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Publication Date

1969-04-01

Submitted to Transactions
of the American Society for Metals

UCRL-18649
Preprint

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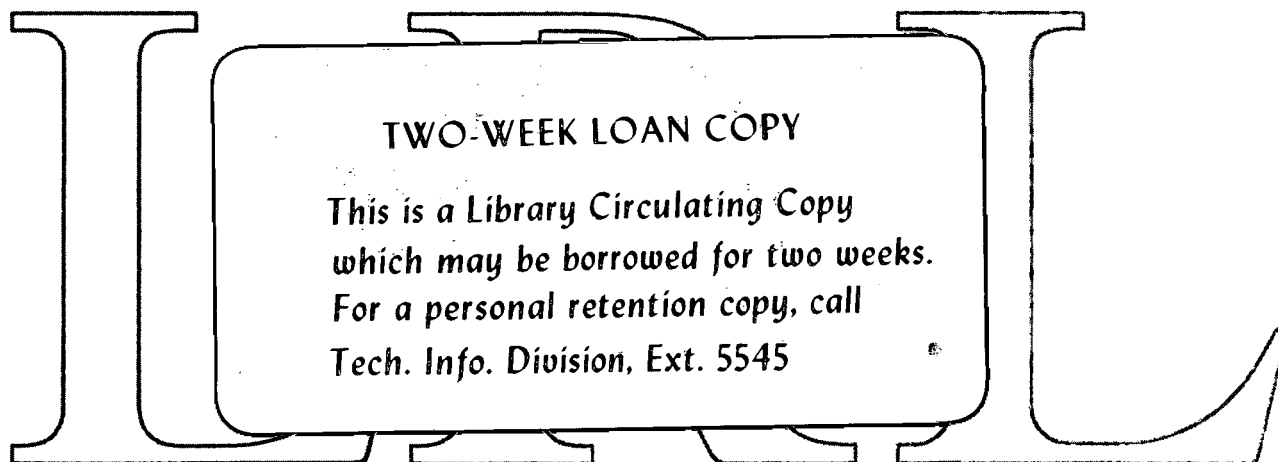
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AEC Contract No. W-7405-eng-48



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PRECIPITATION IN Fe-Ni-Co ALLOYS

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December 1968

ABSTRACT

Precipitation in Fe/Ni/Co maraging alloys occurs by formation of austenite plates from martensite on {110} planes. The crystallography follows the Kurdjumow-Sachs orientation relationship. Complexities in the electron diffraction patterns are explained as a result of multiple diffraction due to interactions between bcc and fcc reflections. If this phenomenon is ignored, erroneous identification of other phases in maraging type alloys can result during electron microscopy investigations.

The presence of small amounts of Ti results in in-situ formation of Ni₃Ti from austenite. A possible mechanism for this to occur is by way of faulting. This mechanism may apply generally to maraging alloy steels.

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INTRODUCTION

Maraging steel is based on the Fe-Ni-Co system (Refs. 1,2), and some attempts have been made to delineate the hardening mechanisms and identify the precipitation that occurs in maraging steel by studying relatively simple systems (3,4). Both X-ray work and electron microscopy and diffraction show conclusively that the decomposition of the martensite occurs with precipitation of a fcc phase with a $a_0 \approx 3.58\text{\AA}$ [austenite] (3,4). When small amounts of titanium are present, Ni_3Ti may also be identified (4). The electron diffraction patterns obtained during the course of thin foil electron microscopy are very complicated and problems may arise as to the interpretation of these patterns. It is the purpose of this paper to explain and identify such patterns, to draw attention to the importance of multiple diffraction, and to suggest a possible mechanism for in-situ precipitation of compounds such as Ni_3Ti within austenite.

Experimental

Fe-Ni-Co (3) and Fe-Ni-Co-Ti (4) alloys that had already been investigated were used in this study, (Table 1). The heat treatments were the same as those used previously and thin foils were prepared in the usual way for the electron microscopy and diffraction investigations.

Results and Discussion

Figure 1 shows a series of bright-field and dark-field micrographs corresponding to the diffraction pattern shown in Fig. 1(e). This pattern is in the $[0\bar{1}1]$ matrix (martensite) orientation with three variants of austenite patterns all in $\langle 111 \rangle$ orientation superimposed. The orientation relationships correspond to that of Kurdjumow-Sachs, viz., $(111) \text{ bcc} // (011) \text{ fcc}$; $[0\bar{1}1] \text{ bcc} // [\bar{1}\bar{1}\bar{1}] \text{ fcc}$. The pattern is complicated, however,

TABLE 1

Alloys Used In This Investigation

Alloy	Fe	Ni	Co	Ti	Al
A (Ref. 3)	balance	20.53	25.06	<.01	<.01
B (Ref. 4)	balance	20	23	0.17	0.07

and extra spots are produced as a result of multiple diffraction. This effect has been noted previously (4,5), but until now, the origins of double and multiple diffraction have not been derived. The interpretation is based on the simplest situation, viz., in Fe/Ni/Co where only martensite and austenite are present. By considering this situation, one can distinguish real diffraction spots due to precipitates from spots that are generated merely by interaction effects. If this is not done, erroneous d-spacings are obtained, leading to errors in identification of phases.

The multiplicity of spots in the diffraction patterns can be accounted for by considering double and multiple diffraction resulting from the combination of fcc and bcc reflections. These combinations produce diffraction maxima at positions which do not correspond to the structure factor predictions for either the bcc or the fcc phases. In single phase bcc or fcc structures, multiple diffraction cannot yield extra spots. For example, if one considers multiple diffraction from interactions of only bcc reflections (or fcc with each other) no extra spots will result, e.g., in the $[\bar{1}10]$ bcc orientation we have possible interactions such as

$$[002] \pm [110] \nrightarrow [112] \text{ or } [\bar{1}\bar{1}2]$$

$$\text{and } [110] \pm [112] \nrightarrow [222] \text{ or } [00\bar{2}] \text{ etc.,}$$

i.e., the interactions yield only bcc positions in the pattern. However, when bcc and fcc reflections are present in the same pattern, and interact, since the magnitudes of the reciprocal lattice (g) vectors for each phase are different (but $g[01\bar{1}]_{\text{bcc}} \approx g[\bar{1}\bar{1}\bar{1}]_{\text{fcc}}$), and since the structure factor rules are different for bcc and fcc materials, interactions can generate "extra" spots in the pattern. Dark-field images of such doubly (or triply, etc.) diffracted spots then yield weak images where reversal of contrast occurs

in those areas of the foil whose diffraction vectors correspond to those involved in the interaction(s). An example is shown for the dark-field image, Fig. 1(a) of the double diffraction spot a, shown in Fig. 1(e), where weak matrix (extinction contours), and weak austenite (precipitate plates) contrast reversal occurs. This result proves the validity of this interpretation. Furthermore, spot c is the (220) austenite reflection and its dark-field image, (Fig. 1c), reverses only those austenite plates in this particular K-S variant. Similar results are obtained for other spots such as f (Fig. 1f).

If this interpretation is correct, it should be possible to explain all the patterns that can be obtained. The particular multiple diffractions are determined only by the reflections that can occur in a given orientation, e.g., in Fig. 1 the multiple pattern is generated by combinations of the [200], [211], [011] bcc reflections with the various [220] austenite reflections from each [111] orientation. Likewise, in [111] bcc orientation, multiple diffraction occurs by interactions of [110] bcc reflections and [200], [111], [220] fcc reflections. This interpretation has been found to apply in all cases after careful analysis of a wide range of orientations. Figure 2(a), (b) shows one example for a [111] bcc orientation, which confirms the multiple diffraction interpretation.

When a comparison is made between the diffraction patterns from the alloy containing no titanium with an alloy containing Ti (Table 1), small, but recognizable, differences can be detected, (Figs. 2 and 3). However, in the images, the morphology of precipitation remains the same, i.e., austenite plates form on the {110} martensite and are oriented by the K-S relationships (compare Fig. 2(a) with Fig. 10, Ref. 4). For example, Fig. 3(a) shows the [111] bcc pattern with the three variants of the {110}

austenite patterns superimposed. A close examination of the pattern reveals spots (triangled in Fig. 3(a), (b), not present in Fig. 2. As shown in another paper (6), this pattern can be interpreted in terms of the superposition of a hcp pattern whose c/a is not quite the same as that for the fcc structure (i.e., $\sqrt{8/3}$). In fact, the spacing of the first order triangled reflection corresponds very closely to the $20\bar{2}0$ spacing of Ni_3Ti .

Figure 4 shows an extraction replica where an Ni_3Ti single crystal pattern in [0001] can be identified uniquely (see e.g. Table 2 of Ref. 7).

A comparison between the present results and those of other workers shows that published unidentified "d" spacings {see e.g., Table 2 of the Review by Floreen (7)} can be explained by multiple diffraction from martensite with austenite and also of course with any other phases that may be present such as the intermetallic compounds Ni_3Mo and Ni_3Ti . The possible complications can be sorted out during electron metallographic investigations by using dark-field imaging and noting possible multiple diffraction in the diffraction patterns, as shown in Fig. 1. Similar techniques apply when extraction replicas are examined when more than one phase is extracted.

It is interesting to note that in several cases where maraging steels have been examined by electron microscopy, few if any, differences exist between images and diffraction patterns of such steels and those from the basis Fe/Ni/Co alloy used here. As an example, compare Fig. 1 of this paper with Fig. 11 of Ref. 5.

Obviously, it is important to recognize the phenomenon of multiple diffraction since otherwise erroneous d-spacings will be obtained, leading to errors in identifying the possible phases that exist. Such effects are likely in any alloy system containing phases of different structures.

Since the corresponding images of Fig. 2 and 3 appear identical, the results indicate precipitation of Ni_3Ti occurs within austenite. This is not unexpected in view of the close lattice correspondence between fcc and hcp phases. A possible mechanism for this to occur is by way of stacking faults. When the alloy is heavily overaged (Fig. 5), it is possible to resolve contrast effects which are typical of those due to stacking faults. The d-spacings from the faulted structure correspond to Ni_3Ti , i.e., the "faults" are actually plates of the Ni_3Ti phase. This is confirmed by the dark-field image shown in Fig. 5(c).

Previous work on austenitic alloys has indicated that strong carbide forming alloying elements such as Ti, Cr, and Mo lower the stacking fault energy when in solid solution (e.g., Refs. 8,9). Cobalt may also behave similarly. It is suggested, therefore, that the precipitation sequence in maraging steels may be martensite \rightarrow austenite \rightarrow faulted austenite -- hcp phase(s) when the precipitating intermetallic compound closely matches the austenite structurally, such as Ni_3Ti . The work of Garwood and Jones (5) lends some support to these views.

Finally, it is interesting to note that since the sequence of structures in aging maraging alloys is so similar, the rapid hardening kinetics in these alloys may be accounted for in the early stages which precludes diffusion process.

Summary

Precipitation in Fe/Ni/Co alloys occurs by formation of austenite from martensite on $\{110\}$ planes. The crystallography follows the Kurdjumov-Sachs orientation relationships. Complexities in the electron diffraction patterns are explained as a result of multiple diffraction due to inter-

actions between bcc and fcc reflections. If this phenomenon is ignored, erroneous identification of other phases can result during electron microscopy investigations.

The presence of small amounts of Ti results in in-situ formation of Ni_3Ti from austenite. A possible mechanism for this to occur is by way of faulting, i.e., Ti lowers the stacking fault energy of austenite so as to favor nucleation of Ni_3Ti . This mechanism may apply generally to maraging steels.

ACKNOWLEDGEMENTS

This investigation came about as a result of written discussions between the authors. Financial support to I-Lin Cheng and G. Thomas was provided by the United States Atomic Energy Commission, through the Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley.

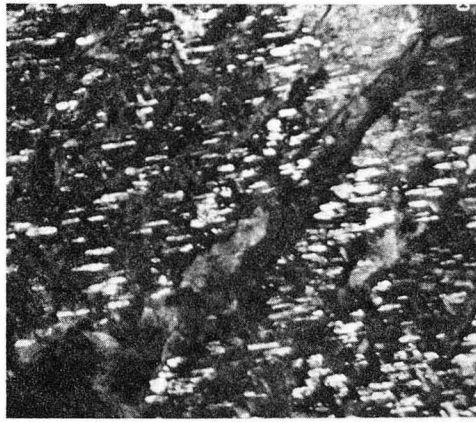
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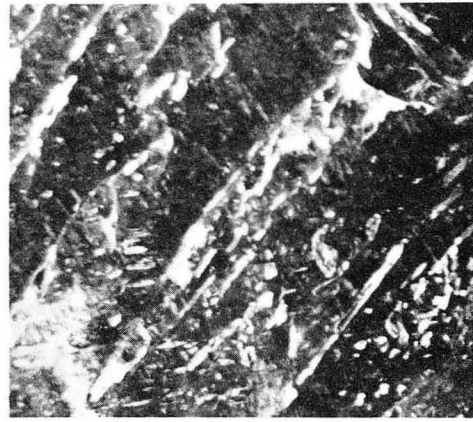
FIGURE CAPTIONS

1. Fe/Ni/Co - 2100°F/4 hrs. air cool, aged 900°F/3 hrs.
 - (a) Dark-field image of double-diffraction spot a.
 - (b) Bright-field image.
 - (c) Dark-field image of spot c (220) fcc, shows only one of the austenite sets on (110).
 - (d) Dark-field image of double-diffraction spot d.
 - (e) Symmetrically oriented $[0\bar{1}1]$ bcc diffraction pattern from the area shown in (a,b,c,d, and f). Other spots not at bcc or fcc positions are due to multiple diffraction from bcc and fcc reflections.
 - (f) Dark-field image of spot f (220) fcc.
2. Fe/Ni/Co, as Fig. 1;
 - (a) Diffraction pattern in $[111]$ bcc orientation. The superimposed pattern is from three orientations of austenite all obeying the K-S relationship. The extra spots near the origin are due to multiple interactions of bcc and fcc reflections.
 - (b) Sketch showing principal indexing of (a). Double-diffraction spots near origin arises from $\bar{1}01$ bcc \leftrightarrow $\bar{1}11$ fcc type interactions.
 - (c) Bright-field image showing Widmanstätten austenite plates.
3. Fe/Ni/Co/Ti alloy aged as for Fe/Ni/Co alloy (Fig. 1,2).
 - (a) Diffraction pattern in $[111]$ bcc orientation. The pattern is similar to that in Fig. 2(a), with the exception of the presence of extra spots (triangled). White-dotted lines in Fig. 2(a) and Fig. 3(a) indicate the same direction.
 - (b) Indexing of the area in (a), (c,f, Fig. 2(a)).

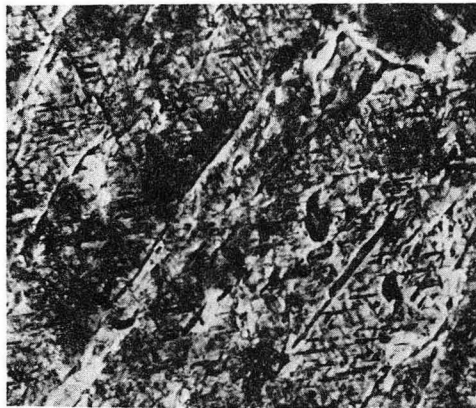
4. Diffraction pattern obtained from an extraction replica of Fe/Ni/Co/Ti alloy aged 600°C/19.5 hrs. The hexagonal pattern indexes uniquely as Ni_3Ti .
5. Fe/Ni/Co/Ti alloy aged 700°C/12 hrs. The results indicate stacking faults, i.e., hexagonal plates within austenite.
 - (a) Bright-field image -- fringes indicate stacking faults.
 - (b) Diffraction pattern.
 - (c) Dark-field image of spot c ($20\bar{2}0$) Ni_3Ti .
 - (d) Dark-field image of spot d (110) martensite.
 - (e) Dark-field image of spot e (220) austenite.



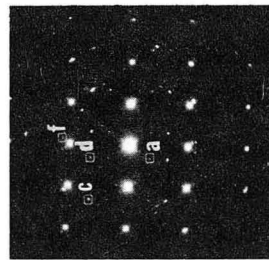
c



f



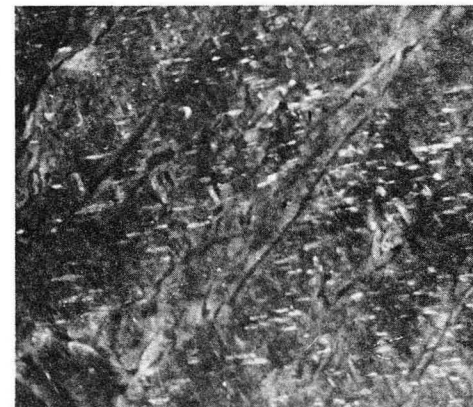
b



e



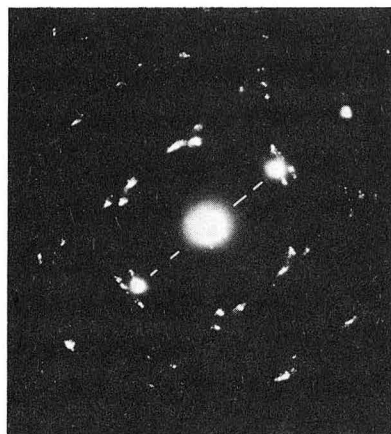
a



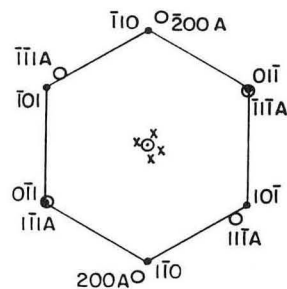
d

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Fig. 1



a



KEY
○ AUSTENITE
• MARTENSITE
x DOUBLE
DIFFRACTION

K-S RELATIONSHIP (011) // (111) BCC
[111]_A // [011] BCC

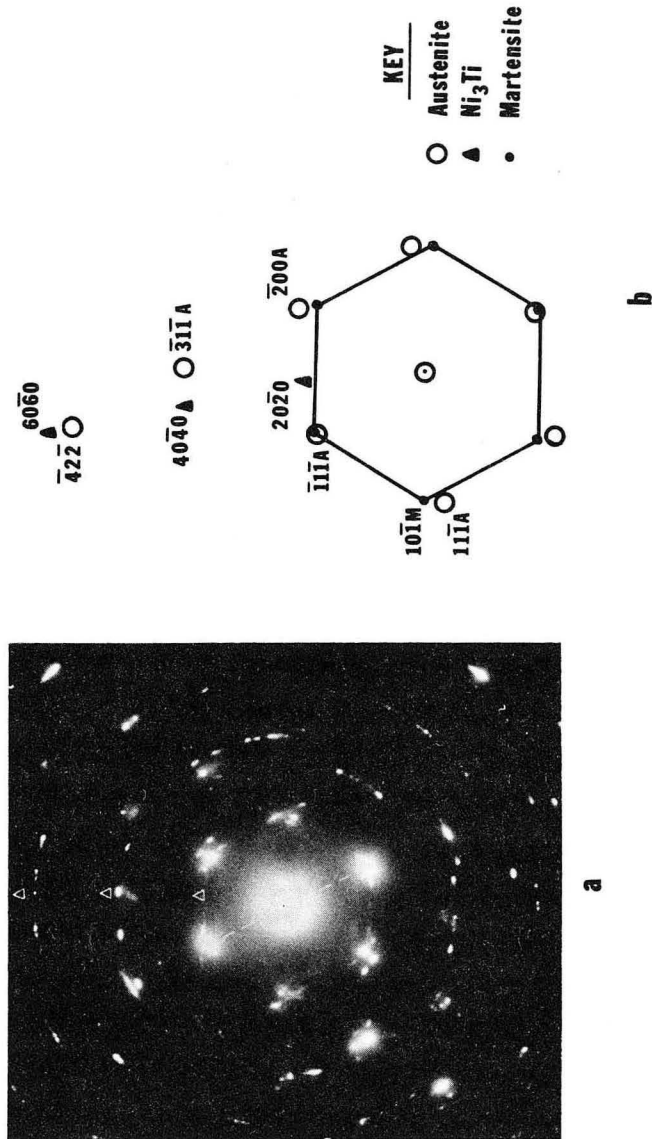
b



c

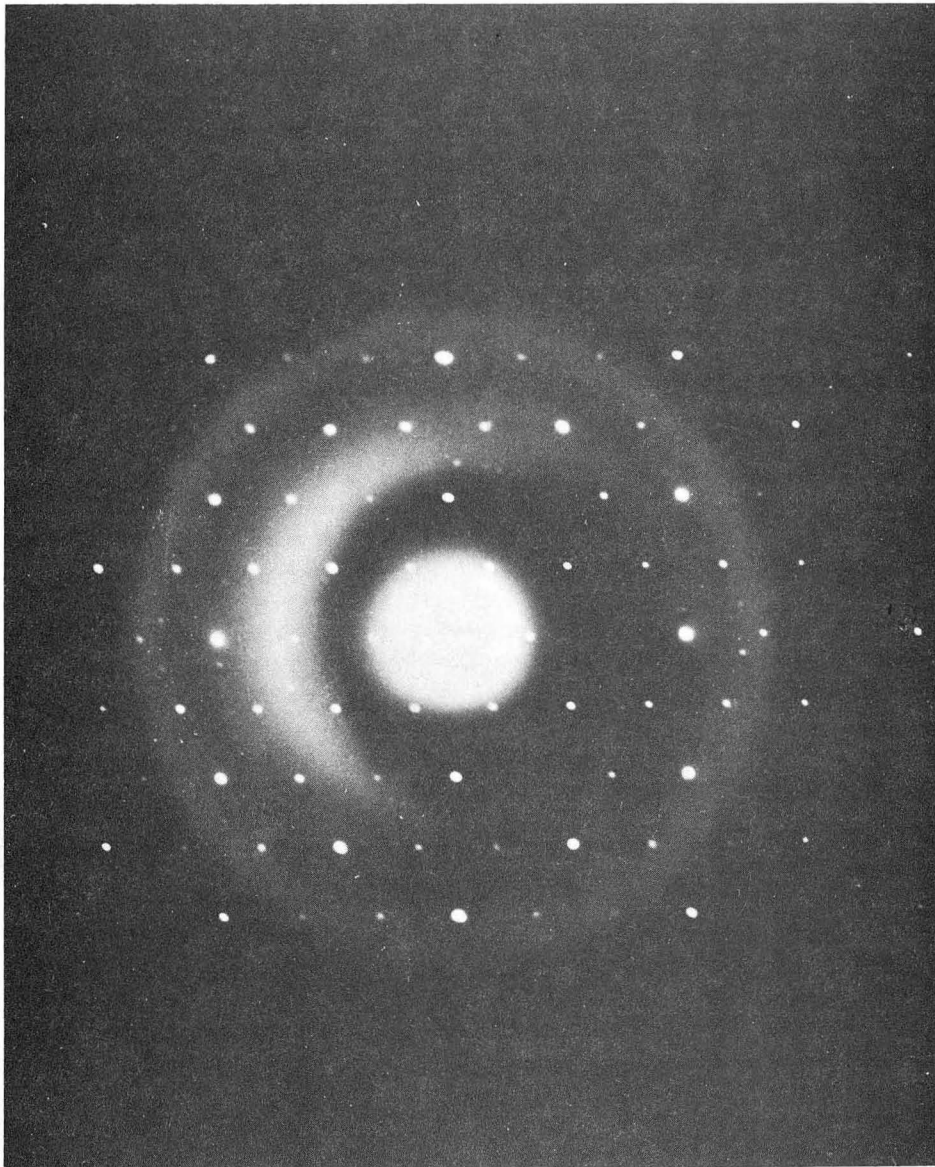
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Fig. 2



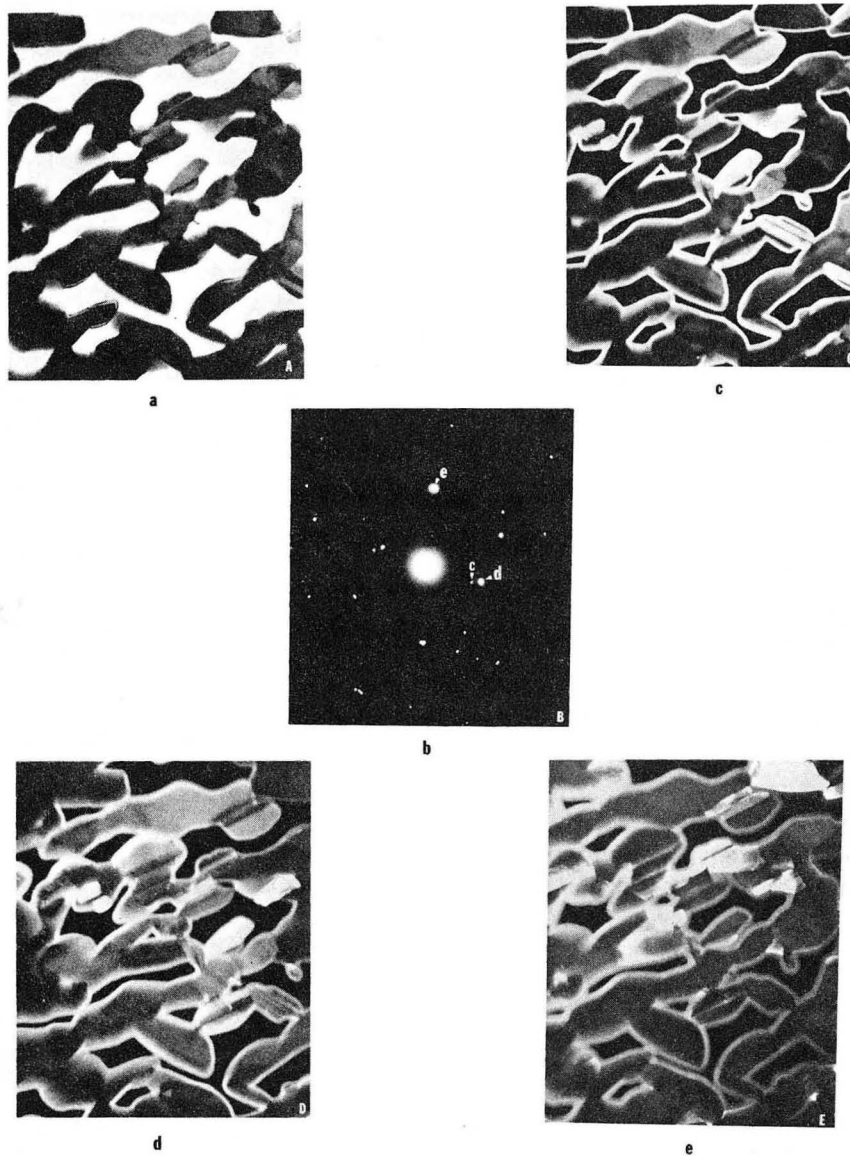
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Fig. 3.



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Fig. 4.



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Fig. 5.

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