to the scatter in Charpy energy at 5°K; the amount of deformation prior to crack instability varies, from sample to sample, from very little to the significant amount shown in the figure (This test employed an A sample having a high Charpy energy at 5°K).

The two-phase processed alloy (D), on the other hand, seemed immune to unstable crack propagation. The specimen was fully plastic, and the pre-induced crack grew slowly until the test was stopped. The ductility of the specimen is visually apparent from the photograph included in figure 5.

The fracture surfaces were examined by scanning electron microscopy. Figure 6 shows scanning electron fractographs taken slightly ahead of the pre-induced fatigue crack along the center line of the sample. The fractographs agree with the trend of the test data. Specimens A, B, and C fractured in a mixed ductile rupture, quasi-cleavage mode, with the fraction of ductile rupture in the fracture surface increasing in the sequence A-C. Specimen D fractured in a fully ductile mode. In contrast to the Charpy impact tests, the fracture toughness tests suggest that D is the superior treatment for imparting cryogenic toughness.

VI. Conclusions.

(1) A variety of grain refinement processes may be used to impart cryogenic toughness to a ferritic, low-interstitial Fe-12Ni-0.25Ti alloy. Through grain refinement the ductile-brittle transition temperature for Charpy impact energy can be suppressed below $5^{o}K$. The grain refined alloys also show excellent toughness in fracture toughness tests at $77^{o}K$, at yield strengths to 150 KSI.

(2) The Charpy impact and fracture toughness tests do not agree on the optimal heat treatment for cryogenic toughness. The Charpy test suggests treatment C (γ cycle + cold work + γ cycle), while the fracture toughness test suggests treatment D (γ cycle + two-phase cycle)(2X). The fracture toughness test seems the more meaningful of the two.

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(9) 1973 Book of ASTM Standards, Part 31, E399-72, p. 960.

CHARPY IMPACT RESULTS

CRYOGENIC TESTING

Heat Treat Series	77°K ft-lbs (Joules)	6°K ft-lbs (Joules)
I	<15 (21)	-
A	168 (228)	25(35) - 148 (201)
B	188 (244)	147 (199)
C	201 (272)	170 (230)
D	115 (156)	99 (134)

TABLE II

TENSILE PROPERTIES AT $77^{o}K$

Treatment	Yield Strength KSI (Newton/m^2)	Tensile Strength KSI (Newton/m^2)	Elong %	R.A. %
I	133 (9.3×10^8)			
A - C	133 (9.3×10^8)	142 (9.7×10^8)	31	74
D	149 (10.3×10^8)	154 (10.6×10^8	27	72

FIGURE CAPTIONS

(1) The Fe-Ni phase diagram with heat treatment (D) shown schematically.

(2) Characteristic microstructures of grain refined Fe-Ni alloys of intermediate Ni content.

(3) Optical micrograph of annealed Fe-12Ni-0.25Ti, prepared as described in text (2% Nital etch).

(4) Optical micrographs of Fe-12Ni-0.25Ti processed through treatments described in text (Etched with 5% picric acid solution saturated with sodium dodecyl benzene sulfonate).

(5) Results of fracture toughness tests at $77^{o}K$, with photographs of the fracture surfaces of the test specimens. Note that specimens A, B, and D have thickness (0.7 in.), while specimen C has thickness (0.625 in.).

(6) Scanning electron micrographs of the fracture surfaces of the specimens shown in figure 5. The areas shown lie on the centerline of the fracture surface slightly ahead of the pre-induced fatigue crack.

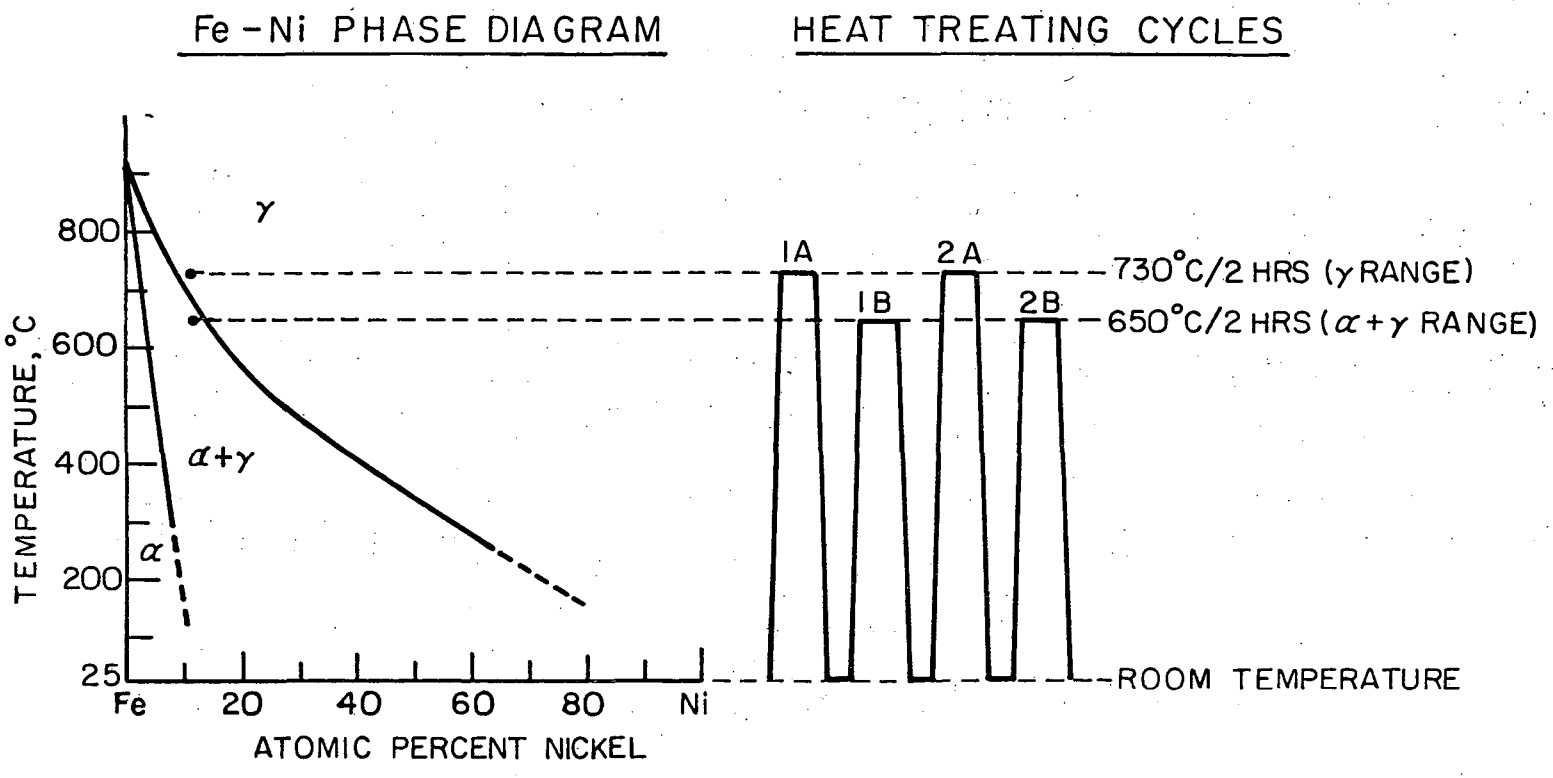

Fe - Ni PHASE DIAGRAM
HEAT TREATING CYCLES
TEMPERATURE, °C
800
600
400
200
25
γ
α+γ
α
Fe
20
40
60
80
Ni
ATOMIC PERCENT NICKEL
1A
2A
1B
2B
730°C/2 HRS (γ RANGE)
650°C/2 HRS (α+γ RANGE)
ROOM TEMPERATURE
XBL 739-1884

Fig. 1.

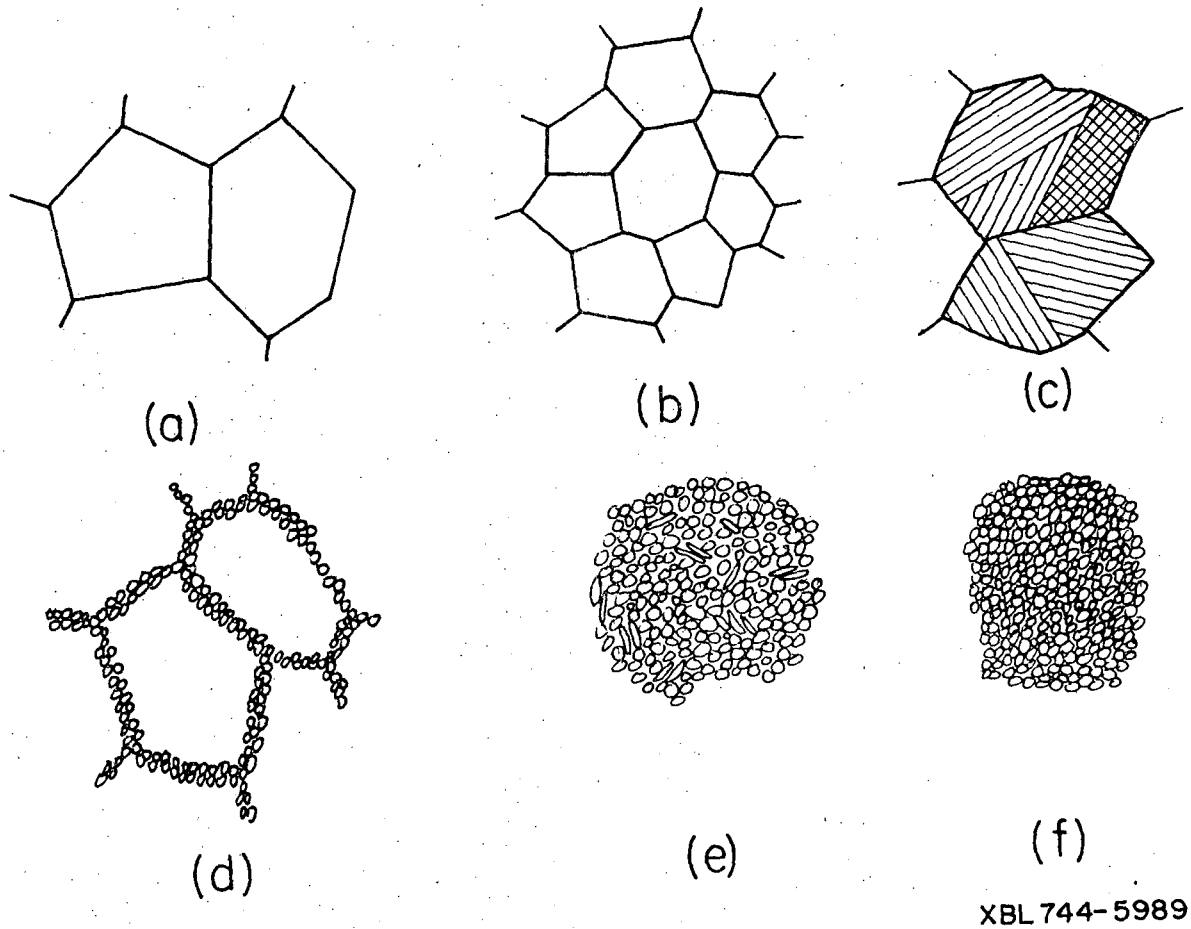
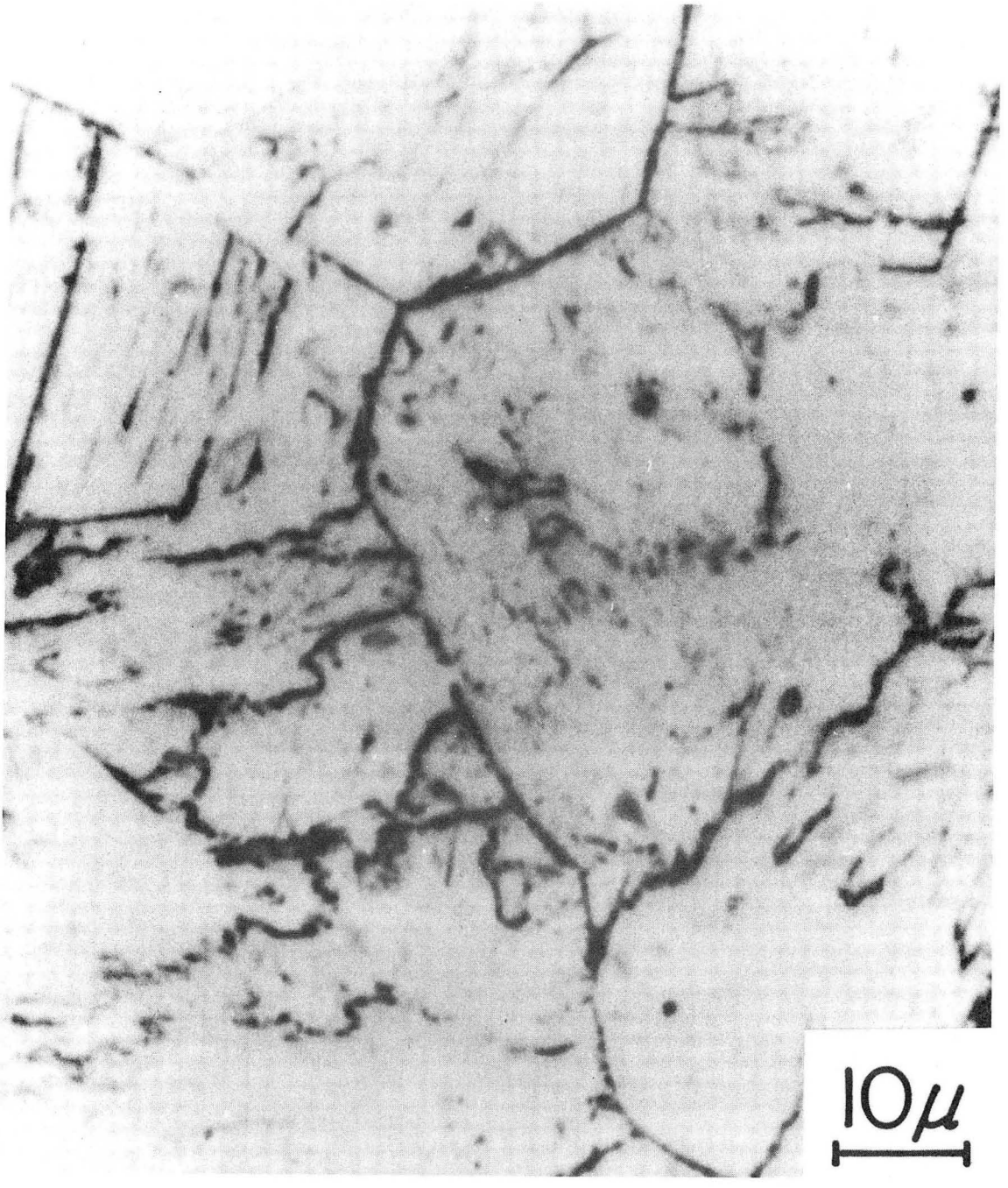
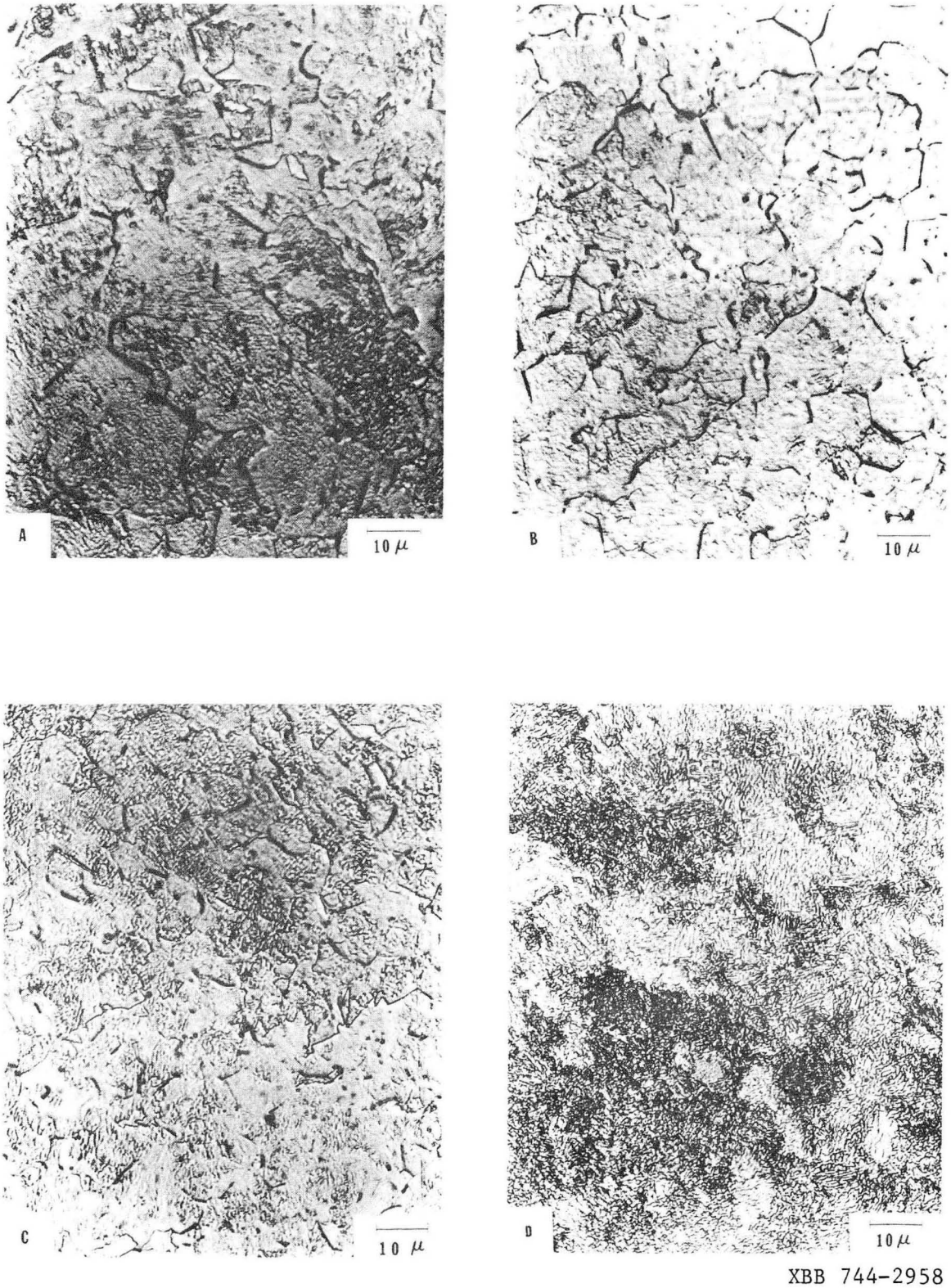


Fig. 2.



XBB 739-5688

Fig. 3.



XBB 744-2958

Fig. 4.

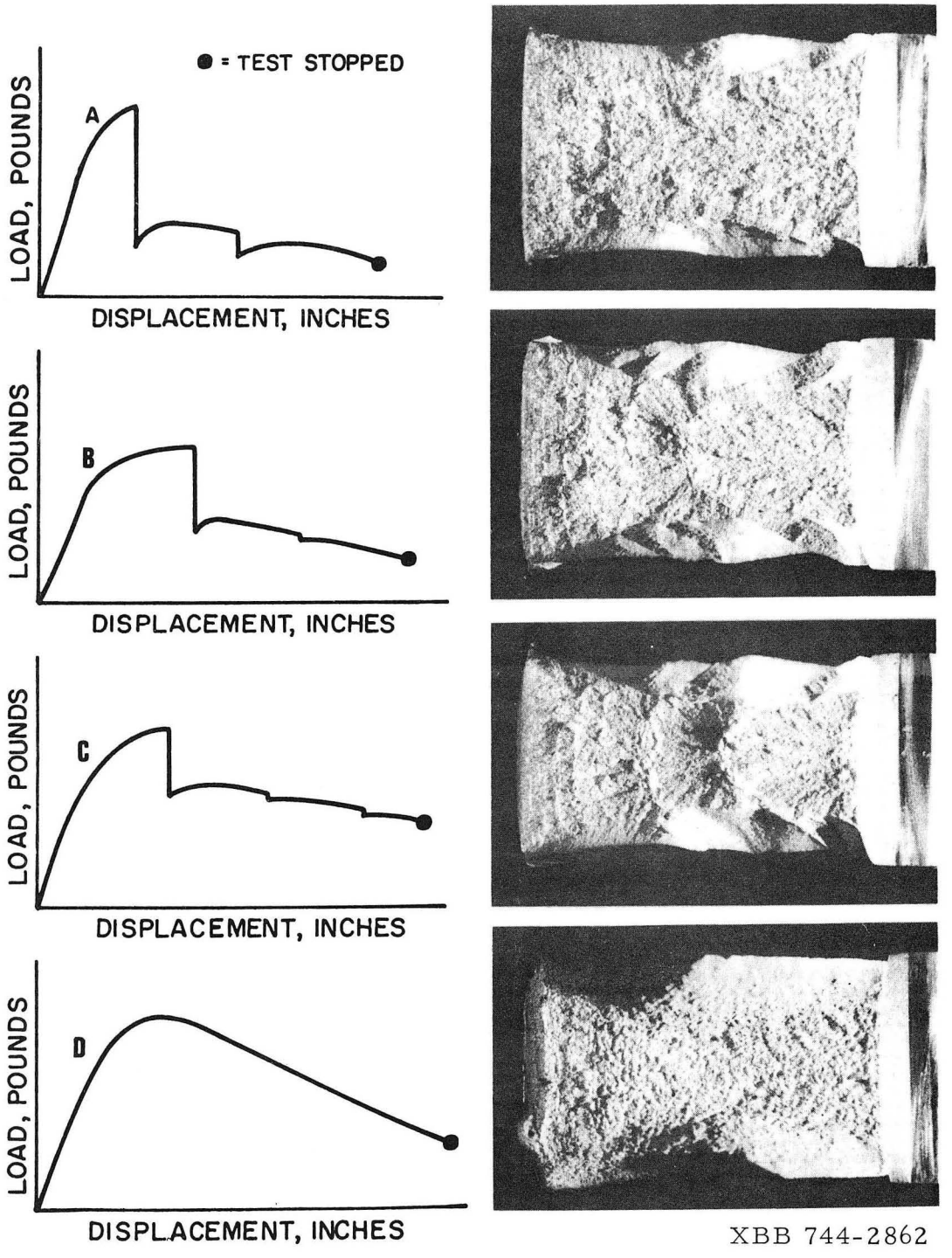
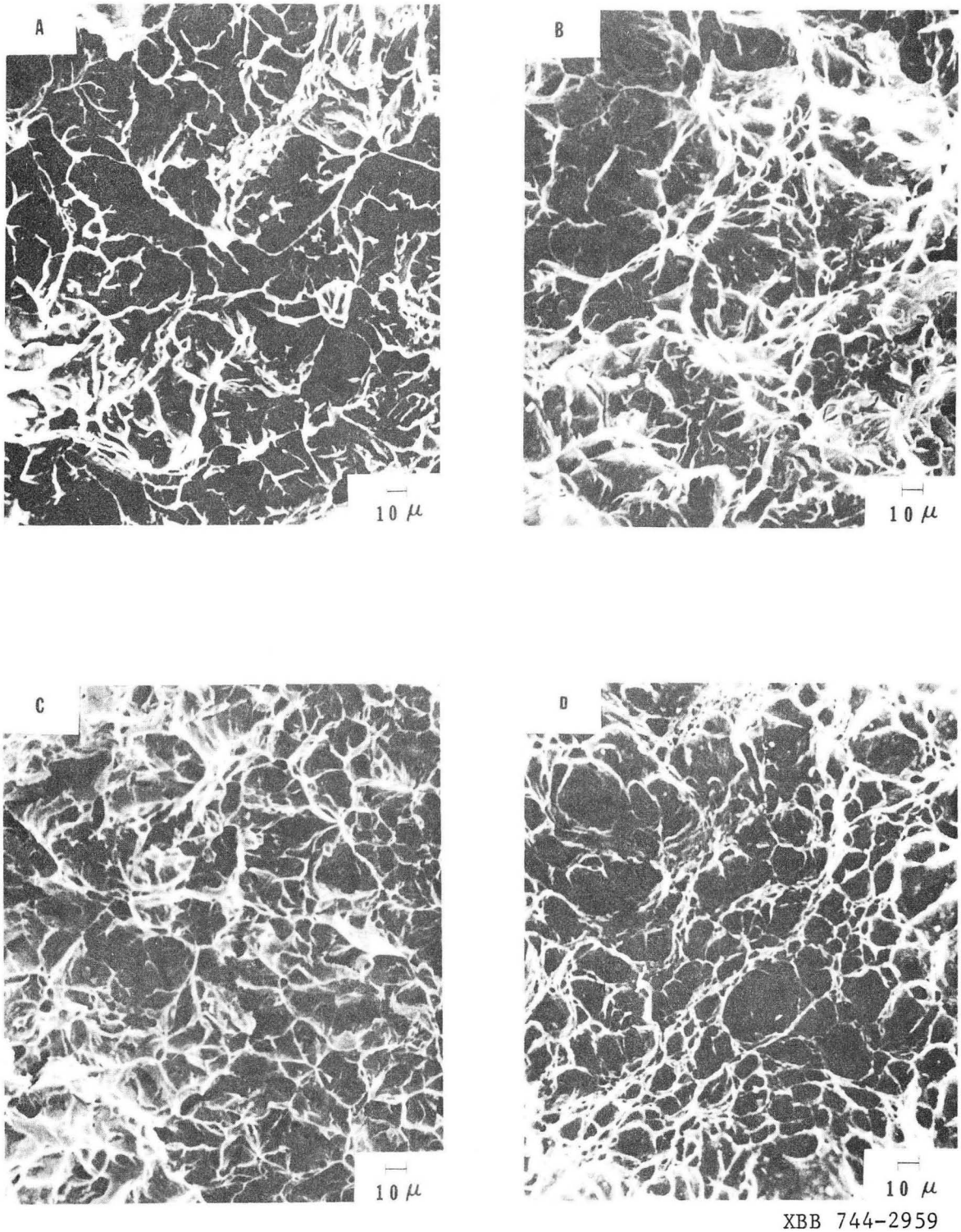

FRACTURE TOUGHNESS TEST RESULTS, 77°K
● = TEST STOPPED
A
LOAD, POUNDS
DISPLACEMENT, INCHES
B
LOAD, POUNDS
DISPLACEMENT, INCHES
C
LOAD, POUNDS
DISPLACEMENT, INCHES
D
LOAD, POUNDS
DISPLACEMENT, INCHES
XBB 744-2862

Fig. 5.



XBB 744-2959

Fig. 6.

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