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D. J. Rowcliffe and G. Thomas

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STRUCTURE OF NON-STOICHIOMETRIC TaC

D. J. Rowcliffe[1] and G. Thomas[2]

[1] Brown Boveri Research Centre, Baden, Switzerland

[2] Department of Materials Science and Engineering, College of Engineering, and Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

ABSTRACT

A detailed electron microscopy and diffraction analysis of TaC alloys obtained by floating zone melting over the range $TaC_{0.7}$ to $TaC_{0.8}$ shows evidence for intrinsic and extrinsic faulting and short range order. A model is presented which is based on the filling of octahedral sites in {111} planes which can account for the observed faulted structures and the formation of the phases Ta_2C, Ta_4C_3.

I. INTRODUCTION

The transition metals vanadium, niobium, and tantalum form monocarbides which have the rock salt structure over a wide range of carbon substoichiometry. Ordered phases occur at compositions $VC_{0.89}$[1] $VC_{0.84}$[2-4] and $NbC_{0.84}$[5] due to the regular incorporation of carbon vacancies in the carbide lattice. No long range order structures have been reported in tantalum carbide. For carbon to metal ratios between about 0.75 and 0.8, intrinsic stacking faults have been observed in vanadium carbide crystals grown from the melt[6] and in tantalum carbide produced by carburizing tantalum sheet[7,8]. In both cases these are Shockley faults, lying on {111} planes, bounded by partial dislocations of the type $a/6\langle 2\bar{1}\bar{1}\rangle$. In melt grown crystals of the same composition range, diffuse scattering intensities visible in electron diffraction patterns are thought to arise from short range order (SRO)[9-11]. However, similar effects have not yet been reported for tantalum carbide prepared in the solid state.

The formation of zeta phase carbides occurs for carbon to metal ratios close to 0.75. Yvon and Parthé[12] have proposed a structure for these M_4C_3 carbides with the metal atoms stacked in the sequence hhcc where h refers to the hexagonal stacking in M_2C carbides and c to the cubic stacking in MC carbides. In their x-ray work, no evidence for ordering in the carbon stacking was found and it was tentatively concluded that the carbon atoms must be randomly distributed over the octahedral interstices in the hhcc lattice. These authors also report that the zeta phases appear to exist over a range of carbon substoichiometry below the ideal composition $MC_{0.75}$. An electron microscopy examination by Billingham and Lewis also failed to show evidence for carbon

vacancy ordering in zeta V_4C_3. Thus it was suggested that the zeta phase forms by a mechanism involving zonal dislocations[13] rather than by vacancy condensation and simple shearing. In the case of tantalum carbide, the electron diffraction investigation of Martin[14] does indicate that carbon ordering occurs but in this case the composition of the zeta phase was thought to be Ta_3C_2.

Clearly, a number of uncertainities still exist in the transition metal - carbon systems, for example whether melt grown carbides differ from those produced by solid state diffusion, the occurrence and exact nature of SRO and the relation between the noncubic phases, stacking faults, vacancy ordering and the FCC phase. The purpose of the present paper is to explain some of the phase relationships based on the results of detailed electron microscopy and diffraction analyses of tantalum carbide crystals, of various stoichiometries, grown by induction floating zone melting.

II. EXPERIMENTAL

Discs were cut from as grown crystals using an ultrasonic drill. Thin foils were prepared by electropolishing and/or ion beam thinning the discs for examination by transmission electron microscopy in a Philips EM 300 at 100 kV and a Hitachi Hu 650 at 650 kV so as to penetrate thicker regions. Stacking faults were imaged in bright and dark field conditions, contrast experiments being done at 100 kV to avoid complications arising from multiple beam conditions which usually occur at high energies.

The carbon contents quoted in this paper are estimated from lattice parameter measurements.

III. RESULTS AND DISCUSSION

A. Electron Microscope Observations

The structures observed by transmission electron microscopy and diffraction are shown in Figures 1-6. Few defects or other metallographic features could be resolved in thin foils of composition greater than $TaC_{0.8}$. However, diffraction patterns from samples close to this composition showed diffuse scattering effects (Fig. 1a,b) especially after prolonged aging at high temperatures. These appear to be identical to the SRO diffuse scattering reported by Billingham et al.[9] and analyzed by Sauvage and Parthé[10], and will be discussed in a separate paper.

In crystals of approximate composition $TaC_{0.8}$-$TaC_{0.7}$ regions were observed which contained random arrays of stacking faults, generally on {111} but also occasionally on other planes, probably {112}. At the highest carbon contents isolated faults were found in material which showed diffuse scattering effects. The coexistence of both structures is demonstrated in Fig. 1b. The diffuse scattering disappeared entirely at compositions below $TaC_{0.78}$ and faulting became much more common. The {111} faults are shear faults, i.e. they have bounding Shockley partial dislocations $\bar{b} = a/6\langle 112\rangle$ as is shown in Figs. 2 and 3, which illustrate the appropriate contrast experiments. In order to study the fringes at the edges of the faults, dark field images such as Fig. 3(d) were used. These show that both extrinsic and intrinsic faults exist e.g. on (111) and $(1\bar{1}\bar{1})$. This contrast is discussed by several authors e.g. Amelinckx[15]. Since the contrast does not disappear entirely even when the phase factor $\alpha = 2\pi(\bar{g}.\bar{R}) = 0$, where $\bar{R}$ is the fault vector, it is likely that this "residual" contrast is probably due to local changes in structure factor, as a result of local compositional changes. These observations can be

accounted for if the faults are disc shaped layers in the{111} stacking sequence where the carbon atoms are completely missing. The effectiveness of this process of reducing the concentration of carbon vacancies in the lattice can be seen from the fact that once the range of composition is reached where faulting occurs, then the diffraction effects due to vacancy SRO are no longer seen. Martin et al.[7] who observed neither residual contrast nor extrinsic faults suggest that the carbon layers may not be completely missing. These authors also never saw any diffuse scattering of the sort shown in Fig. 1. Their samples were prepared by vacuum carburization of tantalum sheet at 2200°C whereas the crystals used in the present investigation were grown from the melt, close to 4000°C. Clearly, SRO and the faults are associated with local vacancy concentrations and it could be that the distribution of carbon vacancies in substoichiometric carbides is dependent upon the temperature at which the crystals are formed.

Specimens observed in the high voltage microscope show high densities of randomly arranged faults in thick areas (e.g. Fig. 4). By trace analysis and by large angle tilting experiments, whereby the faults were maintained in contrast (e.g. using g = <200>), it was found that faults occurred on planes other than {111}. Fig. 4 shows an example. From such experiments it is concluded that the most probable fault planes other than {111} are {112}. In the case of a fault on (112), only one carbon vacancy per unit cell (e.g. at the $00\frac{1}{2}$ site) is required. Such faults are probably growth accidents of non-stoichiometry. The fault density increases rapidly with small decreases in the carbon content and maximises at Ta_4C_3 with the formation of regular {111} faulting, producing sheets of HCP and FCC layers in the material. This occurs in localized regions

of the specimen and coexists with areas of random faults and the fault-free cubic matrix. (Figure 5). This regular faulting gives diffraction maxima at $^{a*}/4$ <111> relpoints in that <111> reciprocal lattice row which is perpendicular to the fault planes. This is shown in Figure 6. The diffraction effects are those which can be expected on the basis of the metal stacking sequence for the zeta phase as proposed by Yvon and Parthé[12]. In addition, they indicate that the carbon vacancies are ordered, i.e. complete carbon layers are missing, rather than the vacancies being randomly situated in the octahedral sites of the metal lattice. The continuous streaks in the <111> direction is further evidence of the faulted nature of the zeta phase. The diffraction pattern of Figure 6d shows the maxima at $^{1}/4[111]$, $^{1}/2[111]$... $^{n}/4[111]$ along the <111> relrods normal to the (111) faults seen in the bright and dark field images of Figure 6a-c. The absence of one plane of carbon in every four and the subsequent shear of the overlying Ta(111) plane giving an intrinsic fault, will, over sufficiently long distances, perturb the {111} periodicity, resulting in a two-phase fcc-hcp mixture, i.e. the zeta phase. The composition in these regions will ideally be $TaC_{0.75}$ if every fourth carbon layer is vacant.

B. Faulting and the Relation Between Structures

On the basis of the results discussed above, the following model is proposed which explains the formation of stacking faults and shows their relationship to zeta-Ta_4C_3, and Ta_2C.

Figure 3 shows that intrinsic and extrinsic stacking faults bounded by Shockley partials of the type $^{a}/6\langle 1\bar{2}1\rangle$ are present in substoichiometric TaC. The stacking sequence of {111} planes in TaC can be designated as follows:

$$A\ \gamma\ B\ \alpha\ C\ \beta\ A\ \gamma\ B\ \alpha\ C\ \beta\ A\ \gamma$$

where ABC represent metal atoms and $\alpha\beta\gamma$ carbon atoms in the corresponding octahedral interstices. The suggested configuration[13] for a stacking fault in the stoichiometric carbide is

$$A\ \gamma\ B\ \alpha\ C\ \beta\ A\ \gamma\ B\ \gamma\ A\ \gamma\ B\ \alpha$$

which requires a shear on both adjoining carbon and metal layers to give a dislocation extended normal to its slip plane. The simpler type of fault requiring only a single shear of the metal such as occurs in FCC metals cannot occur, because the presence of carbon layers prevents such shearing.

In substoichiometric TaC a number of these carbon sites will be vacant and a simple shear in a $\langle 1\bar{2}1\rangle$ direction, analogous to that in FCC metals can take place. The stacking sequence would then be:

$$A\ \gamma\ B\ \alpha\ C\ \beta\ A\ \gamma\ B\ \uparrow\ A\ \gamma\ B\ \alpha\ C\ \beta$$

which gives an intrinsic fault. Exactly the same stacking fault can be arrived at by the removal of a carbon layer from the fault in the stoichiometric compound, as pointed out by Martin et al[7]. However, we believe that the removal of a carbon layer followed by a simple shear of the metal layers above and below it, is the basic mechanism in which all stoichiometry changes are accomodated in the Ta-C system for carbon

to metal ratios below 0.8 and through which all the observed tantalum carbide structures can be constructed.

An extrinsic stacking fault can only form if carbon removal and metal layer shearing takes place on two successive metal-carbon layers:

$$A\ \gamma\ B\ \alpha\ C\ \beta\ A\ \gamma\ B\ \uparrow\ A\ \uparrow\ C\ \beta\ A\ \gamma\ B\ \alpha \quad .$$

Regular removal of carbon atoms followed by shearing every fourth layer gives the following sequence:

$$A\ \gamma\ B\ \overset{\alpha}{\uparrow}\ A\ \gamma\ B\ \alpha\ C\ \beta\ A\ \overset{\gamma}{\uparrow}\ C\ \beta\ A\ \gamma\ B\ \alpha\ C\ \overset{\beta}{\uparrow}\ B\ \gamma\ C\ \alpha$$

This metal atom stacking is exactly that given by Yvon and Parthé[12] for the ξ-phase carbides and the composition corresponds to Ta_4C_3, with carbon atoms ordered as shown in the above scheme. From their diffraction data Yvon and Parthé could not distinguish whether or not the carbon atoms were ordered, but the above interpretation is supported by the electron microscope images of ξ. It is also evident why the ξ cell repeats every 12 metal layers, since this is the minimum distance necessary for the removal of an α, β and a γ carbon layer concurrently.

Ta_2C has the C6 structure [16] which is a derivative of the anti NiAs structure (A γ B γ A γ B γ) with every other carbon layer removed. This structure can be produced from the NaCl structure by an operation of the basic mechanism of carbon removal and shear, on every other pair of metal-carbon layers:

$$A\ \gamma\ B\ \alpha\ C\ \beta\ \ldots \longrightarrow A\ \gamma\ B\ \uparrow\ \overset{\alpha\ C \rightarrow A}{A\ \gamma B}\ A\ \gamma\ B\ \uparrow\ \ldots$$

$$A\ \gamma\ B\ \uparrow\ A\ \gamma\ B\ \uparrow\ A\ \alpha\ B\ \uparrow\ \ldots$$

This model clearly shows the close relation which exists between carbon vacancies, stacking faults and the various carbide phases. When the faulting is periodic a range of structures of different compositions become possible. The regular $^{a*}/4\langle 111\rangle$ faulting accounts for the zeta phase at Ta_4C_3 but deviations from this composition will obviously occur if the periodicity of faulting changes from this $^{1}/4\langle 111\rangle$ sequence. This would account for the difficulties in interpretation of the x-ray data of Yvon and Parthé [12], and also is a reasonable explanation for the co-existence of several phases within a given composition range.

Acknowledgements

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FIGURE CAPTIONS

Fig. 1. Transmission electron diffraction patterns of (a) $TaC_{0.81}$, (211) pole (b) $TaC_{0.78}$, (110) pole. Annealed 200 hrs. at 750°C. The streaks in [111] and split spots in (b) are due to {111} stacking faults. (100 kv).

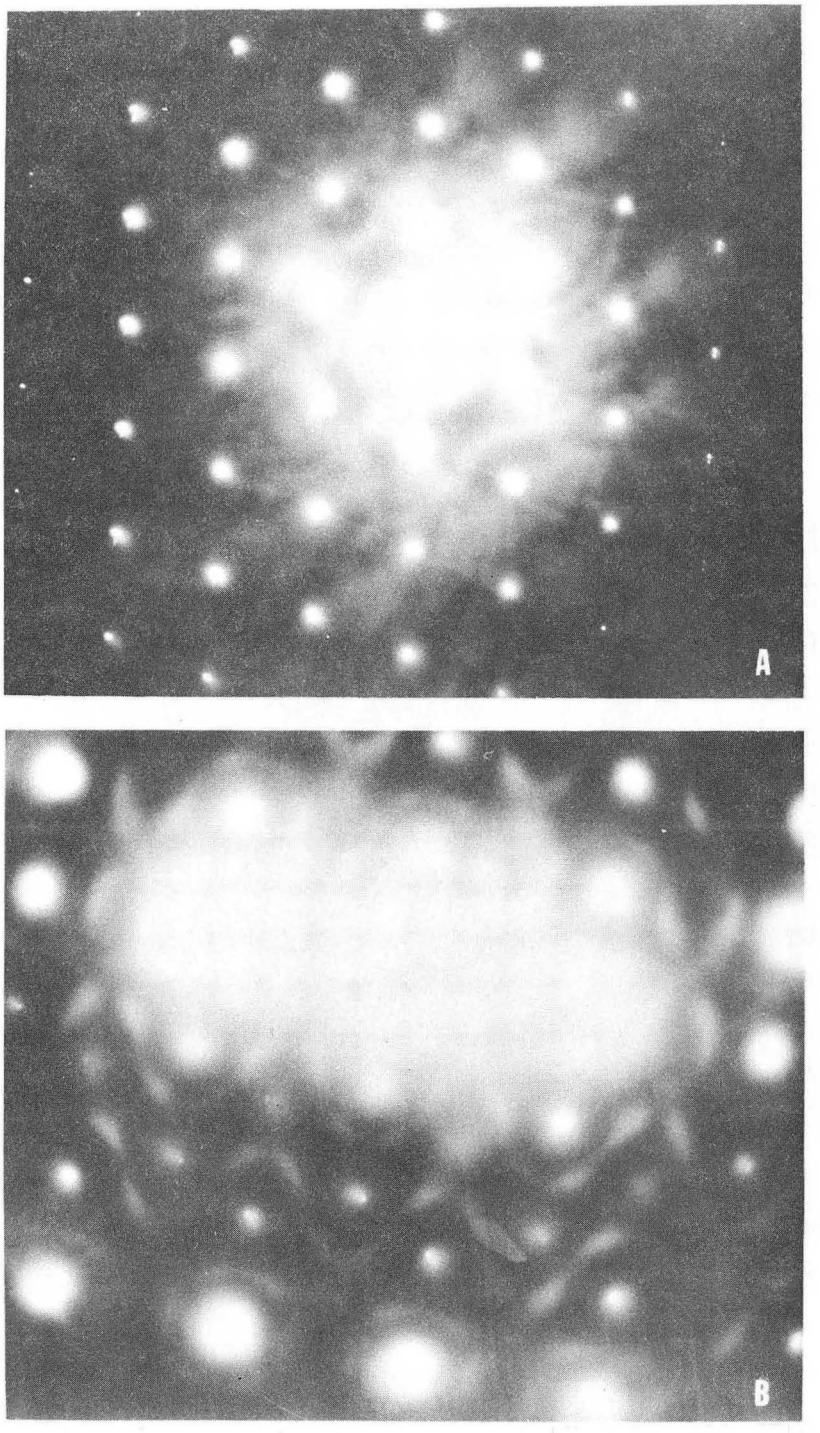
Fig. 2. Disc shaped stacking faults in $TaC_{0.78}$. When the faults are out of contrast (a) the bounding dislocations are in contrast, and vice-versa in (b) indicating that they are the $^{a}/6\langle 211\rangle$ Shockley type. (100kv). Note residual fault contrast in (a).

Fig. 3. Images of stacking faults in $TaC_{0.78}$ under different diffracting conditions. 3(b) and (c) illustrate the structure factor contrast seen when the phase contrast $\alpha=2\pi\bar{g}.\bar{R}$ is zero. The dark field micrograph, (d) shows intrinsic and extrinsic faults on (111) and $(1\bar{1}\bar{1})$. (100 kv).

Fig. 4. Examples of faults with probable (112) habit (A), existing with the principal faults on {111}. Foil orientation near (110) $\bar{g}$ = <200>. (650 kv).

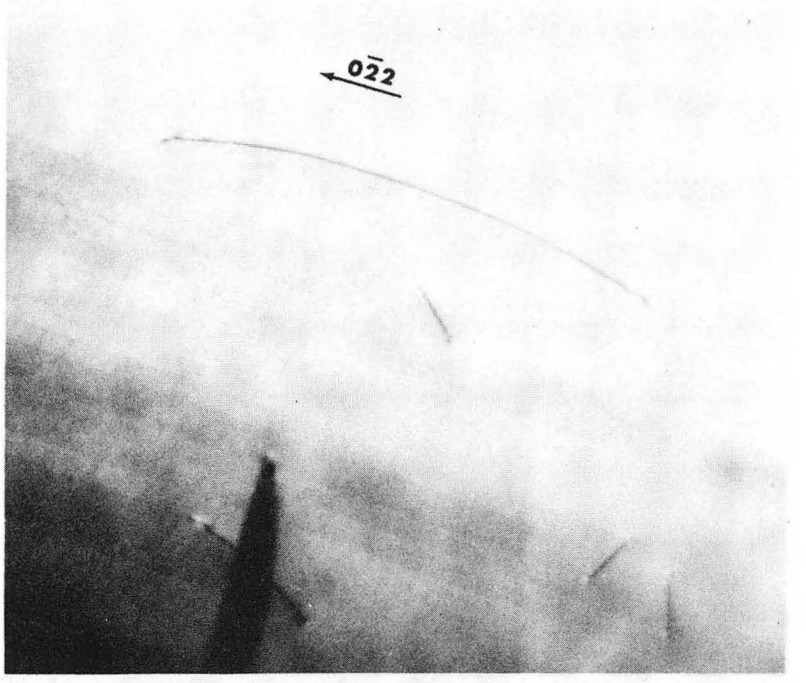
Fig. 5. Coexistence of zeta phase (A), individual stacking faults (B) and fault-free tantalum carbide, in a sample of overall composition $TaC_{0.73}$. (100kv).

Fig. 6. Zeta phase Ta_4C_3, (211) tantalum carbide pole, (a) bright field (b) matrix dark field $(1\bar{1}\bar{1})$ (c) dark field image using the extra reflection at (1/2 1/2 1/2). (d) diffraction pattern. (100 kv).



XBB 743-1387

Fig. 1



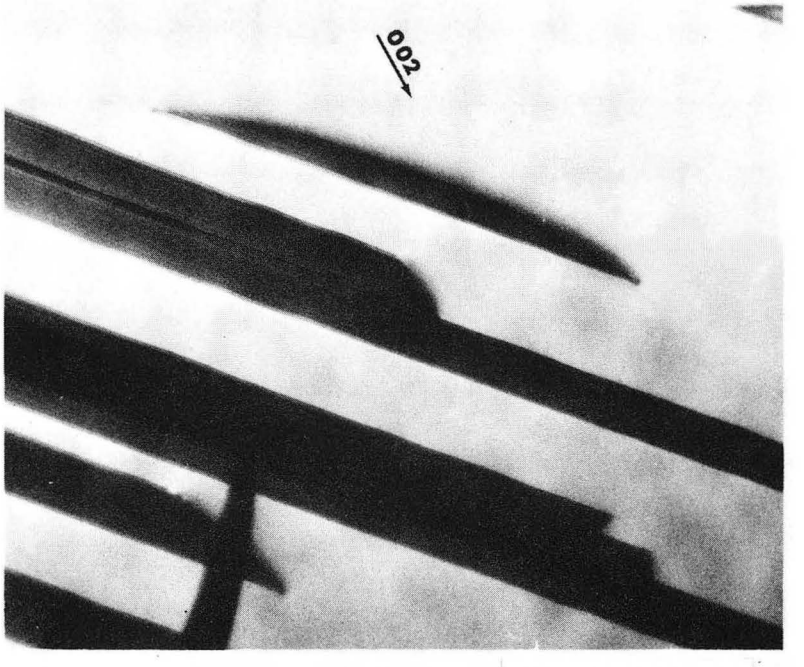


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Fig. 2

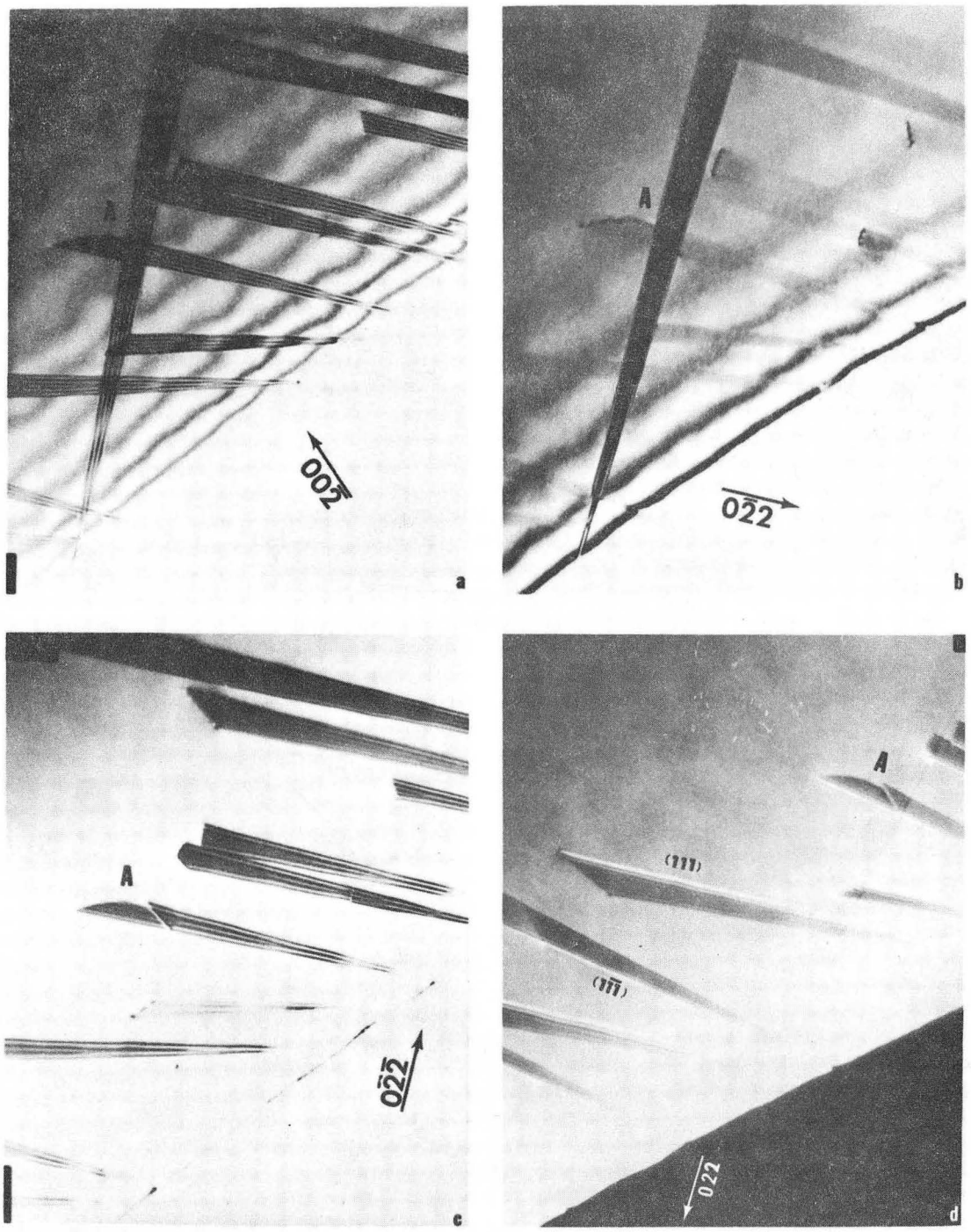

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Fig. 3

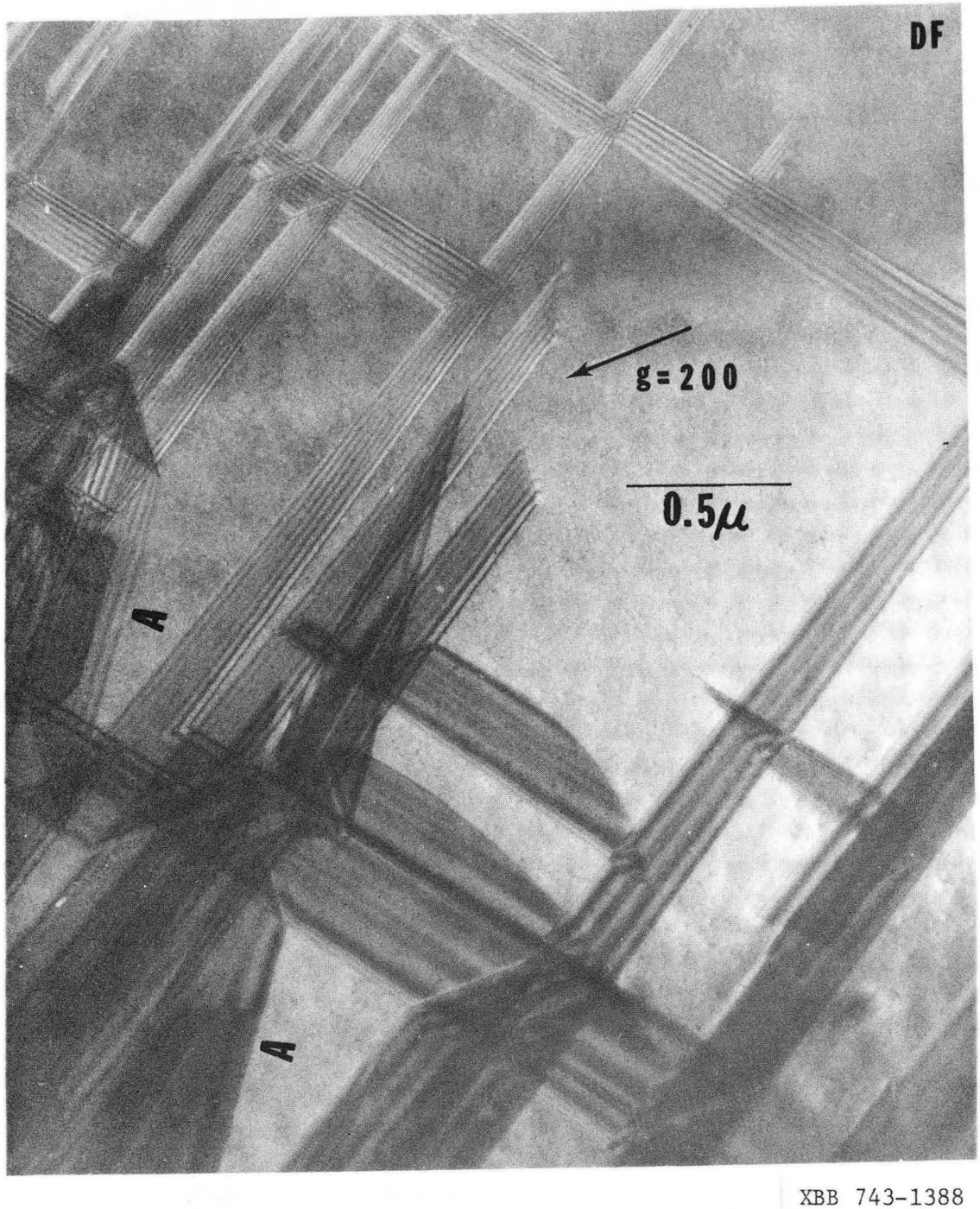

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Fig. 4

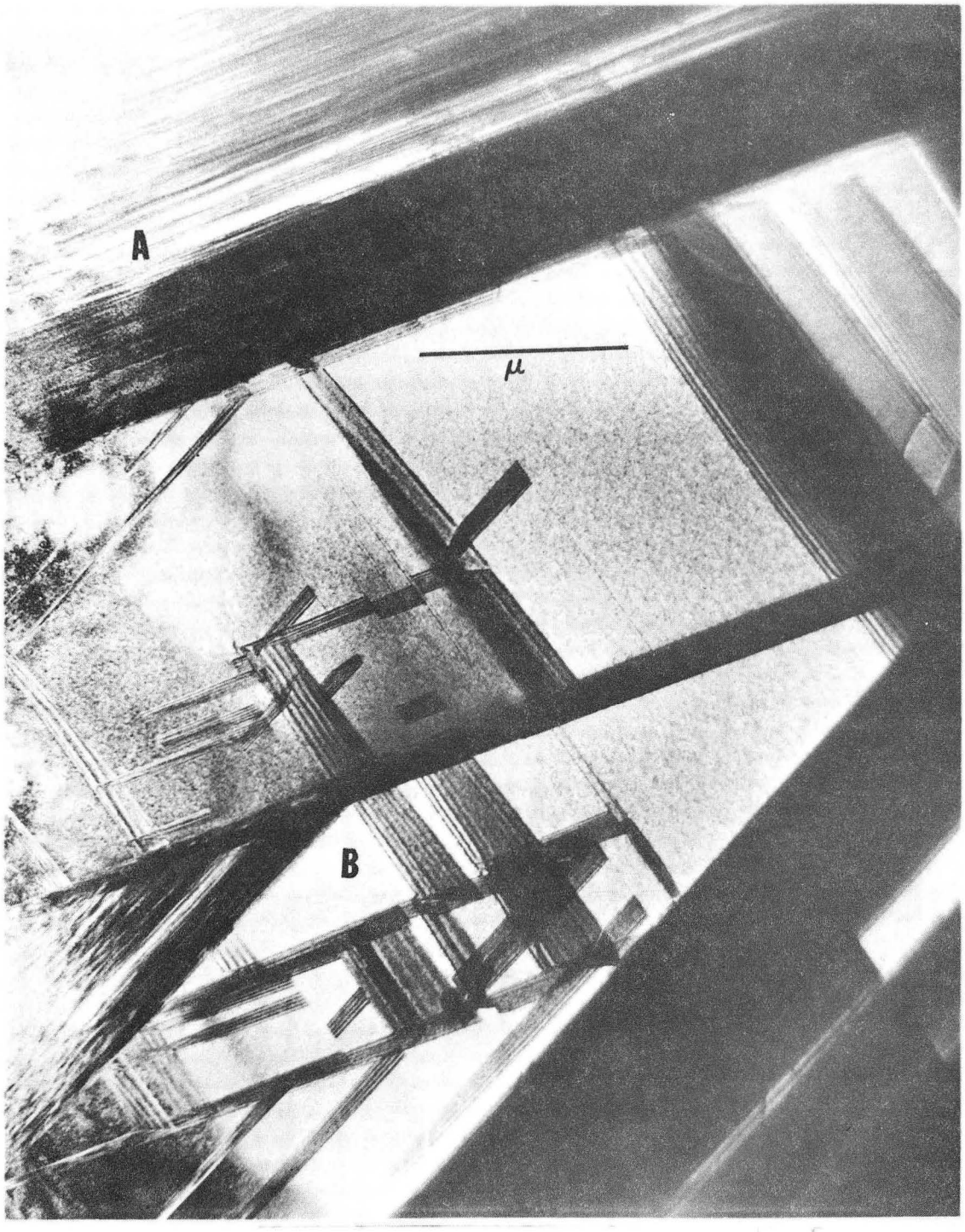

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Fig. 5

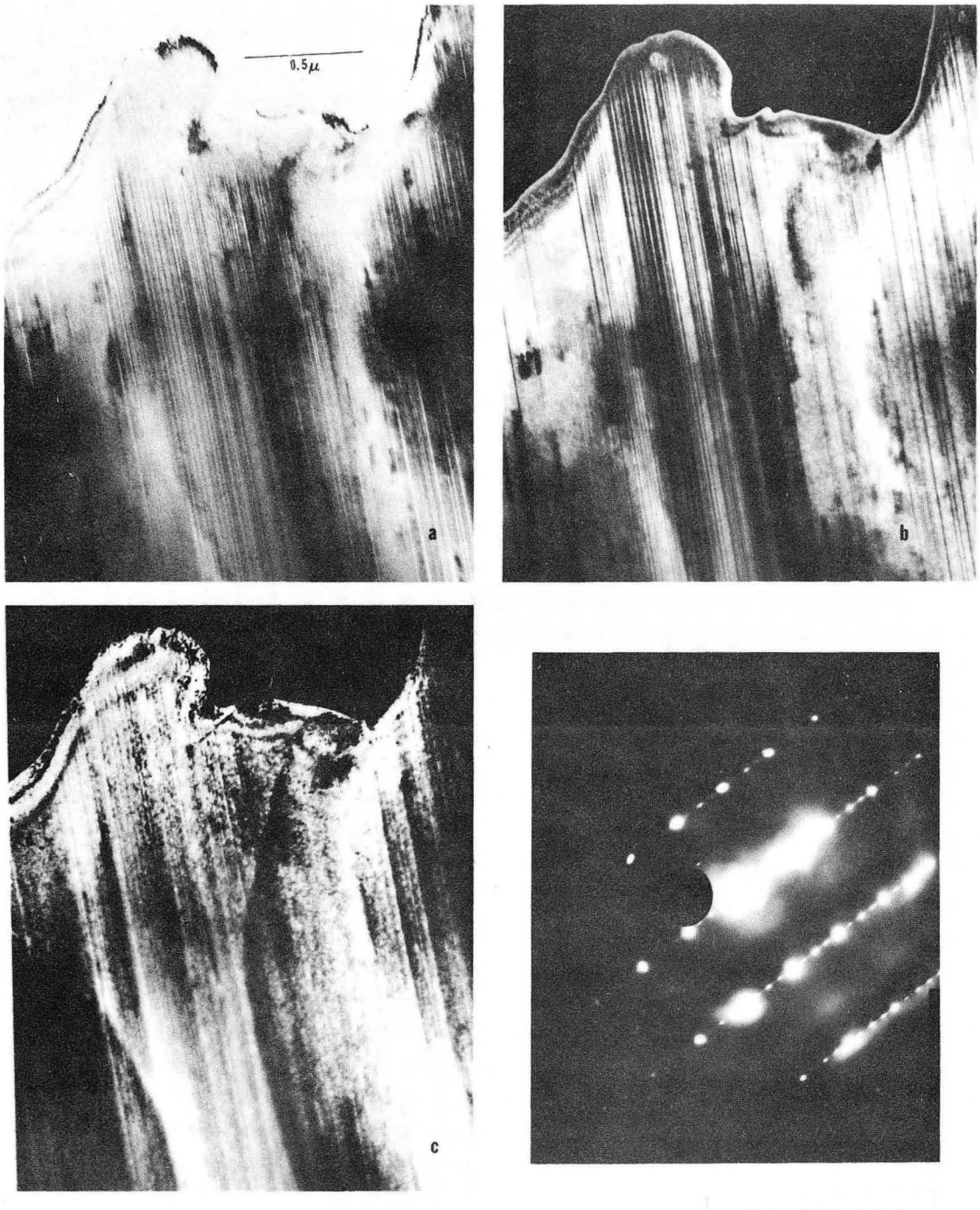

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Fig. 6

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