The Role of Hafnium in Modifying the Microstructure of Cast Nickel-Base Superalloys

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The effects of hafnium additions on the microstructure of ALLOY 713-LC have been investigated using electron microscopy and by a radiographic technique which reveals the grain boundary structure. It is shown that the chinese script MC carbides in ALLOY 713-LC are altered to a particulate morphology in alloy MM-004 (hafnium-modified ALLOY 713-LC). Unlike the script carbides, the discrete MC particles do not provide any easy path for rapid crack propagation and hence, ductility is enhanced. In the hafnium-bearing alloy, the morphology of γ' phase is also modified. Colonies of $(\gamma + \gamma')$ with a rosette morphology are formed and individual γ' platelets exhibit dendritic growth. It is shown that this morphology of γ' causes grain boundaries to be distorted from planar equilibrium interfaces to a convoluted interlocking configuration. It is suggested that the interlocking boundaries retard grain boundary sliding and separation during creep and result in higher stress-rupture life for hafnium-modified alloys.

CAST nickel-base superalloys, used in turbine hardware, are typically composed of approximately 60 vol. pct of a γ' phase coherently precipitated in an fcc matrix, together with eutectic phases and one or more carbide phases. Since these alloys cannot be heat treated, *i.e.* one cannot solution heat-treat and reprecipitate the γ' phase, their properties are governed by the as-cast microstructure. The latter has become increasingly complex in response to the continued need for improvements in elevated-temperature strength. Unfortunately, concomitant with gains in high temperature strength, there has been an associated penalty in that the ambient and intermediate temperature ductility of cast superalloys is usually poor. Recently, however, it has been shown[1,2] that additions of hafnium to nickel-base superalloys can lead to substantial improvement in both ductility and high temperature creep properties. This paper presents results from a study undertaken to define the role of hafnium in modifying the structure and structure-dependent properties of nickel-base alloys.

EXPERIMENTAL PROCEDURE

The experiments reported here were carried out on the commercial alloy ALLOY 713-LC and the hafnium-modified alloy MM-004 kindly provided by the Martin Metals Company in the form of investment-cast test bars. The compositions of these alloys are shown in Table I.

Table I. Alloy Compositions

Composition in Wt Pct	Cr	Mo	Al	Ti	Cb	Zr	B	C	Hf	Ni
713-LC	12.5	4.1	6.1	0.8	2.0	0.10	0.12	0.08	–	Bal
MM-004	12.5	4.1	6.1	0.8	2.0	0.10	0.12	0.08	1.5	Bal

The electrolyte used for etching the specimens prior to replication, and for optical examination, was a 6:8:30 mixture of HF, HNO_3, and glycerol, respectively. Thin foils were prepared by twin-jet electropolishing of 3 mm diam disc specimens in an ethanol-10 pct perchloric acid bath at 32°F. All observations were carried out using a JEM-7 electron microscope operated at 100 kv.

To study the morphology of grain boundaries in ALLOY 713-LC and MM-004 alloys, the boron-mapping technique based on the observations of Fleischer *et al.*[3] was used. By mapping the boron distribution it was possible to reveal, indirectly, the grain boundary structure. This procedure is based upon the observation that certain nuclides can cause highly localized and detectable damage in films of mica, polycarbonate resin, or cellulose nitrate. Of specific interest to the present work is the fact that the energy, 1.8 mev, of the α particle resulting from the B^{10} (n, α) reaction is within the range of values which produce detectable tracks in cellulose nitrate. In this work, 10 mil thick films of cellulose nitrate were glued to highly polished surfaces of the samples. These packages were then irradiated for 5 min in a thermal neutron beam having a flux of 5×10^{11} n per sq cm per sec in the Union Carbide reactor at Sterling Forest, N. Y. The damage tracks left by the α particles in the cellulose nitrate were subsequently revealed as small etch pits by etching the films in a 6.5 N aqueous solution of NaOH for 2 to 3 min at 116°F.

RESULTS

a) Intragranular Carbide Morphology

The "as-cast" alloy ALLOY 713-LC has a coarse-grained, complex microstructure in which the columbium (Nb)-rich MC carbides form a network with a chinese script morphology. A composite micrograph showing the extent of this script carbide substructural network in a longitudinal section of a tensile-test spec-

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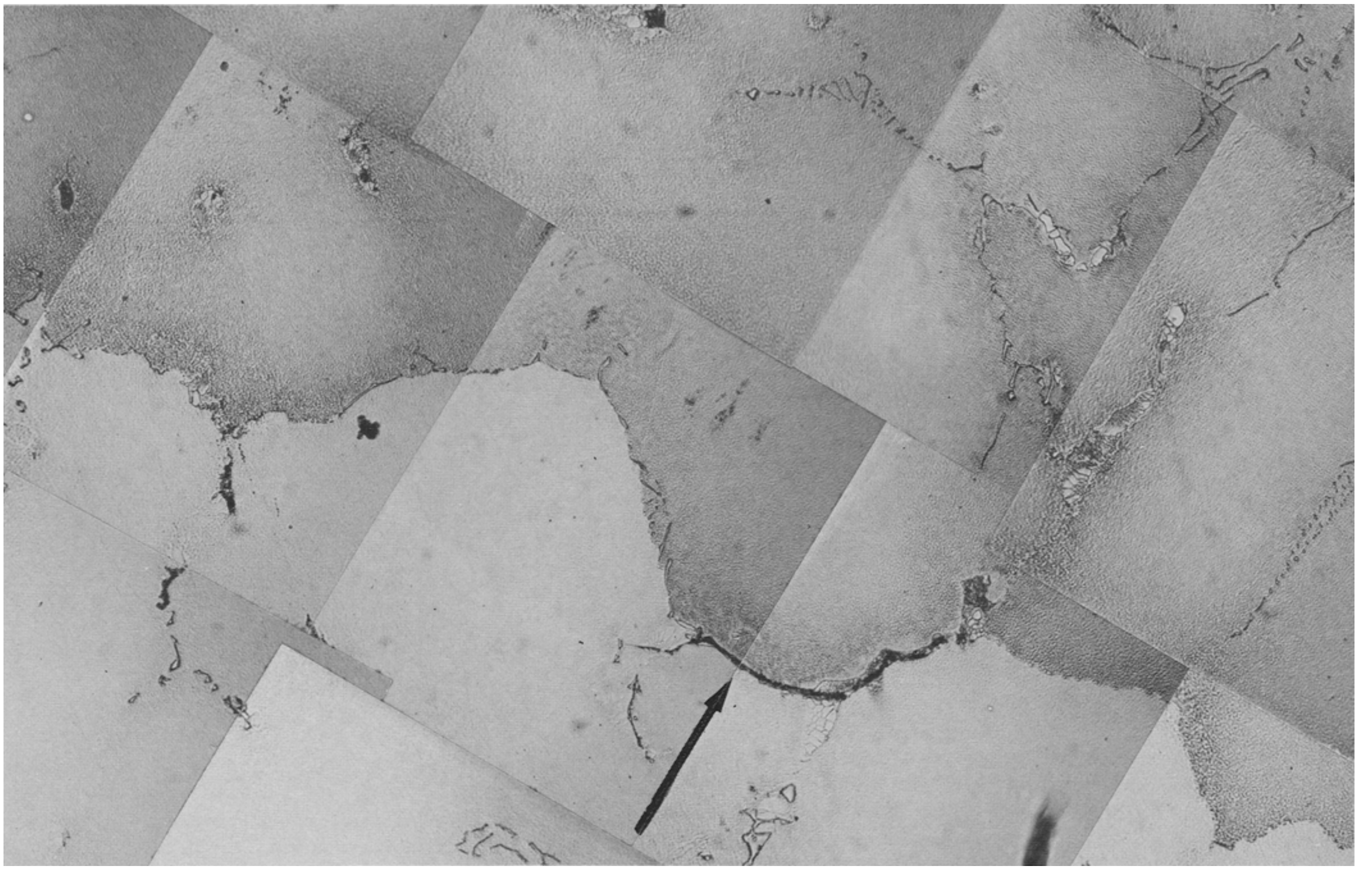

Fig. 1—Optical micrograph of a tensile specimen of ALLOY 713-LC. Longitudinal section. Magnification 236 times.

imen, which fractured after 3 pct elongation at room temperature is shown in Fig. 1. An individual cluster of script carbides is shown in the plastic replica micrograph in Fig. 2(*a*). In contrast, alloy MM-004 in the "as-cast" condition exhibits MC carbides having a discrete particulate morphology, as shown in Fig. 2(*b*).

The differences in carbide morphology found in ALLOY 713-LC and MM-004 seem to be primarily responsible for the enhanced tensile ductility in the hafnium-modified alloy. The regions marked by the arrow in Fig. 1 shows that cracks, perpendicular to the tension axis, are initiated at the script carbide phase. Once crack initiation has occurred, the continuous network of the script carbides greatly facilitates rapid crack propagation. Thus, the MC carbides provide regions, within an otherwise ductile matrix, along which cracks can initiate and propagate in a brittle manner. For example, in Fig. 3(*a*) the scanning electron micrograph shows fracture dimples typical of crack propagation by void coalescence in the matrix, but brittle fracture of the script carbides. This structure provides room temperature ductility in the range of 3 to 5 pct. On the other hand, a scanning electron micrograph of an MM-004 tensile fracture surface, Fig. 3(*b*), shows that the fracture is ductile throughout. The MC carbides, which are distributed as discrete particles, Fig. 2(*b*), in alloy MM-004, may still provide sites for the nucleation of microvoids but their shape and distribution does not provide a preferred path for crack propagation. As a result the ductility of MM-004 is considerably enhanced, and typically, MM-004 exhibits tensile ductility in the range 12 to 15 pct.

b) γ' Morphology

In addition to its influence on the morphology of carbides, the addition of hafnium to ALLOY 713-LC also modifies the distribution of γ' phase in the as-cast condition. For example, Fig. 4 shows a region of the interdendritic $(\gamma + \gamma')$ eutectic in the ALLOY 713-LC, with the so-called "blocky" γ' morphology, together with the intragranular homogeneously-nucleated γ' phase, which forms on cooling after solidification. The γ' strengthening precipitates have a typical $\{001\}_\gamma \parallel \{001\}_{\gamma'}$ morphology and each particle is distinctly cubic.

The morphology of γ' phase in as-cast MM-004 alloy is considerably different. As shown in the optical micrograph in Fig. 5, regions of $(\gamma + \gamma')$ with a rosette-like morphology can be observed. The fingers of γ', which interpenetrate the γ matrix within each rosette, exhibit a blocky morphology, and extend up to the interface between the rosette colonies, as is evident in Fig. 6(*a*). Locally, serrations can be observed at the γ/γ' interface, "*S*" in Fig. 6(*b*), of the γ' platelets in a given colony. These serrations are more closely revealed by thin foil transmission electron micrography, Figs. 7(*a*) and 7(*b*). These micrographs show that, in fact, the fingers or platelets of the γ' phase in MM-004 exhibit a distinctly "dendritic" morphology, with primary, "1" in Fig. 7(*a*), and secondary, "2" in Fig. 7(*b*), growth directions. The second-order dendrite

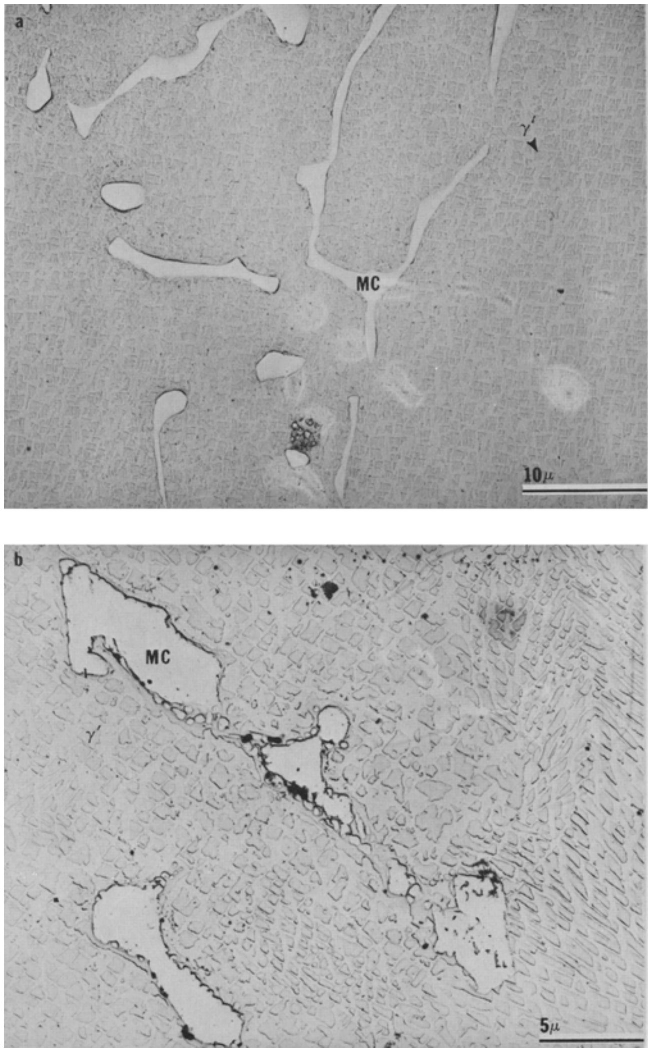

Fig. 2—Plastic replica micrographs showing the morphology of MC carbides. (*a*) "Chinese script" carbides in ALLOY 713-LC, and (*b*) discrete particles of MC in MM-004 alloy.

arms exhibit serrated facets which correspond to $\{001\}$ interfaces for normally cube-shaped precipitates. This suggests that the typical γ/γ' orientation relationship is maintained in the hafnium-modified alloy, despite growth in a preferred $\langle 110 \rangle$ direction.

c) Grain Boundary Structure

Figs. 8(*a*) and 8(*b*) are radiographic maps of the boron distribution in ALLOY 713-LC and MM-004, respectively. As is generally observed in cast superalloys, the boron is concentrated principally at interfaces such as grain boundaries and subgrain boundaries.[4] Inspection of Fig. 8(*a*) indicates that the 713-LC alloy exhibits a conventional type of grain structure, in which the grains are bounded by relatively planar interfaces. By contrast, the grain boundaries of the MM-004 alloy exhibit a convoluted structure, in which the grains appear to interlock with each other, as shown in Fig. 8(*b*). This unusual grain boundary morphology seems to be related to the tendency, for the γ' phase in MM-004 alloy, to form in the dendritic manner described above. Thus in Fig. 9, it is

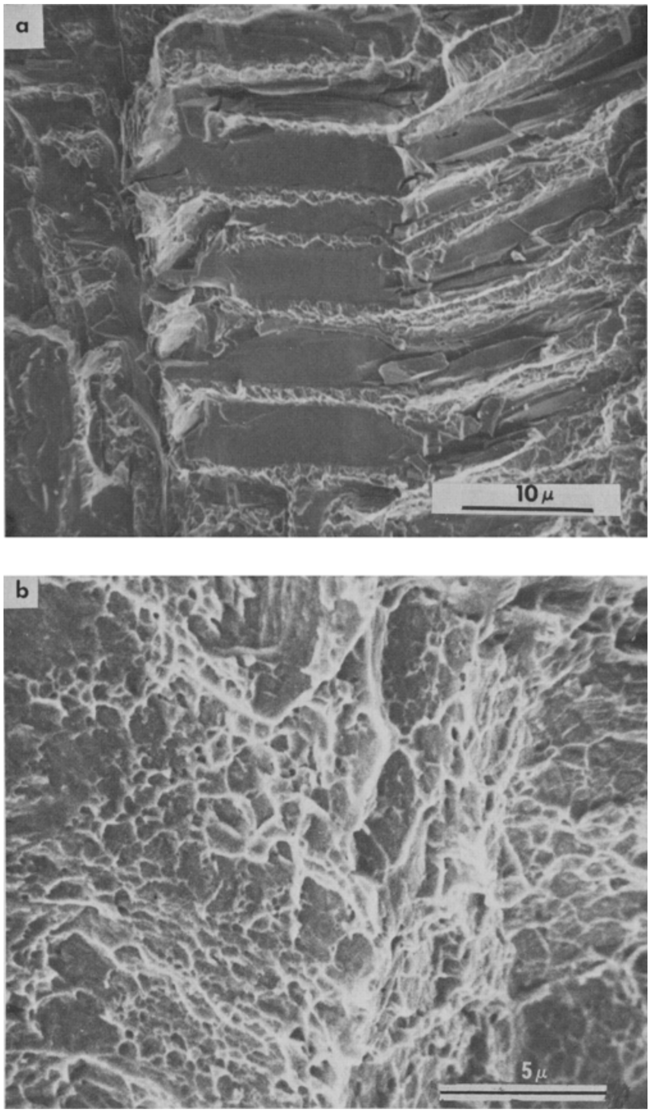

Fig. 3—Scanning electron fractographs showing (*a*) brittle fracture of MC platelets and ductile fracture of the matrix in ALLOY 713-LC, and (*b*) ductile fracture in alloy MM-004.

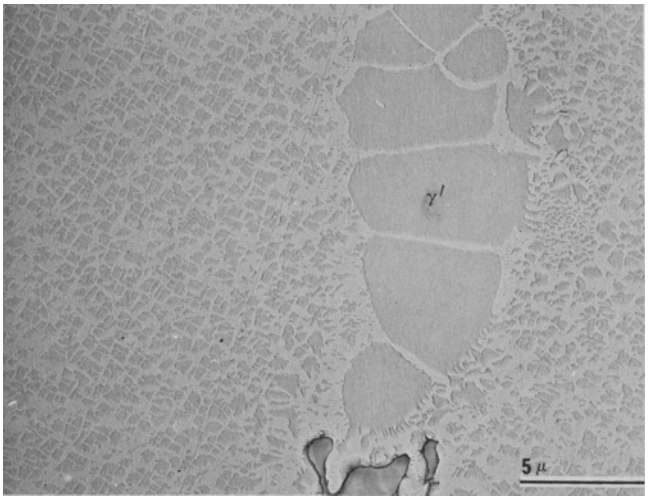

Fig. 4—Plastic replica micrograph of as-cast ALLOY 713-LC alloy showing "blocky" γ' together with intragranular γ' precipitate.

evident that under the influence of the dendritic γ' phase growing in two adjacent grains, the grain boundary has been distorted from an equilibrium planar interface.

DISCUSSION AND CONCLUSIONS

It is evident from the results presented above that the addition of hafnium to ALLOY 713-LC has the following effects upon the microstructure: i) the chinese script MC carbides are modified to a discrete particulate morphology, ii) the γ' phase exhibits a "dendritic" morphology instead of the usual cube-like arrangement in the unmodified alloy, and iii) the grain boundaries are modified from planar interfaces to a convoluted configuration as a consequence of the dendritic morphology of γ'.

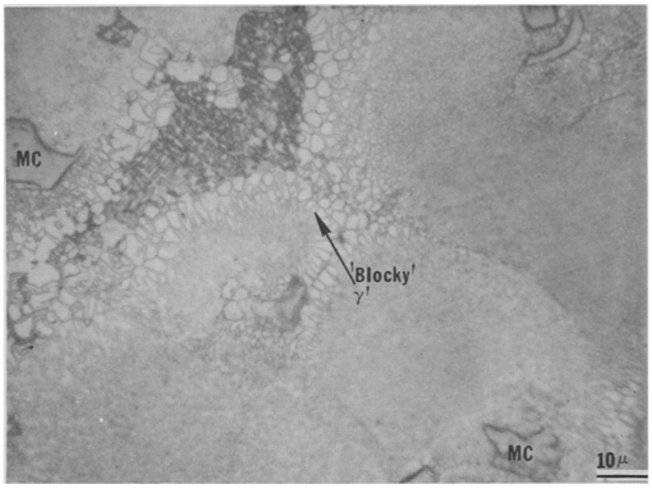

Fig. 5—Optical micrograph showing rosette-like $\gamma + \gamma'$ colonies in MM-004 alloy.

It is suggested that these changes are responsible for the improved low temperature ductility and high temperature creep resistance of MM-004[1,2] relative to the corresponding properties of ALLOY 713-LC. Thus, it is expected that the modified carbide distribution would reduce the available paths for brittle fracture, thereby improving ductility. Secondly, alteration of the grain boundary structure from planar interfaces to an interlocking configuration would be expected to provide increased resistance to grain boundary sliding and separation during creep. Indeed, the importance of microstructural features which retard grain boundary sliding and, hence, prolong stress-rupture life, has long been recognized. For example, Sims[5] and Gresham[6] have proposed that improved intermediate and elevated temperature stress-rupture life in cast nickel-base alloys is dependent upon the existence of a film of γ' phase at the grain boundaries. This γ' at the grain boundary serves to delay the onset of fracture by accommodating the local shear associated with grain boundary sliding—both in the case of grain boundaries which are relatively free of carbide precipitates, and in the case where (due to a high carbon concentration as, for example, in MAR-M-200 or IN-100 alloys) carbides such as $M_{23}C_6$ occur at the grain boundaries. In hafnium-modified alloys, such as MM-004, it appears that, rather than a grain boundary film, the interlocking dendritic γ' in adjacent grains, shown in Fig. 9 and depicted schematically in Fig. 10, provides the resistance to grain boundary sliding.

Other factors, not explicitly considered in this investigation, may also contribute to the superior mechanical properties of hafnium-modified alloys. Consider-

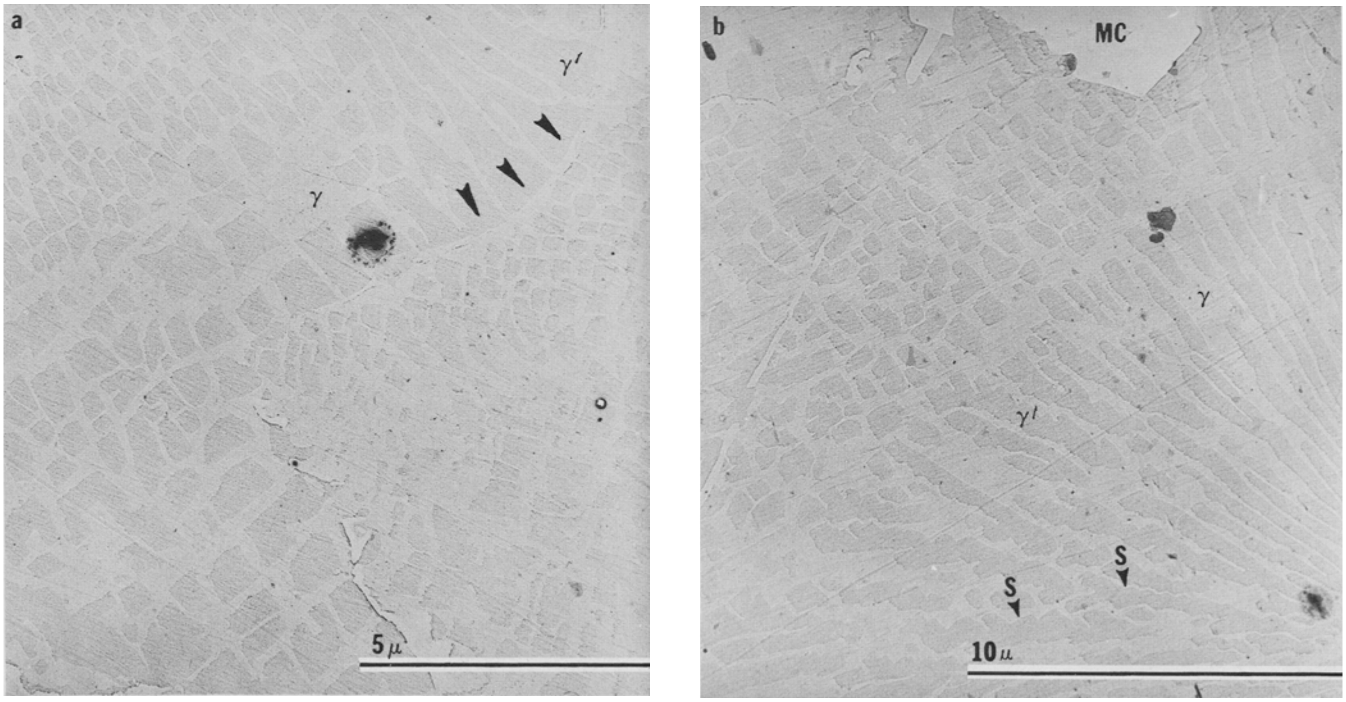

Fig. 6—Plastic replica micrographs of as-cast MM-004 alloy showing morphology of γ' phase. (*a*) "Blocky" γ' at an interface between adjacent $\gamma + \gamma'$ rosettes; (*b*) serrations at γ/γ' interface.

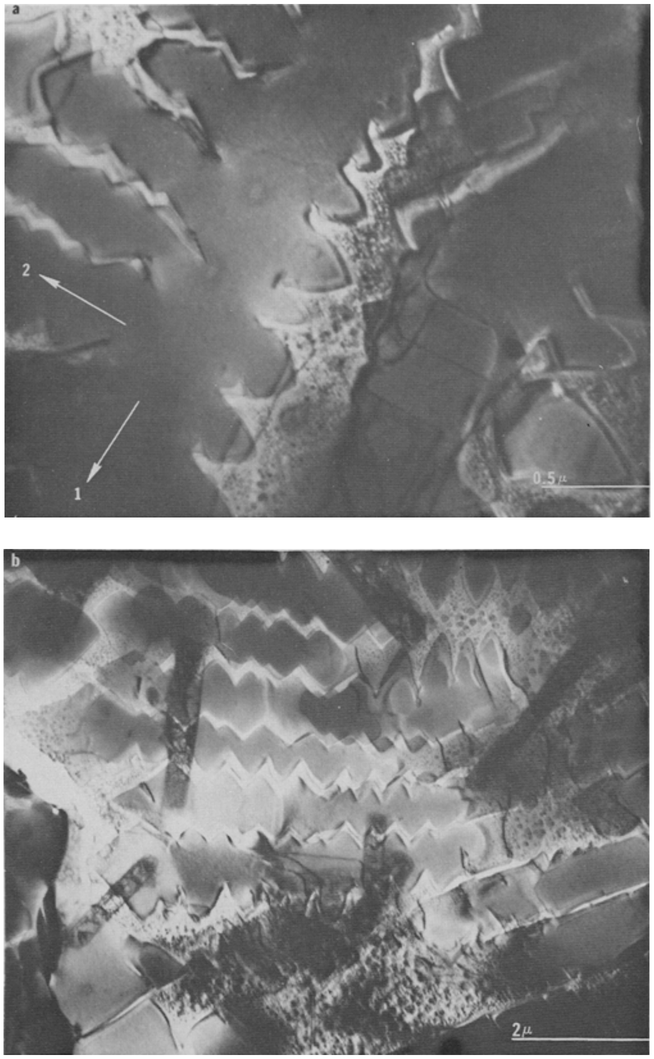

Fig. 7—(*a*) and (*b*). Thin foil micrographs of "as-cast" alloy MM-004 showing the directional growth and dendritic morphology of γ'.

ing that hafnium has a low solubility (<1 at. pct)[7] in the γ matrix but a considerably higher solubility (~7 at. pct) in Ni_3Al,[8] it is expected that hafnium would tend to segregate to the γ' phase rather than to γ during solidification. Recently, Doherty *et al.*[9] have shown that hafnium does indeed segregate to the γ' phase in MAR-M-200 alloy and that it strengthens the γ' regions. It is not known whether the segregation of hafnium to γ' has any influence on the "dendritic" growth in MM-004 alloy; but the fact that the γ' is further strengthened by hafnium segregation is consistent with the fracture-retarding effect of the interlocking γ' configuration at the grain boundary.

Finally, it is worth noting that the observed directional growth of γ' in hafnium-modified MM-004 alloy has implications with regard to obtaining directionally solidified superalloys under more relaxed growth conditions than are normally considered feasible. As yet, the mechanism whereby hafnium causes directional growth of γ' is not clear, but the fact that it does raises the interesting possibility that directional so-

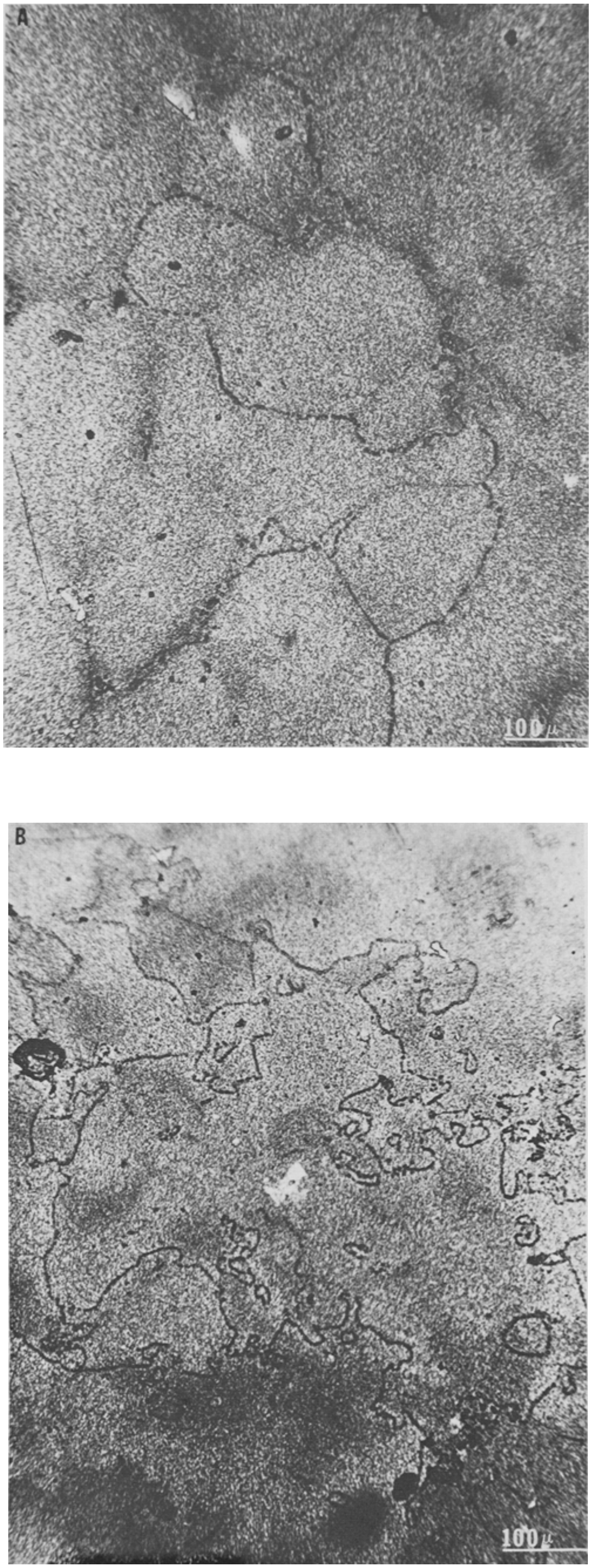

Fig. 8—Optical micrographs of cellulose nitrate films showing the distribution of boron in (*a*) ALLOY 713-LC, and (*b*) MM-004 superalloys.

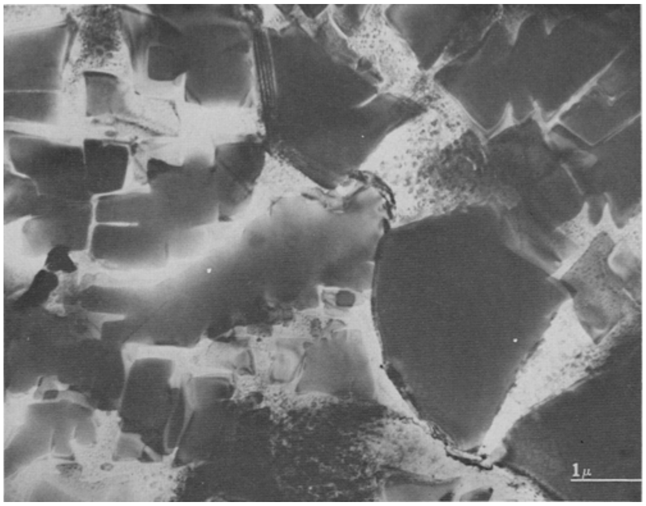

Fig. 9—Thin foil micrograph of as-cast MM-004 alloy showing a grain-boundary distorted from a planar interface.

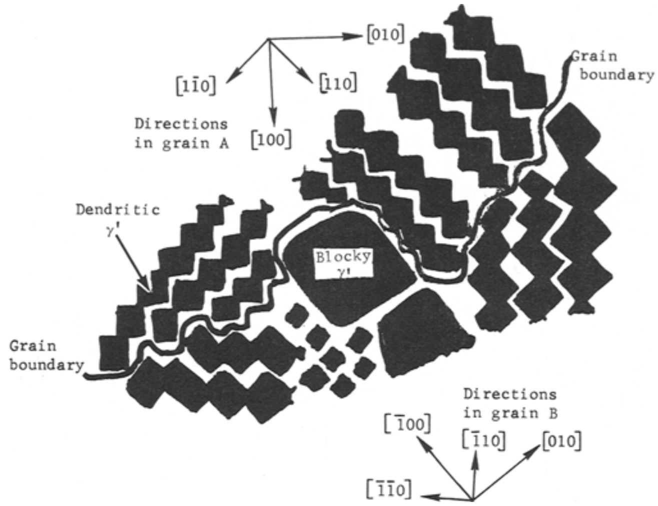

Fig. 10—Schematic representation of a convoluted grain boundary in a hafnium-modified cast nickel base superalloy. The coarse convolutions are defined by the overall orientation of a $\gamma + \gamma'$ rosette colony, see Figs. 6(*b*) and 8(*b*), whereas the fine convolutions result from the dendritic growth of the γ' phase, see Fig. 9.

lidification can be induced by constitutional factors as well as by control of thermal parameters during solidification.

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