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PHASE EVOLUTION DURING NEUTRON IRRADIATION OF COMMERCIAL Fe-Cr-Mn ALLOYS

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Phase Evolution during Neutron Irradiation of Commercial Fe-Cr-Mn Alloys

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Abstract

Earlier irradiation studies on simple Fe-Mn and Fe-Cr-Mn alloys in the annealed condition showed that these alloys exhibited a higher level of phase instability than do comparable Fe-Cr-Ni alloys. Contributing to this instability was the tendency of iron to segregate at microstructural sinks due to the operation of the inverse Kirkendall effect. This segregation, combined with the addition of various solutes and the application of typical thermomechanical treatments to produce the commercial alloys, added complexity to the phase evolution of Fe-Cr-Mn alloys. This complexity included the intergranular and intragranular precipitation of $M_{23}C_6$ carbide, alpha ferrite, and sigma. These phases can have detrimental effects on mechanical and corrosion properties. Provided that the phase transformations to sigma and carbides can be controlled, the commercial austenitic Fe-Cr-Mn alloys appear to be suitable starting compositions for the development of low activation alloys for service in fusion reactors.

Key Words

Epsilon martensite, alpha martensite, inverse Kirkendall, sigma phase, carbide, ferrite, ternary alloys, binary alloys, intergranular, precipitation, corrosion, intergranular failure, phase instability, commercial alloys, reduced activation

Introduction

Fe-Cr-Mn alloys are being considered as a replacement for Fe-Cr-Ni stainless steels in the construction of fusion reactors due to their reduced intermediate-term radioactivity following service.[1,2] This reduced activation simplifies the disposal of structural components to class C shallow burial. Four commercial Fe-Cr-Mn alloys irradiated in the Fast Flux Test Facility Materials Open Test Assembly to a dose of 75 displacements per atom (dpa) at 420°C and 520°C and to a dose of 60 dpa at 600°C were characterized following irradiation using analytical transmission electron microscopy.

Previous studies proved that simple Fe-Mn binary alloys in the 85-90wt% Fe range, have a pre-irradiation microstructure composed of epsilon and alpha martensite and retained austenite. In the 72 to 85wt% Fe range only epsilon martensite was present in the austenite.[3] These alloys are also susceptible to sequential transformations from austenite to epsilon martensite and then to alpha martensite when subjected to stress.[4] The addition of chromium to these binary alloys increases the austenite stability and provides corrosion resistance. However, enhanced diffusion during the irradiation of the simple ternary Fe-Cr-Mn alloys leads to segregation by the inverse Kirkendall effect and, consequently, local compositions at which transformations to alpha and epsilon martensite are likely even with the addition of austenite stabilizers.[5,6] See Figure 1. The addition of carbon and chromium adds to these instabilities making the formation of carbides and sigma probable.

Insert Figure 1 here

Results and Discussion

The compositions of the commercial alloys in this study are designed to stabilize austenite and avoid embrittling transformations to alpha and epsilon martensite that were observed to occur in simple binary and ternary alloys. These alloys contain moderate amounts of manganese with minor additions of austenite stabilizers, carbon, and elements believed to improve performance for the particular purpose for which the alloy was originally designed. See Table 1. Consequently, these alloys showed less alpha and epsilon martensite to be present following irradiation when examined in a transmission electron microscope. However, phases such as tetragonal sigma and fcc $M_{23}C_6$ did precipitate on grain boundaries which is a concern because these brittle phases can be the nucleation sites for cracks that can lead to intergranular failure. The precipitation of these chromium rich phases also depletes the matrix of chromium, reducing corrosion resistance and increasing iron content near the grain boundary.[7] This iron enrichment near the grain boundary, coupled with iron segregation due to inverse Kirkendall, caused the nucleation and growth of alpha ferrite in the aged conditions of AMCR [8], 18/18 Plus, and the cold worked condition of NMF3. In the low chromium alloy NMF3 irradiated at 520°C, this mechanism produced decomposed regions 10 microns wide centered on the original austenite/austenite grain boundaries.

The decomposed regions contained three phases; $M_{23}C_6$, bcc alpha ferrite and retained austenite.[7] See Figure 2. The effects of this grain boundary decomposition were observed in a corrosion study in which AMCR was heat treated in lithium at 600°C. Lithium penetrated along grain boundaries and incoherent twin boundaries and resulted in intergranular failure during post-irradiation testing.[9]

Insert Table 1 here

The high chromium alloy, 18/18 Plus, contained neither alpha nor epsilon martensite following irradiation. However, there was heavy homogeneous and heterogeneous $M_{23}C_6$ carbide precipitation at 420°C and 520°C. In contrast Nitronic Alloy 32 with 6wt% less manganese and reduced minor additions of nickel, copper and molybdenum, showed no homogeneous and less heterogeneous carbide precipitation. The high chromium alloys, 18/18 Plus and Nitronic Alloy 32, contained sigma following irradiation at 600°C. See Figure 3. Low chromium alloys, AMCR and NMF3, did contain alpha and epsilon martensite prior to and following irradiation for some thermomechanical treatments and irradiation temperatures. See Figure 4 and 5. They did not however contain sigma following irradiation at 600°C.

Insert Figure 2

Insert Figure 3

Insert Figure 4

Insert Figure 5

To summarize the dependence of phase transformations on composition in the commercial Fe-Cr-Mn alloys, increasing iron content increases susceptibility to transformations to epsilon and alpha martensite. Increasing chromium content decreases susceptibility to martensite transformations but increases susceptibility to carbide and sigma precipitation. Decreasing manganese content decreases carbide precipitation.

In addition to composition, prior thermomechanical treatment can change phase stability during irradiation. Several of these commercial alloys were irradiated in multiple thermomechanical conditions with varying results. See Table 1 and Figure 6. As shown in figure 6, aging produces larger heterogeneous precipitates at the expense of smaller homogeneous precipitates. Aging also has an effect on alpha ferrite formation in the alloys 18/18 Plus and AMCR. Alloy 18/18 plus in the cold worked condition precipitates $M_{23}C_6$ carbides on grain boundaries during irradiation at 420°C, however, in the cold worked and aged condition, alpha ferrite also precipitates there. Sufficient iron segregation occurred at void surfaces by the inverse Kirkendall mechanism to precipitate alpha ferrite there only in solution annealed and aged (SAA) AMCR of the three thermomechanical conditions irradiated. See Table 1 and Figure 7

Insert Figure 6

Insert Figure 7

Conclusions

Provided that the phase transformations to sigma and carbides can be controlled, the commercial austenitic Fe-Cr-Mn alloys appear to be suitable starting compositions for the development of low activation alloys for service in fusion reactors. The austenite of the commercial Fe-Cr-Mn alloys is more stable than that of the simple ternary and binary alloys with respect to alpha and epsilon martensite transformations. However, the Cr and carbon content of these alloys leads to the formation of $M_{23}C_6$ carbides at all irradiation temperatures and at 600°C leads to sigma formation in the high chromium alloys Nitronic Alloy 32 and 18/18 Plus. If the precipitation occurs at grain boundaries the mechanical and corrosion properties of these alloys are degraded. Grain boundary decomposition is more likely to occur in aged alloys and be most severe in low chromium alloys such as NMF3 (4wt%Cr).

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Table 1. Composition of Commercial Fe-Cr-Mn Austenitic Alloys

Designation	Vendor	Composition wt%	Conditions
Nitronic Alloy 32	ARMCO	18Cr-12Mn-1.5Ni-0.6Si-0.2Cu-0.2Mo-0.4N-0.1C-0.02P	CW
18/18 Plus	CARTECH	18Cr-18Mn-0.5Ni-0.6Si-1.0Cu-1.1Mo-0.4N-0.1C-0.02P	CW, CWA
AMCR	CREUSOT-MARREL	10Cr-18Mn-0.7Ni-0.6Si-0.06N-0.2C	CW, CWA, SAA
NMF3	CREUSOT-MARREL	4Cr-19Mn-0.2Ni-0.7Si-0.09N-0.02P-0.6C	CW

Note: CW = 1030°C/0.5 h/air cool + 20% cold-work.
CWA = cold worked condition + 650°C/h/air cool.
SAA = 1030°C/1 h/air cool + 760°C/2 h/air cool.

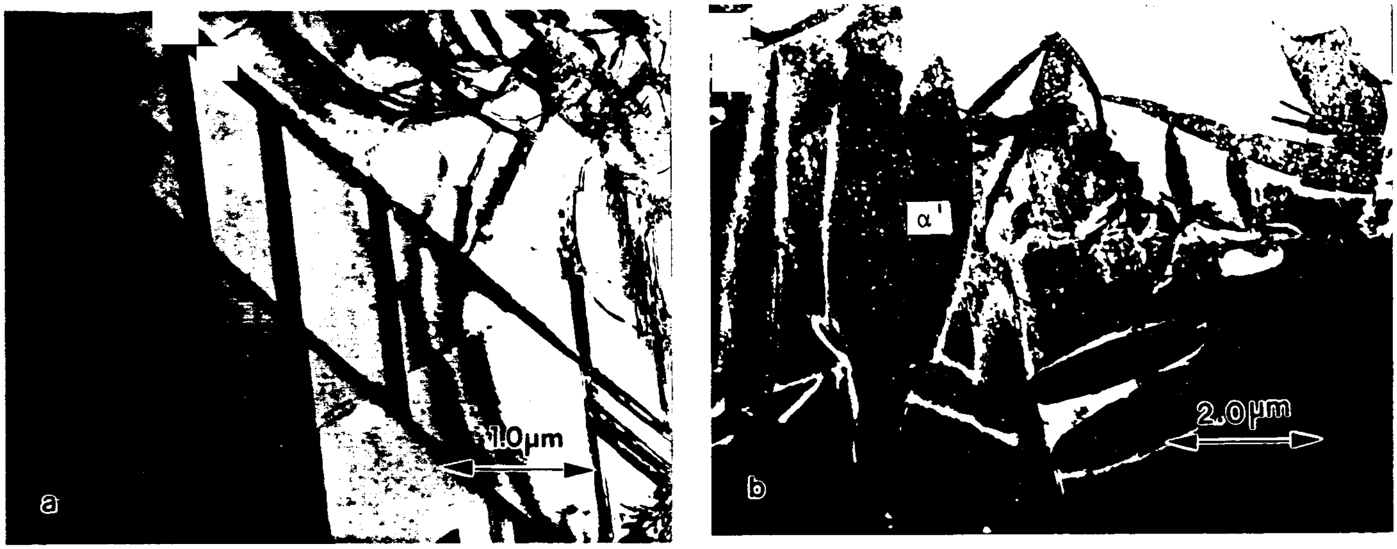

Fig. 1a. Brightfield transmission electron micrograph (TEM) of unirradiated annealed Fe-5Cr-15Mn composed of large austenite grains with stacking faults.

b. Brightfield TEM image of some material following irradiation at 420°C to 9 dpa, lenticular alpha martensite and retained austenite with epsilon martensite were present.

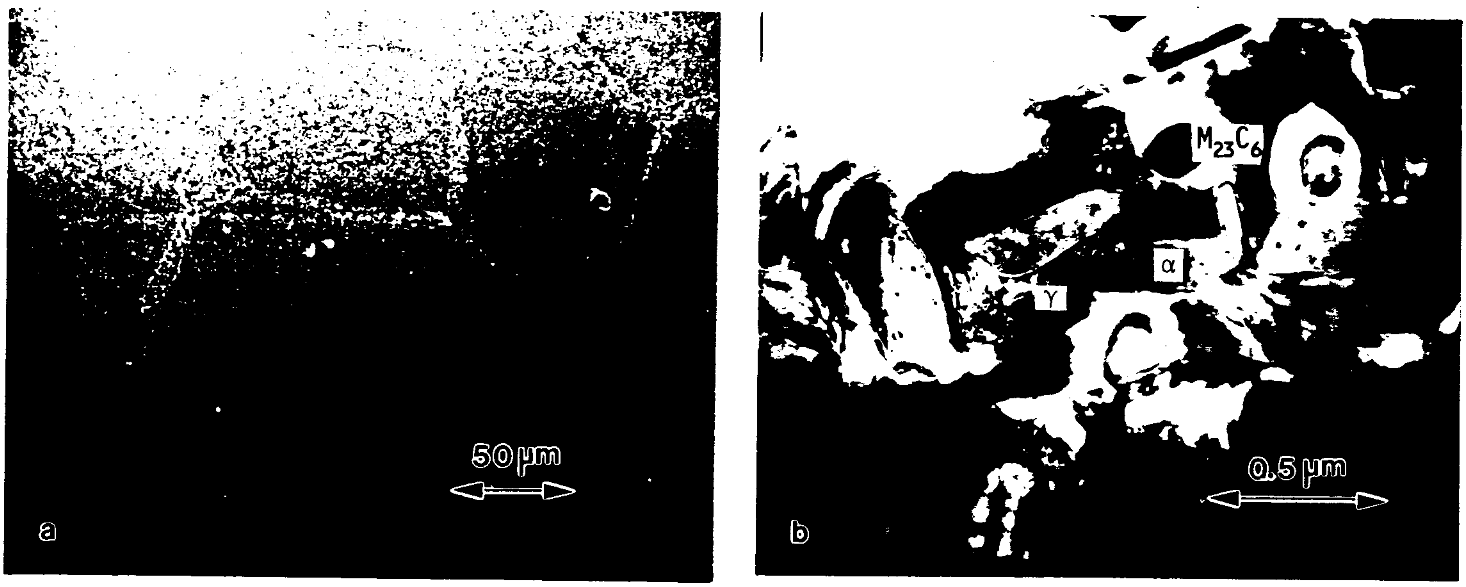

Fig. 2a. Scanning electron micrograph (SEM) of surface of electropolished NMF3 irradiated at 520°C to 75 dpa showing decomposed austenite/austenite grain boundaries.

b. Brightfield TEM image of one of the decomposed grain boundaries in 2a.

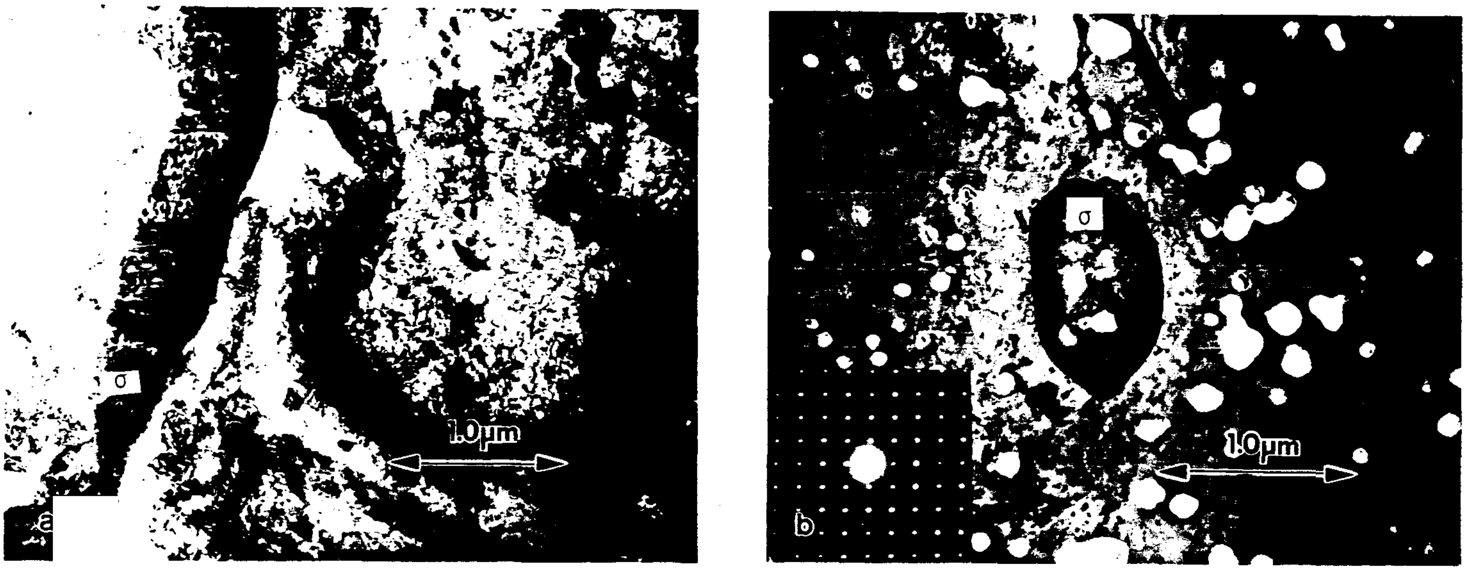

Fig. 3a. Brightfield TEM image of the intermetallic tetragonal sigma phase coating a grain boundary in cold-worked 18/18 Plus irradiated at 600°C to 60 dpa.

b. Brightfield TEM image and inset diffraction pattern of sigma in Nitronic Alloy 32 irradiated at 600°C to 60 dpa.

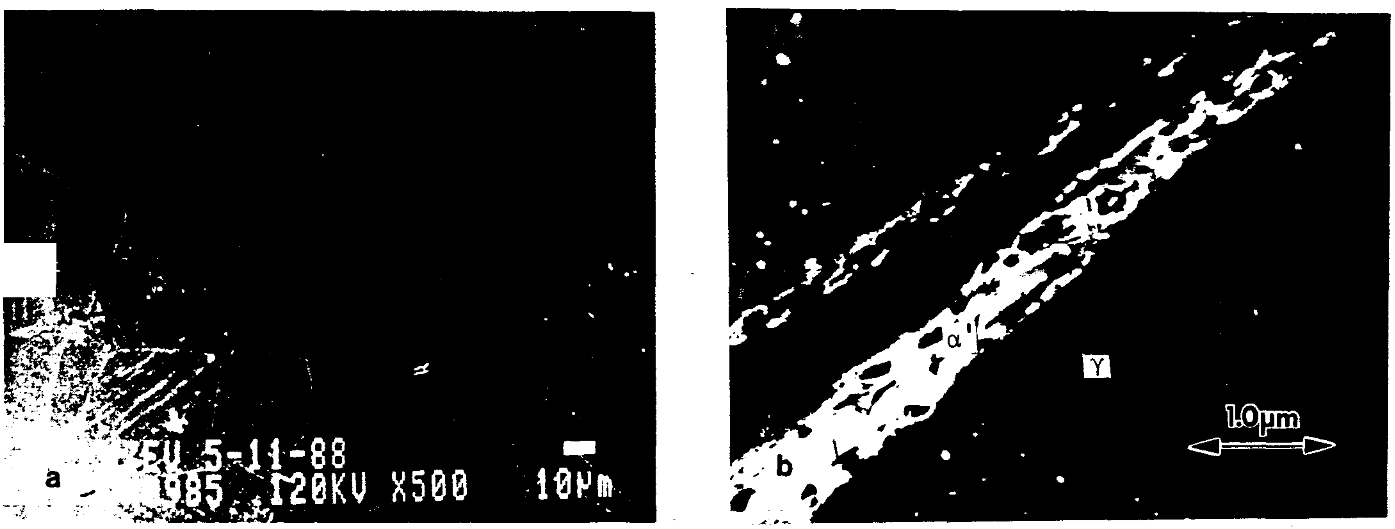

Fig. 4a. SEM image of surface of electropolished foil of cold-worked AMCR irradiated at 520°C to 75 dpa showing a high density of alpha martensite plates.

b. Brightfield TEM image of the martensite plates with $M_{23}C_6$ carbides visible within the plates and at the austenite/martensite grain boundary.

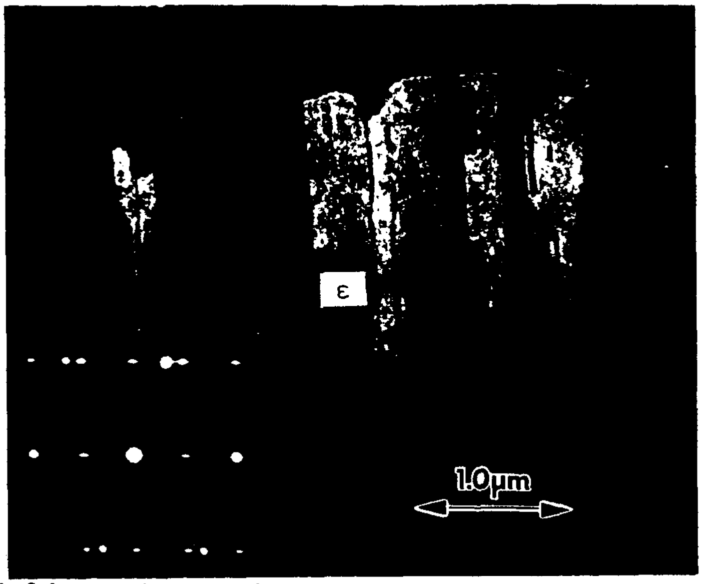

Fig. 5. Darkfield TEM image with inset diffraction pattern of epsilon martensite $\langle 1210\rangle_{\epsilon} \| \langle 110\rangle_{\gamma}$ in NMF3 irradiated at 600°C to 60 dpa.

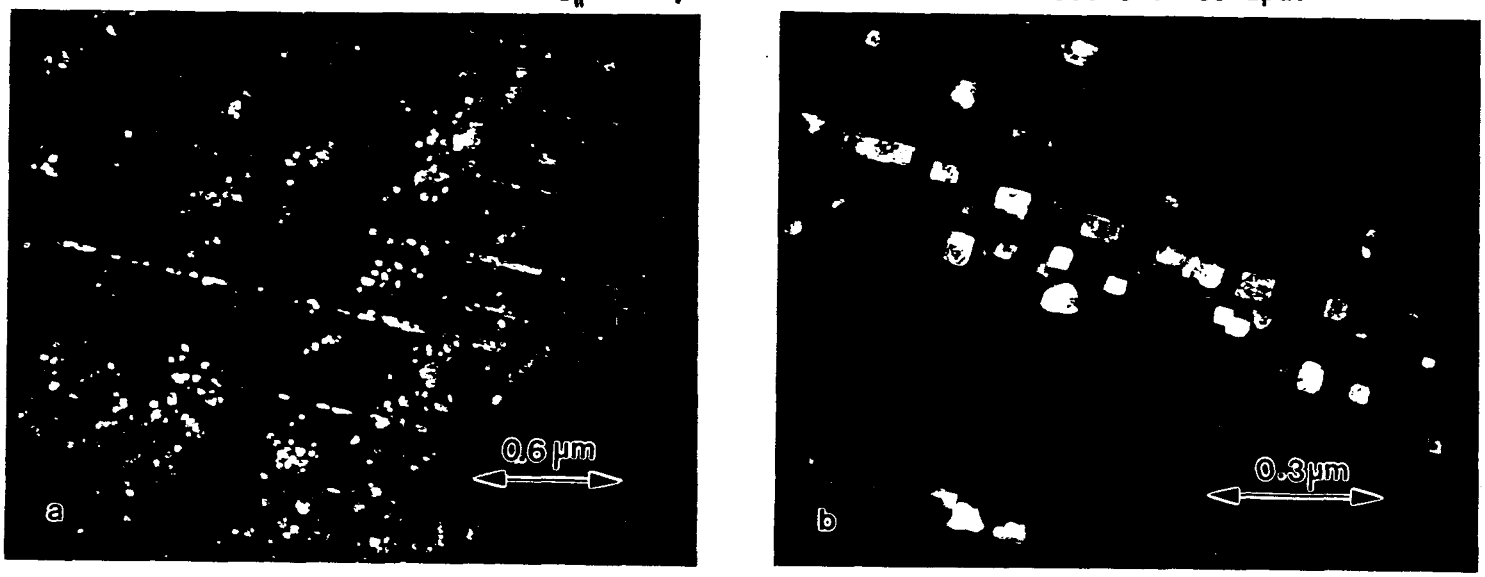

Fig. 6a. Darkfield TEM image of $M_{23}C_6$ carbides in cold-worked 18/18 Plus irradiated at 520°C to 75 dpa.

b. Image of the same carbides in the same alloy with aging prior to irradiation

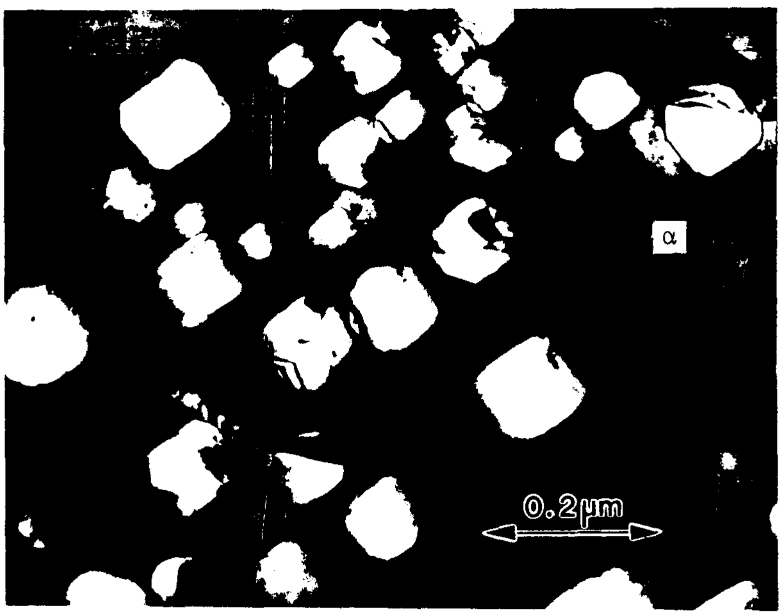

Fig. 7. Brightfield TEM image of alpha ferrite in the austenite of solution annealed and aged AMCR irradiated at 520°C to 75 dpa.