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June 1985

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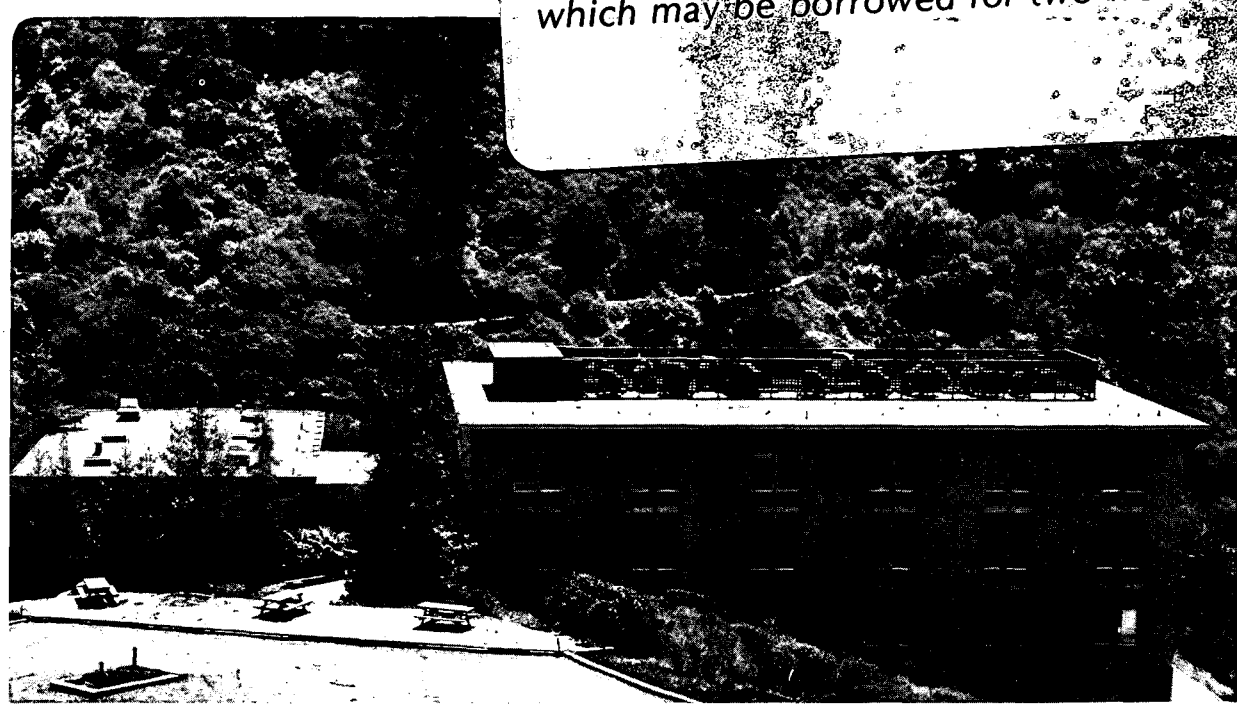

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A TEM STUDY OF AN UNUSUAL ORDERING REACTION IN PLATINUM-CARBON

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ABSTRACT

In platinum containing carbon in solid solution an ordered phase with twice the lattice parameter of the matrix has been found in regions near grain boundaries and inclusions. The ordering was observed after quench-aging treatments as well as during electron irradiation above 300kV in the temperature range of 250 to 650°C. Outside this temperature range disordering took place thermally at high temperatures (>650°C) and athermally by irradiation at low temperatures (<250°C). The threshold voltage for athermal disordering was ∿ 400kV, well below the 1300kV threshold for displacement damage in Pt. The simplest ordered structure consistent with the diffraction evidence is face-centered-cubic Pt_7C, isomorphous with Pt_7Cu. An important implication of these observations is that substantial amounts of carbon can be effectively transferred from interstitial to substitutional sites under certain conditions. This is linked to the earlier observation of a large binding energy between interstitial carbon and platinum vacancies (∿0.6eV).

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INTRODUCTION

Platinum has a very small interstitial solid solubility for carbon and until recently it was believed that only graphite precipitated from solid solution, at least in materials prepared by conventional methods (1-3). One early study had, however, indicated the possibility of an alternative reaction. In a thin film prepared by cyclic vapor deposition of platinum and carbon followed by a homogenization treatment at 1100° C, superlattice reflections were observed in electron diffraction patterns at the primitive unit cell positions (4). A 1% shrinkage in the lattice parameter of the Pt was also noted, indicating that carbon had replaced some Pt atoms on the lattice, and by implication, had moved from interstitial to substitutional sites.

It is now known that in spite of its limited terminal solubility the Pt-C system is more complex than originally believed and exhibits several unusual features. In recent transmission electron microscopy studies (5) it was shown that carbon is precipitated from Pt in a sequence of metastable phases analogous to that found in substitutional Al-Cu alloys. Furthermore, precipitation occurs only in the presence of quenched-in vacancies. It was inferred that a strong coupling between carbon atoms and vacancies exists leading to a close interplay between the vacancies, the precipitation of the carbon from supersaturated solid solution, and the matrix structural rearrangements accompanying formation of the metastable phases. The vacancies are systematically condensed in the parent lattice to change the atom stacking sequence and spacing to that of the product phase. These effects are not peculiar to Pt-C and the structural role of vacancies in precipitation in other classes

of alloy system has also been discussed (6).

From these studies questions regarding the meaning of solid solubility have arisen. Should a carbon atom closely bound to a vacancy be treated as substitutional? and if so, is the solubility of carbon in such a system the sum of the interstitial and substitutional solubilities, $C_i + C_s$, where C_s is a function of the vacancy concentration C_v. Is it possible to extend solubilities by "alloying" with vacancies? and is this the same process that operates in alloys prepared by rapid solidification?

Related questions are; how is the diffusion of interstitial solutes affected by binding to vacancies? and is the magnitude of the binding energy directly related to atomic size misfit (relative to the octahedral or tetrahedral interstices) as some believed to be the case in substitutional alloys.

Partial answers to these questions have come from recent studies of carbon diffusion through polycrystalline Pt foils under isothermal conditions (7). Foils were heated in the temperature range 700-900° C and exposed to a carburizing atmosphere at one surface and a decarburizing gas at the other. It was observed that the carbon diffusion through the foil was accompanied by a counter flow of platinum atoms. As a result, mounds of platinum formed at the carburized surface and pitting occurred at the decarburized surface. The effects were particularly pronounced in the grain boundaries and analysis by TEM and Scanning Auger Microscopy showed that considerable concentration of the carbon had occurred in these regions. In studying these carbon-enriched regions by High Voltage Electron Microscopy an unusual

ordering reaction was observed which throws further light on the relationship between carbon atoms and vacancies. This is the topic of the present paper.

EXPERIMENTAL

The platinum foil used in the experiments was from the same stock as that used in earlier studies (5). It was nominally 99.9% pure and in the as-received condition contained 740 at. ppm carbon. Some discs for TEM examination were prepared from as-received foils which had been quenched from the melting point in ultra-high vacuum and subsequently aged at 400° C. Others were made from foils which had been subjected to a carburizing/decarburizing treatment for 16 hours at 800° C. Details of the specimen treatment and preparation are given elsewhere (7).

The foils were examined in a Kratos 1.5 MV (variable voltage) High Voltage Electron Microscope (HVEM) at various temperatures (using a hot stage) and at voltages below and above the various threshold voltages established in earlier radiation damage studies (8). The microscope is fitted with LaB_6 as well as conventional tungsten filaments and an Ion Beam Stop to prevent heavy negative ions from reaching the specimen. Using the tungsten filaments the electron flux in the fully focussed beam was 5-10 x 10^{23} e/m^2/sec, and with the LaB_6 it was an order of magnitude higher.

Other examination and analysis were carried out on various JEOL microscopes at accelerating voltages of 100 or 200 kV.

RESULTS

1. General Observations

Direct evidence of an ordering reaction has been obtained from

both the as-received platinum Pt(A-R) and the carburized material, Pt(C). However, the regions over which the reaction occurs are quite small, evidently reflecting local variations in the carbon concentration. A graphic illustration of this variation was found in the electropolishing behavior of the two materials. In pure platinum there is a tendency for the grain boundary regions to polish preferentially whereas the converse is true for Pt(C). Fig. 1 shows a low magnification micrograph of a foil that was carburized on one surface and decarburized (probably incompletely) on the other in nominally dry argon. The resistance to polishing of the grain boundary regions clearly evident in Fig. 1 has been related to the presence of a high concentration of carbon (7).

These local concentration variations present difficulties in making a direct quantitative analysis of an ordering reaction involving carbon since conventional analysis of the entire sample will be misleading and microanalysis is notoriously prone to errors in the case of carbon. Consequently, the proposed interpretation is based on the electron diffraction evidence and on the fact that ordering is found only in certain distinctive regions of the foils rich in carbon.

Most of the observations were made on Pt(C) samples using the HVEM, but supplementary information was obtained on quenched and aged Pt (A-R); these results are presented first.

2. Ordering Induced by Quench-Age Treatments

Evidence for the ordering reaction in the Pt(A-R) was found only in foils given a 400 °C aging treatment following quenching, and only in regions surrounding certain inclusions. An example is shown in Fig. 2. The lower magnification bright field image (2a) shows a high density

of fine (10nm) domains (A) in a shell around the inclusion (B). In addition, another type of precipitate is seen associated with the complex dislocation configurations (C) emanating from the inclusion-matrix interface. A contrast analysis of these features suggests that they are the α'-Pt_2C phase identified earlier (5) precipitated on dissociated dislocations. However, at present the analysis is not yet unambiguous. In regions more remote from the inclusion, matrix precipitation of α' is observed (D) separated from the ordered region by a denuded zone (E).

A selected area diffraction pattern taken from the regions containing the fine domains is shown in Fig. 2(b). It is seen to be composed of the matrix Pt reflections corresponding to the 001 section of the reciprocal lattice with a second, superposed pattern, having half the periodicity. A large number of patterns taken with different zone axes all showed the same characteristics. In all cases the intensity of the superlattice reflections was significantly less than those of the matrix.

A dark field image formed with a 011 superlattice reflection is given in Fig. 2(c). It is seen that the diffracted intensity originates from the domains and to some extent the inclusion also. Fig. 2(d) is a high magnification bright field image showing the morphology of the ordered zones.

The concentration of domains in the shell around the inclusion was estimated to be $\sim 2\times10^{16}cm^{-3}$. Tilting experiments performed to investigate further their morphology revealed them to be plate-shaped with a diameter to thickness ratio of $\sim$5:1. Taking the mean size as

10nm, the concentration of atoms contained in the domains was calculated as $4x10^{-3}$.

3. HVEM Studies of the Ordering Reaction

3.1 General

An HVEM offers several advantages over conventional TEM's for studying ordering reactions (9). In the present work, ordering was studied as a function of temperature and accelerating voltage to establish the stability range, the role of point defects and the effects of irradiation on the formation and dissolution of the ordered phase. All the observations were made in different parts of the grain boundary regions of the same Pt(C) specimen that had been carburized at 800°C for 16h.

Two noteworthy features were, (i) ordering was observed only in the thick grain boundary regions of the Pt(C) specimen imaged in Fig. 1 and (ii) these regions contained large inclusions around which the reaction was most noticeable. The crystal structure of the inclusions has not been determined but electron diffraction evidence shows it is non-cubic. A typical micrograph of radiation-induced ordering near a particle is given in Fig. 3(a) and the corresponding selected area diffraction pattern in Fig. 3(b). The similarity to the structures produced by quenching and aging (cf. Fig. 2) is evident.

3.2 HVEM In-situ Observations

(i) Effect of Accelerating Voltage on Radiation-Induced Ordering

By varying the accelerating voltage it was established that threshold voltages exist for both inducing ordering in the initially

disordered lattice* and for disordering a previously radiation-induced (RI) ordered region.

Observations over long periods at 200kV produced no changes in microstructure in the as-prepared foil over the temperature range 25-550° C. Irradiation at 300kV and 300-550°C for 30 minutes produced resolvable ordered zones. Evidence for ordering at shorter irradiation times was found in the diffraction patterns. Over the voltage range 400-1500kV ordering occurred at temperatures between about 300-600°C. With increasing voltage the time for ordering decreased, and at 1300kV and above it occurred in seconds.

A typical example of an ordering sequence is shown in Fig. 4. The nucleation and growth of small ordered domains during irradiation with 500 kV electrons at 500°C is illustrated in the series Fig. 4(a-d) in which a 100 superlattice reflection was used to form the image. However, the first appearance of extra spots in the diffraction pattern provided a more sensitive indicator for the onset of ordering; this is seen in the series Fig. 4 (e-h).

At voltages of 900kV and above, displacement damage in the form of dislocation loops nucleated and grew in the same region as the ordering occurred. An example obtained at 1300kV is given in Fig. 5. An analysis of the loop nature was not performed but they are presumably interstitial in accordance with earlier work (8).

(ii) The Effect of Accelerating Voltage on Radiation-Induced Disordering

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*It is in fact likely that short-range ordered regions are already present in the specimen since diffuse scattering was observed in the diffraction patterns.

In a second series of experiments, regions of order created by an irradiation at 500°C were irradiated further at room temperature with a fully focussed beam at various voltages to study radiation-induced disordering.

The threshold voltage for disordering was found to be about 400kV at which voltage small changes in microstructure were observed after 30 minutes ($\sim 9 \times 10^{26} e/m^2$). As the accelerating voltage was increased the reaction time decreased so that at 1000-1500kV disordering was already evident in the few seconds necessary to expose a film. In addition to disordering the specimen, irradiation above 900kV again produced displacement damage but on a much finer scale than that produced during ordering at elevated temperature.

The various radiation-induced processes were followed by bright field and superlattice dark field imaging and by changes in the diffraction patterns. A typical example of the disordering reaction at room temperature and 700kV is shown in Fig. 6. After irradiation for 10 minutes ($\sim 3 \times 10^{26} e/m^2$) the central region of the dark field micrograph in Fig. 6(a) where the electron beam was fully focussed had disordered whereas the ordered domains were still present in surrounding un-irradiated areas. Clear evidence to support this is found in the diffraction patterns. When a large selected area aperture was used, the normal pattern indicating ordering was obtained (see Fig. 6b). However, when a smaller aperture was centered on the irradiated area the matrix diffraction spots only were found (Fig. 6c).

(iii) The Effect of Temperature

The temperature range over which radiation-induced ordering

occurred in times of 30-40min was established using a fixed voltage of 1000kV. Very small domains were observed in superlattice dark field images after irradiation at 280°C. After 30 m irradiation at 260°C superlattice spots were faintly visible in the diffraction patterns. Thus the lower temperature limit for ordering was ∿250 °C. To establish the upper temperature limit, a series of diffraction patterns were taken from the same previously ordered region during continuous heating. These observations were made both below the threshold voltage (300kV) and above it (1500kV). The sequence obtained at 300kV is given in Fig. 7. It is seen that a decrease in the intensity of the superlattice spots has occurred at 650 °C and the original diffraction pattern has been restored at 675° C (c.f. Figs. 4e and 7d). When the same experiment was performed at 1500kV a slight shift to higher dissolution temperatures was observed. A decrease in superlattice spot intensity was found at 665°C and faint residual intensity was just evident at 700°C. After cooling the specimen to 505° C the original ordered pattern was re-established within a minute. Both sets of results could be readily reproduced by cycling the specimen temperature over this range. An upper temperature limit for the stability of the ordered phase under irradiation is thus 650-700°C. The conditions for RI ordering and disordering are summarized in Fig. 8.

Discussion

The general topic of ordering in metallic alloys has been comprehensively covered in many reviews and books (see e.g. 10,11). In a number of studies an HVEM was used not only to follow in-situ ordering and disordering reactions and derive parameters for comparison with

theory, but also to induce or accelerate the reactions using an electron beam (12-14). The unique aspect of the present study is that the order/disorder reaction occurs in an alloy system normally considered interstitial, whereas all earlier work has been conducted on substitutional systems. This difference is the main emphasis of the present paper.

It is evident from both the quenching and irradiation results that the ordered phase forms only in certain regions of the Pt foils, and only under special circumstances. In each case the regions adjacent to unidentified inclusions apparently satisfy the conditions for ordering to occur under the right stimulus. Although indirect, all the evidence points to the requirement of a lattice rich in carbon and vacancies. An earlier Auger analyses of the specimen used in the irradiation experiments(7) showed that carbon was present in the grain boundary regions in amounts far in excess of the solid solubility limits established by conventional methods(1-3). No definite mechanism has been established for this enrichment process. However, since previous diffusion experiments (7) demonstrated directly that some carbon atoms diffuse in association with a vacancy, it is reasonable to hypothesize that the excess carbon is present in pseudo-substitutional solid solution. One possibility is that when the carbon atom is a nearest neighbor to a vacancy in a closely bound pair, atomic relaxations effectively remove it from interstitial solid solution into a pseudo-substitutional site(15). The resulting shift in equilibrium between free vacancies, free carbon and pairs will allow further absorption of carbon into interstitial sites. Thus, a progressive increase in the carbon concentration would

occur spreading into the matrix from vacancy sources (free surfaces, grain boundaries and dislocations). This picture is consistent with earlier TEM and Auger analyses which provide direct evidence for such enrichments around vacancy sources.

The situation is in some ways analogous to "constant activity aging" which has been extensively studied and exploited by Jack and his co-workers (see e.g. 16). In this process, nitrogen concentrations far higher than the usual equilibrium level are dissolved isothermally in iron-base substitutional alloys by virtue of the concurrent co-precipitation of the nitrogen and the substitutional element as a stable nitride. Final equilibrium of the iron matrix and interstitial nitrogen is established only after all the substitutional solute atoms are precipitated from solution.

In the present case, since continuous sources of vacancies exist in a crystal, no such limitation exists and, given favorable kinetics and sufficient time, carbon would continue to be dissolved until the matrix is saturated with "substitutional" and interstitial carbon. The total carbon concentration (C_T) is then $C_T = C_s + C_i$ where $C_s >> C_i$. The observation of diffuse scattering intensity in the diffraction patterns from the unirradiated grain boundary regions is consistent with this picture since some short range ordering could occur during the carburization treatment or during cooling. A rationalization of the irradiation results then follows logically. In the temperature range 300 - 650° C electron irradiation induces long range ordering of the substitutional carbon on the fcc Pt lattice. With increasing temperature the number of domains decreases while their size increases until at the higher temperatures completely ordered structures containing

a typical maze of antiphase boundaries is observed (see Fig. 9).

1. Structure of the Ordered Phase

The crystal structure of the ordered phase was obtained from analysis of the electron diffraction patterns. In all the zones examined extra superlattice spots were observed bisecting the matrix Pt spots indicating a structure with a lattice parameter twice that of Pt(4). Assuming the phase is a carbide, the simplest structure consistent with the diffraction evidence is that shown in Fig. 10. It forms when an 8 unit cell region of the Pt matrix containing 28 Pt atoms and 4 carbon atoms orders so that the carbon occupies (substitutionally) the face-centered sites of the new larger (x2) unit cell. The stoichiometric composition is Pt_7C and the structure is isomorphous with $CuPt_7$(10). Since in some experiments the domains grew throughout the whole foil thickness, the local carbon/vacancy concentration must be at least 12.5 atomic percent, assuming the phase is stoichiometric.

2. The Mechanism of Radiation-Induced Order/Disorder

In earlier HVEM studies of displacement damage in Pt-C alloys (8) threshold voltages for several different processes were found.

The lowest threshold occurring at ∿380 kV was related to the minimum energy transfer from an electron to a carbon atom to displace it from a Pt-C precipitate plate. A second threshold occurred at 560 kV when the energy transferred to a carbon atom was sufficient for it in turn to produce a Frenkel pair in the Pt matrix. Above this voltage interstitial loops were formed in the matrix. Finally, at voltages above 1300kV a third process occurred as electron-Pt atom collisions

directly produced Frenkel defects in the matrix. One other result relevant to the present work was the observation that radiation-stimulated growth of pre-existing precipitates could occur under certain conditions. At room temperature the threshold for this process was 600 kV. These results are invaluable in forming the basis for understanding the present work.

The observed 300 kV threshold voltage for ordering must be related to the minimum energy transfer necessary to stimulate an atom jump of the complex. It is clear that direct or indirect displacement of Pt atoms is impossible at 300 kV, hence the ordering reaction must involve the local rearrangement of pre-existing carbon-vacancy complexes. However, there is clearly a large discrepancy between the 300 kV threshold for ordering and the 600 kV value for electron stimulated growth of carbide plates. Several differences in the experimental conditions may be the cause of this variance. For example, the precipitate growth studies were performed at room temperature, using a conventional tungsten filament ($\phi=10^{24} e/m^2$), and involved long range diffusion of the complexes (the mean separation of the precipitates was $\sim$100 nm). On the other hand the ordering reaction occurred at intermediate temperatures ($\sim 260 < T_C < 650°C$), during irradiation with a LaB_6 filament ($\phi= 10^{25}$ e/m^2) in times that decreased with increasing temperature, and required mass transport over much shorter distances (the mean separation of the domains was $\sim$10 nm in the 300 kV irradiation). Of these various factors, only the temperature would reduce the threshold voltage for stimulated complex migration, while the dose rate and diffusion distance would affect the incubation time. Nevertheless, the experimental increase in jump

probability with increase in temperature could certainly decrease the required electron energy transfer by a significant factor.

A quantitative analysis of sub-threshold electron-stimulated vacancy migration has been carried out by Tenenbaum and Doan (17) using computer simulation by the molecular dynamics technique. Calculations for copper showed a marked dependence of the induced vacancy jump frequency on the incident beam direction and a maximum value between 60 and 100kV. Even allowing for the difference in mass between Pt and Cu, there appears to be a large discrepancy between the calculated energy for maximum jump frequencies and those measured in the present work. This may reflect the increase in energy that will be required to move the complex compared to the monovacancy.

Kiritani (18) used a simpler cross-section averaging approach to estimate point defect jump frequencies of one to ten jumps per second with a maximum frequency at 250kV for Pt.

Within the given temperature range it is evident that once formed the ordered phase is quite stable over the voltage range 300 kV to 1500 kV. However, above 900 kV matrix displacement damage in the form of dislocation loops developed after extended irradiation. This threshold is considerably higher than the 580 kV measured for secondary displacement in the purer Pt and may again reflect the greater stability of the ordered structure.

3. Ordering by Quench-Aging

If the proposed necessary preconditions for the formation of the ordered phase by irradiation are accepted, namely, the presence locally of a high concentration of carbon atom/vacancy pairs, a credible mechanism

for its formation by quench-aging also follows.

Assuming the unidentified particles centering the shells of ordered zones are rich in carbon, it would be possible for the matrix region surrounding the particle to become carburized during the pre-quench heating close to the melting point (Tm). Taking the equilibrium vacancy concentration at Tm, $C_V = 5x10^{-4}$, and B = 0.6eV (7) the fraction of carbon atoms bound to vacancies is $\sim$0.1. If attaching a carbon atom to a vacancy effectively moves it from interstitial to substitutional solution, as noted earlier the resulting shift in equilibrium will allow further carbon to be interstitially dissolved. This process will be particularly efficient if the particle/matrix interface is also a good vacancy source. It allows progressive enrichment of the matrix with carbon, vacancies and C/v pairs to occur, and if followed by an appropriate quench-aging treatment, all the necessary conditions for the local formation of ordered zones of Pt_7C by purely thermal processes may be fulfilled.

The observation of the helical dislocations emanating from the particles is also explained readily. These may be punched from the interface to relieve stresses generated by a differential contraction between the particle and matrix by the well-known loss of coherency mechanism. They will perturb the formation of the ordered phase only by locally creating zones denuded of vacancies and carbon atoms. Indeed, detailed analysis of the dislocation features suggest that they act as heterogeneous nucleation sites for precipitation of one of the more concentrated carbide phases reported earlier(5).

Formation of the ordered phase by quenching (albeit in small zones dispersed in the Pt matrix) in addition to its generation under the more esoteric conditions of electron irradiation, suggests that the Pt_7C phase, and perhaps other related phases, might be encountered more frequently under appropriate circumstances. For example, Pt supported catalysts are often exposed to carboneous environments and temperatures where local or surface formation of such phases could take place (19).

SUMMARY AND CONCLUSIONS

An unusual ordering reaction has been observed near grain boundaries of carburized platinum foil during high-energy electron irradiation in the temperature interval of 250-650°C. The same ordered phase was found near inclusions in quench-aged dilute Pt-C alloys and its proposed structure of Pt_7C is fcc with twice the lattice parameters of Pt. In this structure carbon occupies substitutional sites, in contrast to its usual state where it is dissolved interstitially. Using the present results in conjunction with earlier data that show strong binding between interstitial carbon and platinum vacancies it is concluded that near vacancy sources excess carbon can combine with its associated vacancy and go from interstitial to psuedo-substitutional solid solution. As a result carbon concentrations far in excess of the established interstitial solubility limit can be built up locally. The rearrangement of carbon-vacancy pairs effecting the ordering occurs in the electron beam for accelerating voltages above 300kV. This is substantially lower than the thresholds of 1300kV for displacement damage in pure Pt and 600kV for dilute Pt-C alloys and must therefore be due to electron stimulated migration of carbon-vacancy complexes.

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FIGURE CAPTIONS

Fig. 1. Low magnification STEM micrograph of a thinned Pt specimen illustrating the resistance to electropolishing of the grain boundary regions compared to the grain interiors. The foil was carburized on one surface and decarburized on the other in dry argon. (Micrograph supplied by C. Echer).

Fig. 2. TEM diffraction contrast analysis of Pt (A-R) quenched from the melting point and aged at 400°C. a) shows ordered domains A around an inclusion B. Dislocations C emanating from the inclusion are associated with another type of precipitate. Far from the inclusion normal matrix precipitates of α' Pt_2C are found (D) separated from the ordered region by a depleted zone E. A selected area diffraction pattern from the ordered region A, shown in b), exhibits extra spots halfway between matrix reflections. In c) a dark field image taken with one of the extra spots shows the ordered domains. The bright field image in d) shows the plate-like morphology of the domains.

Fig. 3. Dark field micrograph (a) and corresponding selected area diffraction pattern (b) of radiation-induced ordering showing high density of ordered zones and corresponding superlattice spots midway between matrix spots.

Fig. 4. Sequence of micrographs showing radiation induced ordering at 500 kV and 500° C. (a)-(d) are dark field images using the 100 superlattice reflections, taken after 10 mins. (a), 30 mins (b), 50 mins. (c) and 60 mins. (d). The ordered domains are visible in (c) and (d) as fine white zones. In (e)-(h) the same sequence is followed by selected area diffraction in a 110 orientation. The original pattern

containing only matrix spots (e) exhibits weak extra spots after 10 min. irradiation (f). The superlattice spots have increased in intensity after 30 min. (g) but thereafter are hardly changed, 50 min. (h).

Fig. 5. Micrograph formed by shifting the objective aperture over a diffracted beam showing dislocation loops in central bright field area due to displacement damage during irradiation at 1300 kV. Note fine ordered domains in dark field areas due to the same irradiation.

Fig. 6. (a) Dark field micrograph of ordered zones with central dark region disordered by room temperature irradiation at 700 kV. (b) Selected area diffraction from entire initially ordered area and (c) from the central disordered region only. The absence of superlattice reflections in (c) is evident.

Fig. 7. Thermal disordering sequence at sub-threshold electron energy (300 keV), (a) 600 °C, (b) 625° C, (c) 650° C and (d) 675° C. In (d) the crystal is completely disordered.

Fig. 8. Schematic representation of conditions for radiation-induced ordering, disordering and displacement damage as a function of temperature and accelerating voltage.

Fig. 9. Completely ordered region obtained by high-temperature irradiation. Note large domains separated by antiphase boundaries and nearby inclusion.

Fig. 10. Face centered cubic unit cell of Pt_7C, the simplest structure consistent with the observed superlattice reflections.

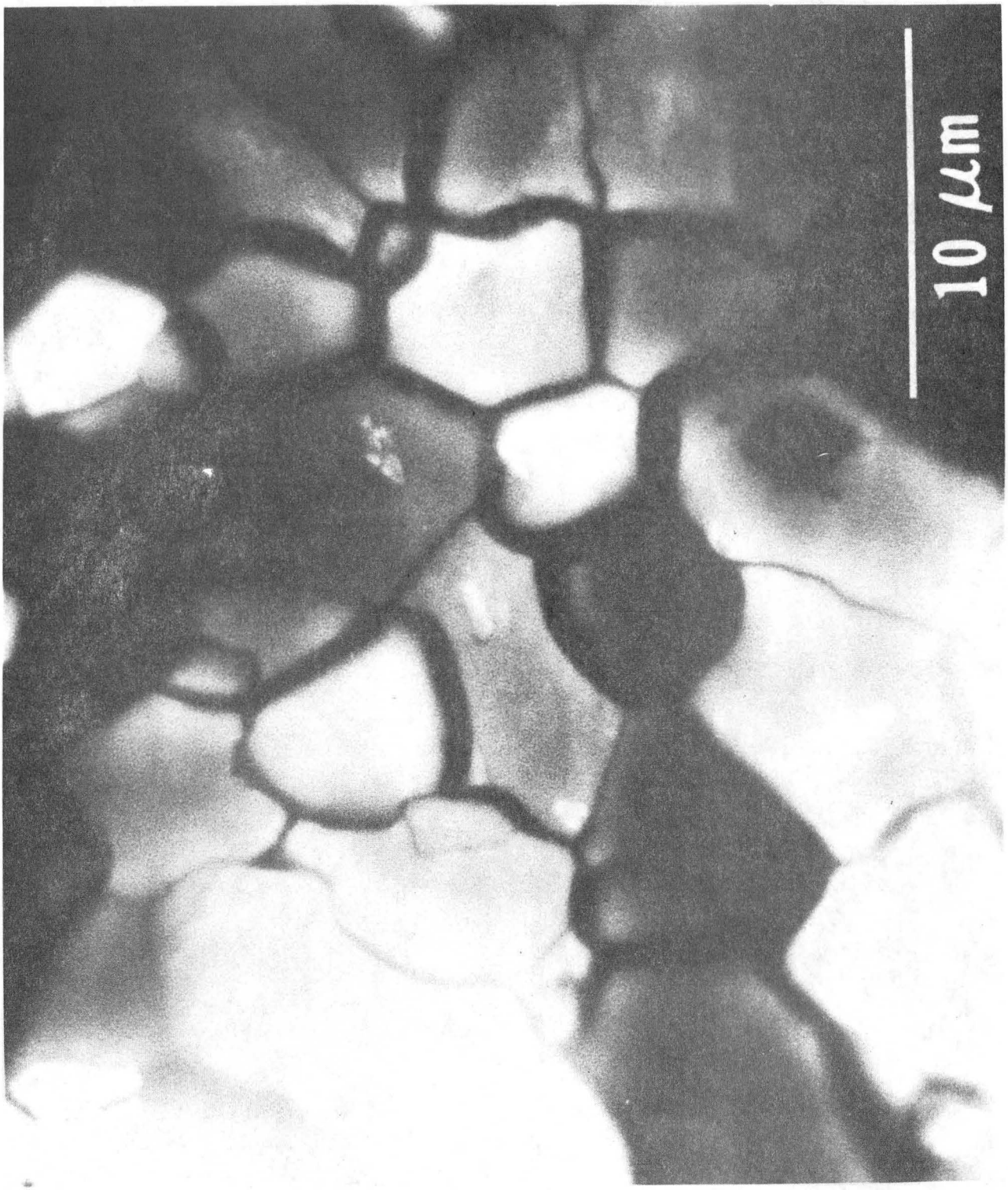

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Fig. 1

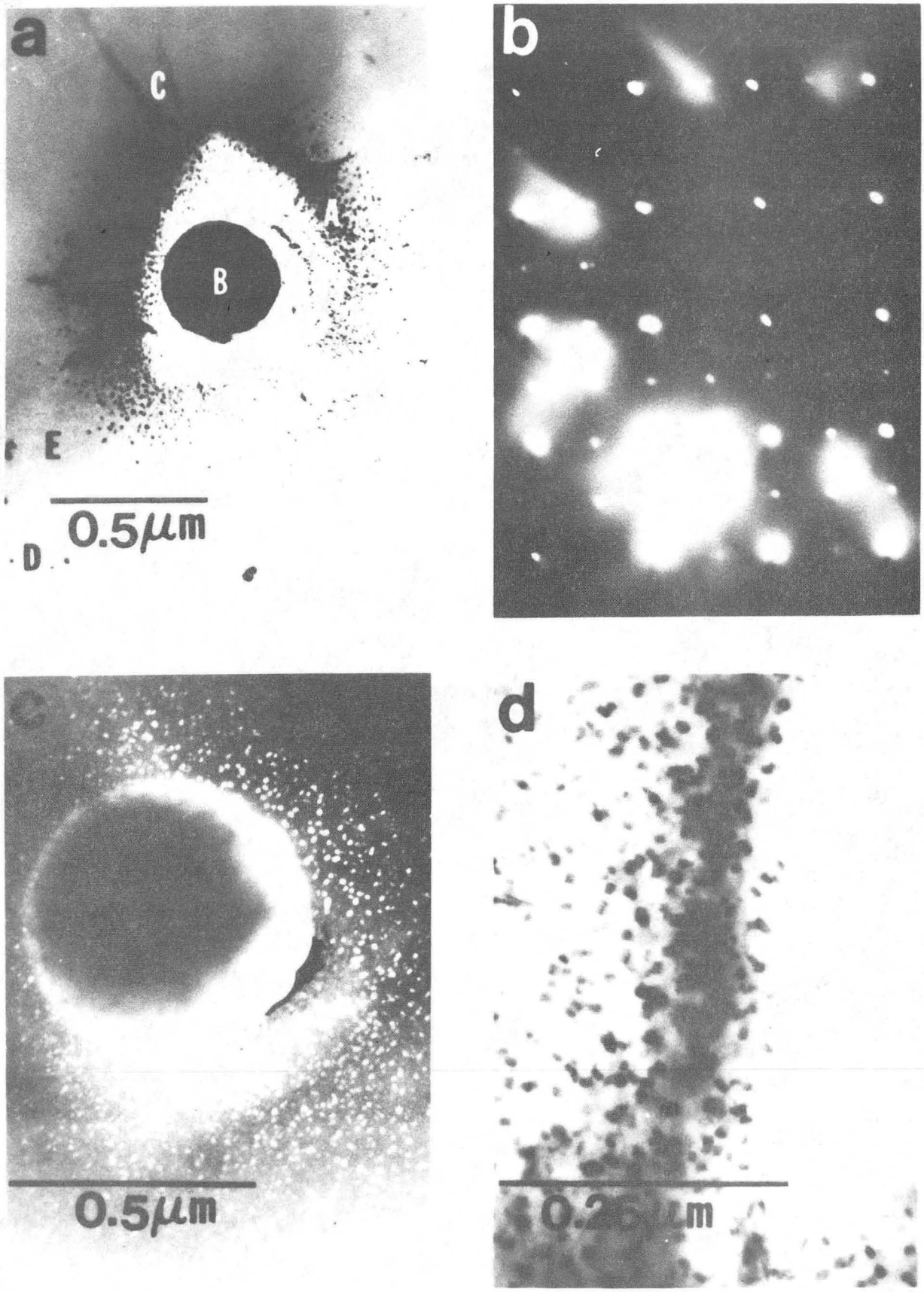
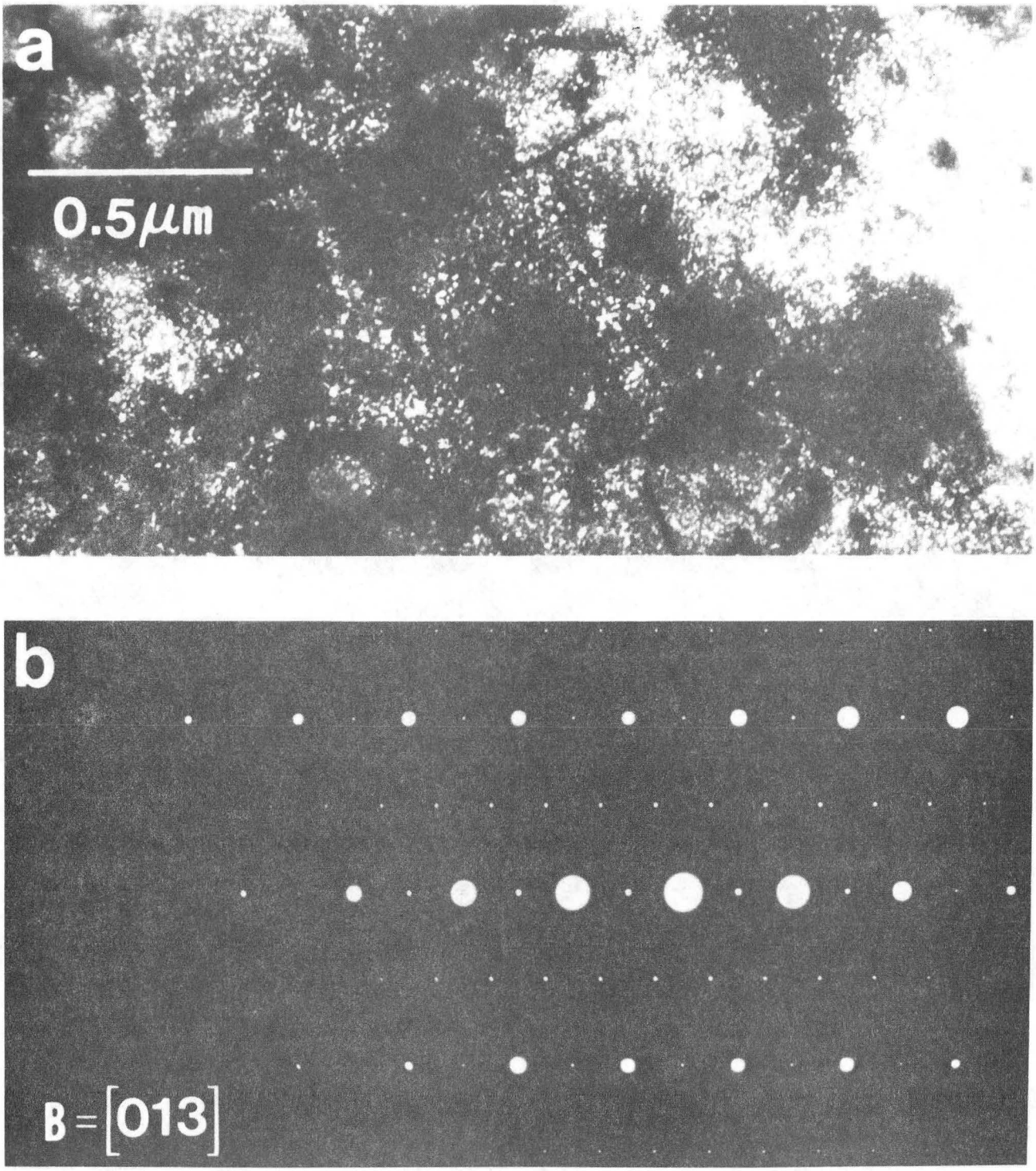


Fig. 2

XBB 854-3292



XBB 856-4260

Fig. 3

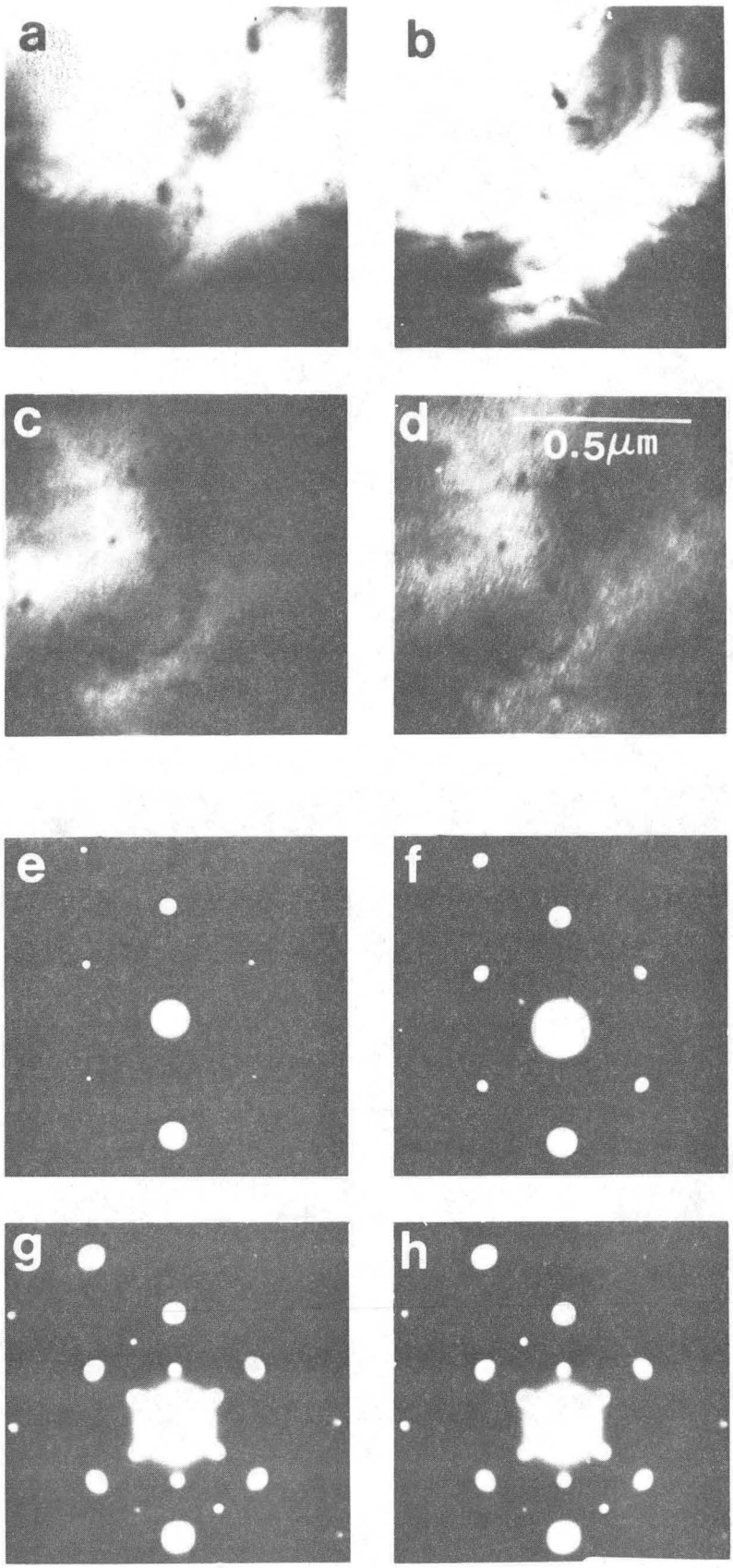
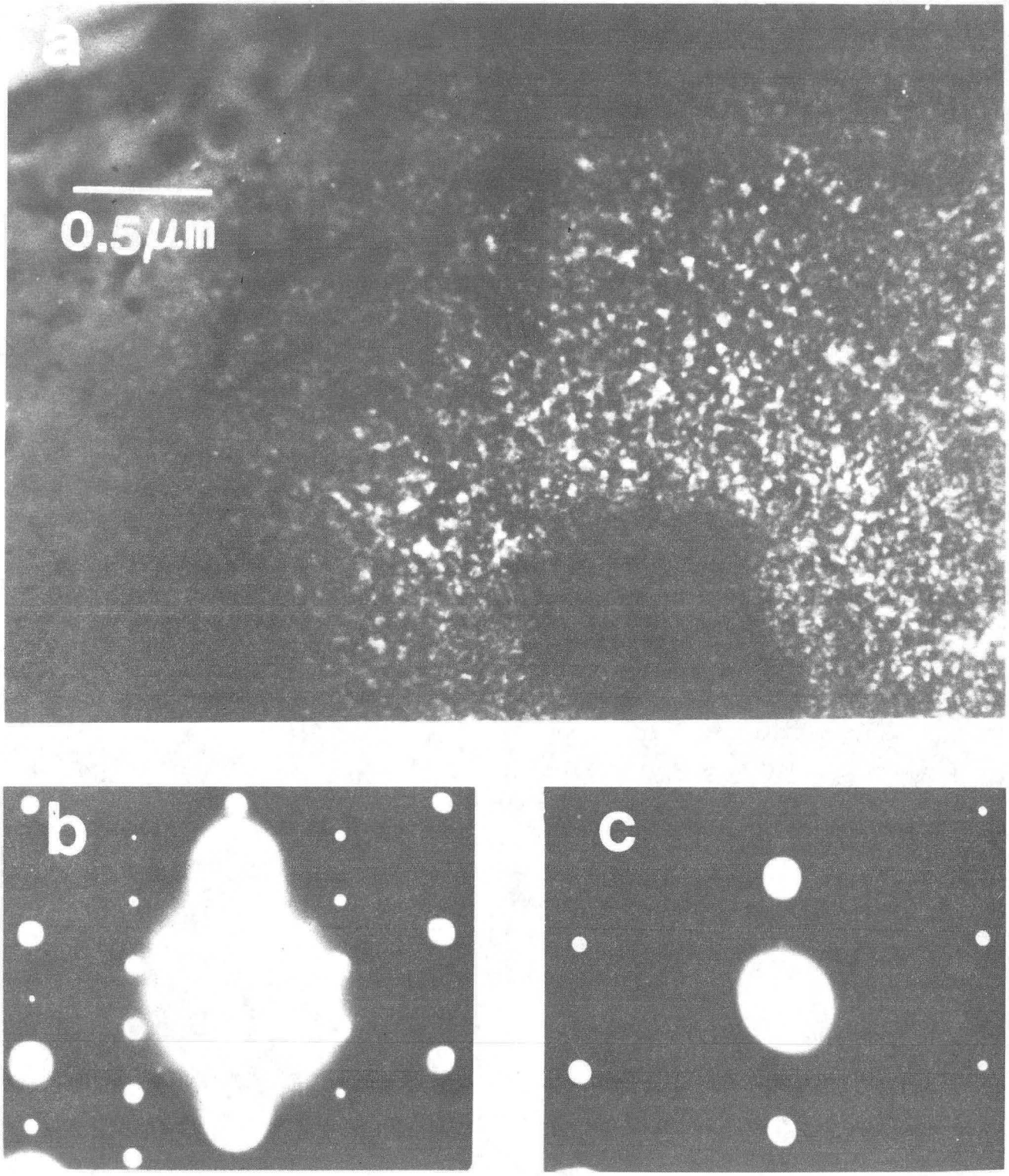


Fig. 4

XBB 854-3296

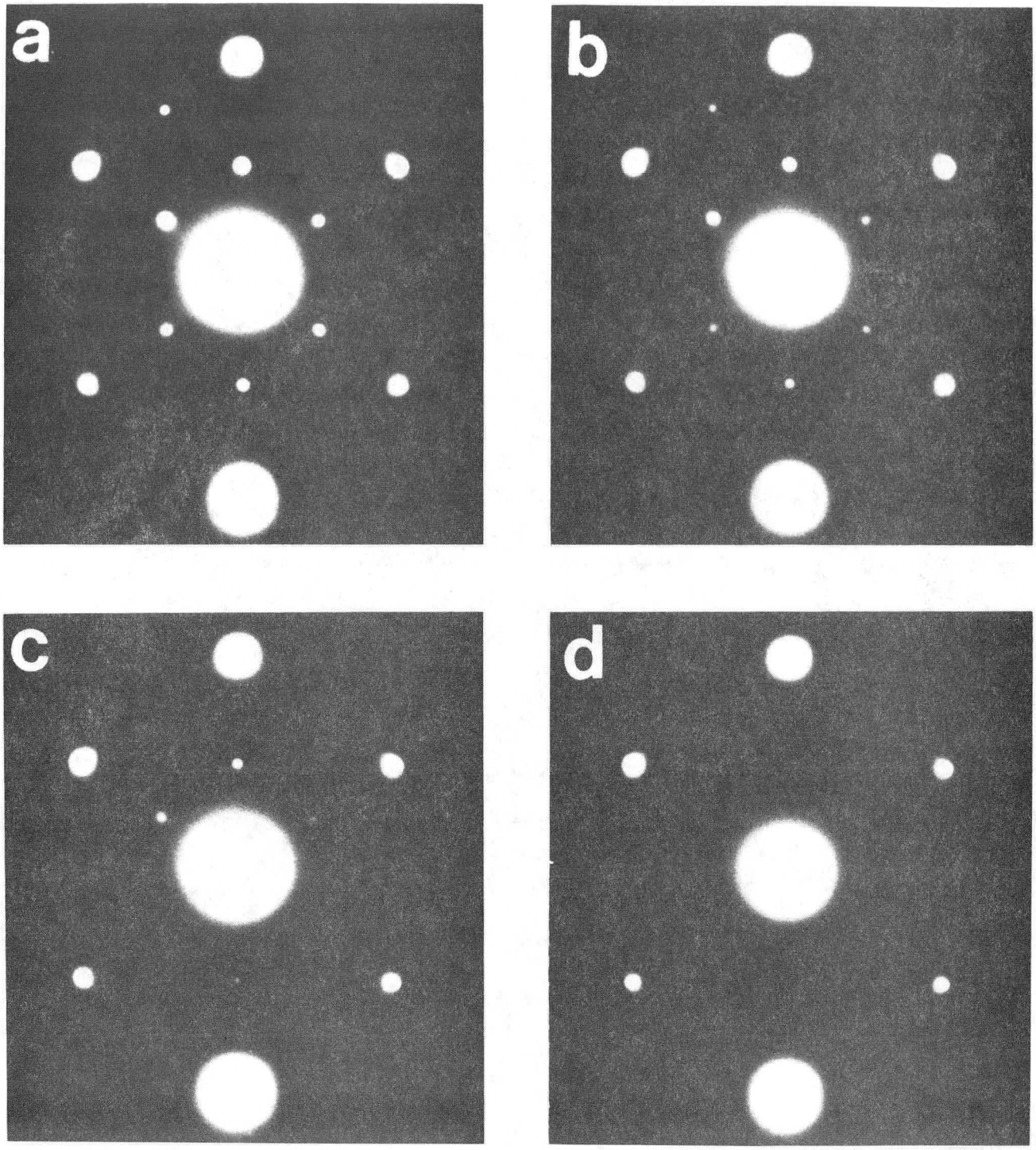
Fig. 5

XBB 854-3295



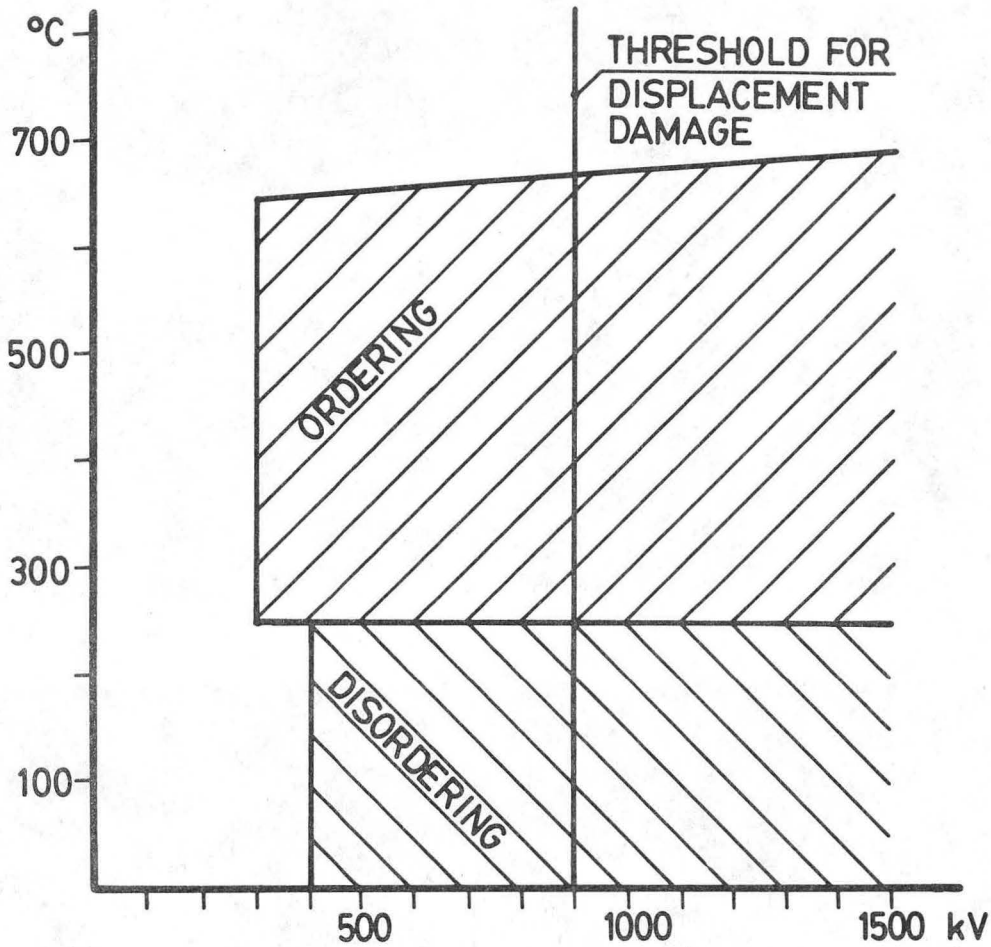
XBB 854-3291

Fig. 6



XBB 854-3290

Fig. 7

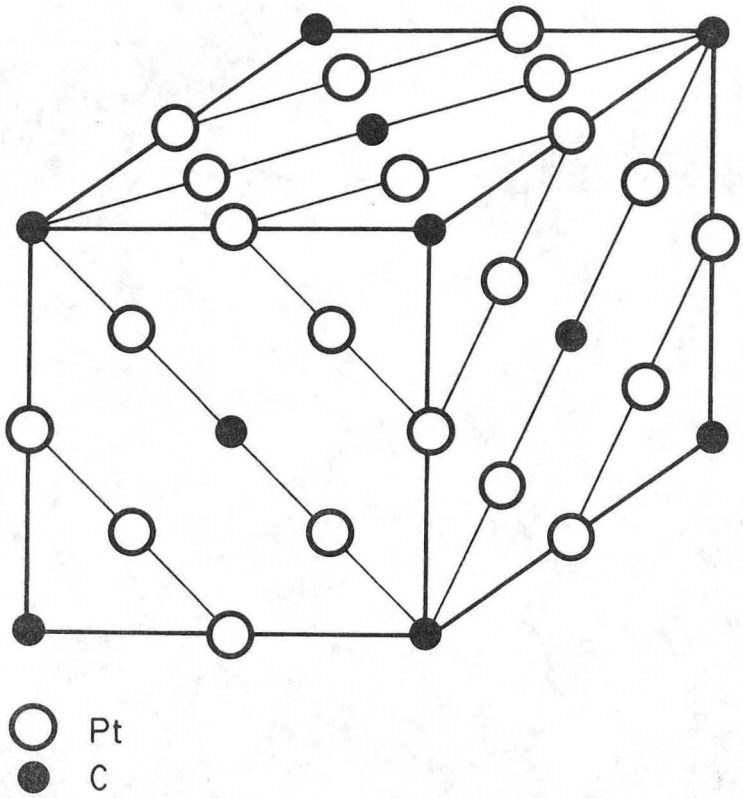


XBL 855-2647

Fig. 8

Fig. 9

XBB 854-3294



XBL 854-2220

Fig. 10

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