OBLIQUE INCIDENCE EFFECT ON THE CRYSTAL STRUCTURE OF THIN VACUUM-DEPOSITED CHROMIUM FILMS

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SUMMARY

It has been found that thin films of chromium made by oblique incidence in vacuum deposition consist of the new modification of chromium (δ-Cr[1].) in addition to ordinary b.c.c. α-Cr. For uniform films with thicknesses between approximately 10 and 70 Å, the ratio of the amount of δ-Cr to α-Cr increased as the obliqueness of the incident vapour stream increased. When the mean thickness exceeded about 100 Å, δ-Cr ceased to be observed and only b.c.c. α-Cr remained, irrespective of the incidence angles. On the other hand, when the mean thickness was about 10Å diffuse halo patterns were observed. Dark field electron microscopy revealed that the crystal size of the δ-Cr was much smaller than that of the α-Cr.

1. INTRODUCTION

It is well known that metallic films condensed in vacuum from vapour which is incident obliquely on the substrate exhibit anisotropy in their optical[2], magnetic[3–5] and electrical[6] properties. Many studies have also been reported on the effect of oblique incidence on the structure of metallic thin films, *i.e.* on the surface appearances of the films[7], the external shape of the grains[8] and the crystal orientation of the microcrystals in the films[9, 10]. The observation, however, that causing the metallic vapour to strike the surface obliquely instead of normally has a strong influence on the crystal structure of the thin films produced has not been reported as far as these authors are aware.

In the present experiments it was found that the thin chromium films produced by condensation at oblique incidence in vacuum consisted of the new modification of chromium (δ-Cr) in addition to the well-known b.c.c. α-Cr, and further, that

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for films of equal thickness within a range of approximately 10–70 Å the ratio of the amount of the new modification of chromium to b.c.c. α-Cr increased as the incidence angle of the vapour stream to the substrate surface increased. The intensities of the electron diffraction Debye pattern and the lattice constant of the new modification of chromium in the present experiments agreed with those of the crystal structure found by the present authors[1] in the fine particles produced by evaporation and condensation of chromium in argon at low pressures. This new modification was called δ-Cr and its electron diffraction pattern was interpreted in terms of a disordered structure derivable from the A-15 type structure.

Forssell and Persson[11] found a new phase in very thin vacuum-deposited chromium films prepared at various substrate temperatures between room temperature and 450 °C on NaCl and KCl, cleaved either in ultra-high vacuum or in air. This phase was found to exist in the coalescence stage of the growth and ceased to be observed when the film became thick enough to be continuous. The lattice constant was found to agree with that of the fine particles of chromium reported by the present authors. Forssell and Persson, however, interpreted their electron diffraction spot patterns as consistent with the genuine A-15 type structure, contrary to the present authors.

The purpose of this paper is not to discuss the details of the crystal structure analysis of this new phase of chromium, which will be postponed until more data are available, but to report the effect that oblique incidence tends to favour the occurrence of δ-Cr.

2. EXPERIMENTAL

Condensation of chromium was carried out in a conventional vacuum evaporation unit with a metal bell jar of about 20 litres in volume. The vapour source consisted of an electrically heated conical tungsten basket containing spectrographically standardized chromium from Johnson, Matthey and Co. The rate of condensation was about 1–5 Å/s and the pressure during evaporation was approximately 1×10^{-5} torr. The substrates were amorphous carbon film, Formvar film, thin flakes of single crystal graphite and KCl and NaCl crystals cleaved in air. A supporting frame with steps, as shown in Fig. 1, was used to make the thickness of each film the same, irrespective of the angle of incidence of the vapour stream on the surface of each substrate. The substrates were placed on each step and films with a given thickness but with various incidence angles were made at a single evaporation. The incidence angle θ was varied from 0° (vapour stream normal to the surface of a substrate) to 80° stepwise in intervals of 10°. The distances between the source of evaporation and the substrate were 15 cm for normal incidence and 6.3 cm for 80° incidence in one frame and 8.0 cm and 3.3 cm, respectively, in another frame. The condensation was always carried out at room temperature.

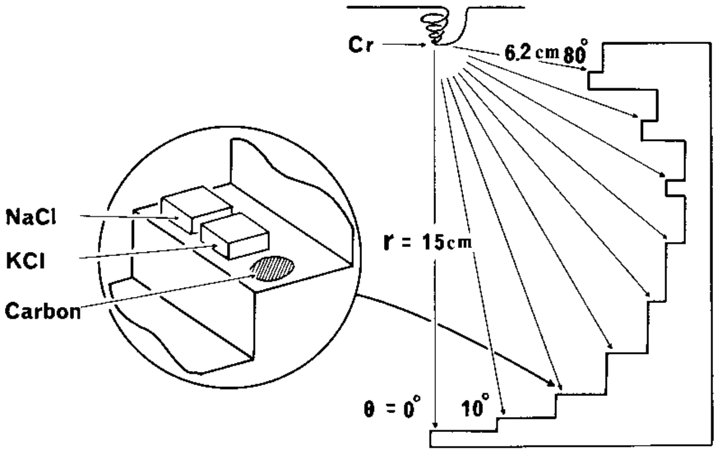
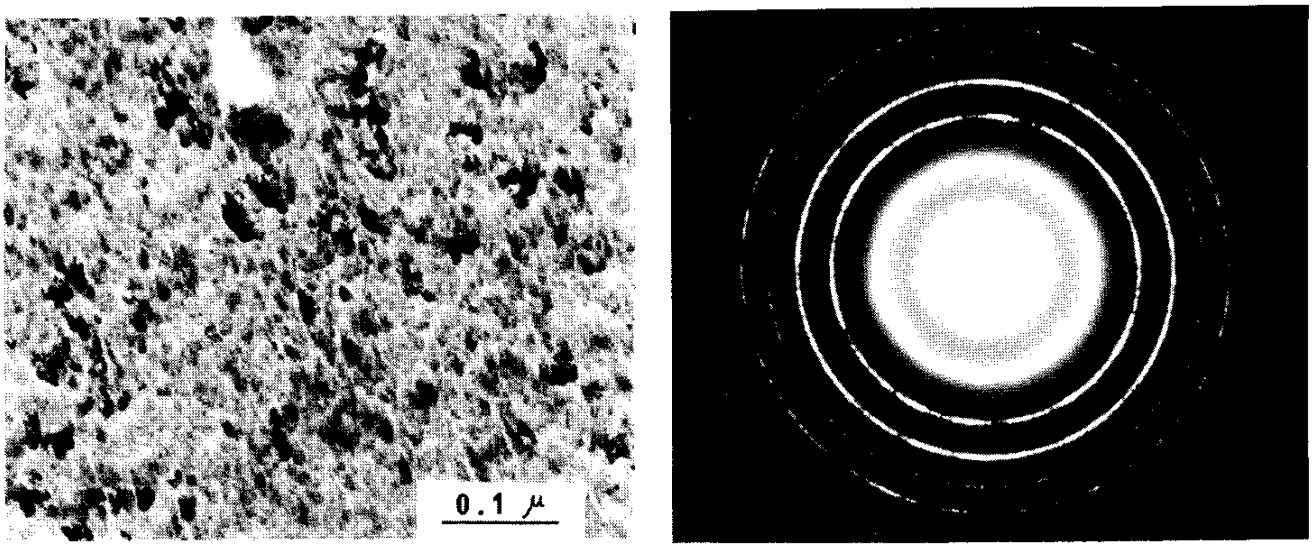


Fig. 1. Supporting frame for substrates to make films of constant thickness irrespective of incidence angles: $\cos\theta/r^2 =$ const. In one frame the maximum value of r was 15 cm and in another frame it was 8 cm.

3. EXPERIMENTAL RESULTS

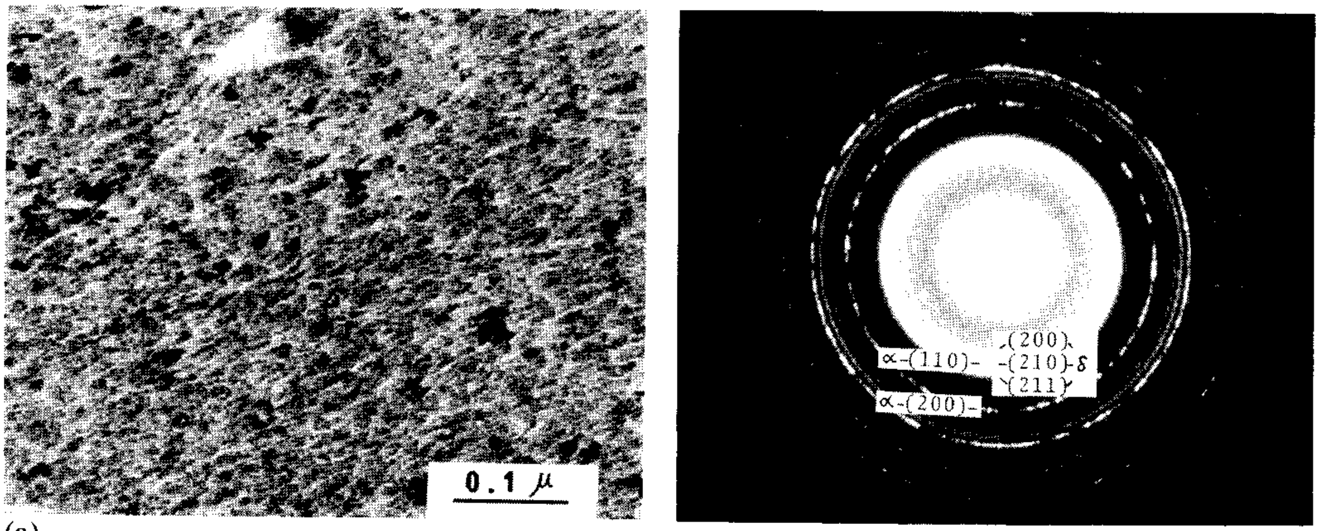
3.1. Electron micrographs and electron diffraction patterns— effect of incidence angles and thickness on the structure of the chromium films

Figures 2 and 3 show electron micrographs and electron diffraction patterns obtained from chromium films of 60 Å mean thickness prepared at normal incidence ($\theta = 0°$) and oblique incidence ($\theta = 80°$), respectively. Generally speaking, as shown in these micrographs, the films prepared at normal incidence appeared to have a flat surface and uniform structure in any direction of the film surface. However, as the incidence angle θ became larger, the films exhibited a coarse structure which consisted of columnar grains tending to tilt towards the direction of the incident vapour stream. These columnar crystals increased in size as the mean thickness of the film increased and the coarse structure could always be observed if the thickness of the film was between about 20 Å and about 100 Å



(a) (b)

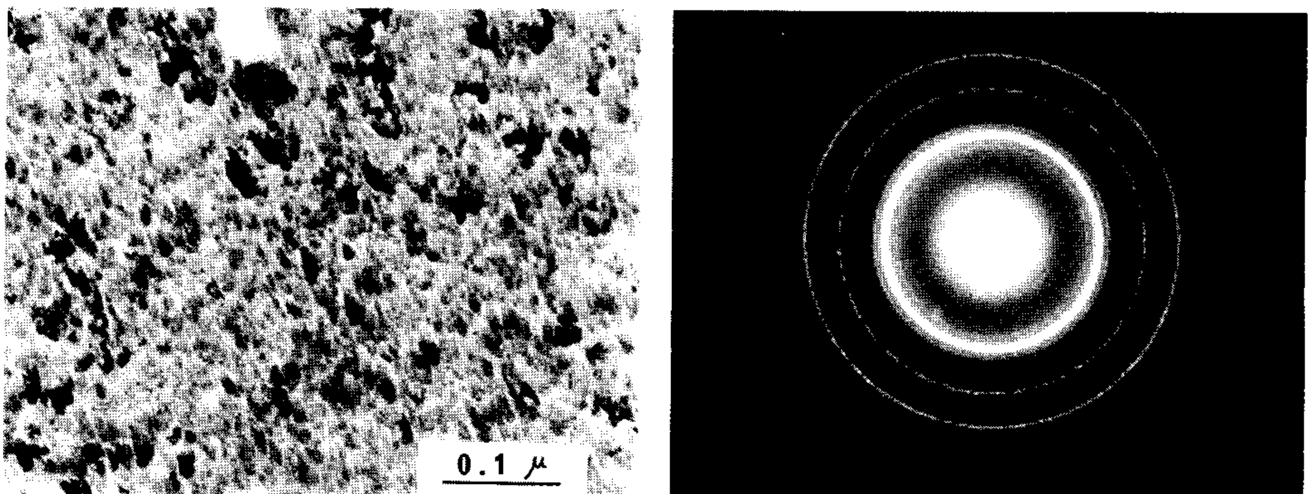
Fig. 2. (a) Electron micrograph of a Cr film of 60 Å thickness made at normal incidence ($\theta = 0°$). (b) Electron diffraction pattern from (a), b.c.c. α-Cr.



(a) (b)

Fig. 3. (a) Electron micrograph and (b) diffraction pattern from a Cr film made simultaneously with the film shown in Fig. 2 but at oblique incidence ($\theta = 80°$). In (b) the diffraction pattern from δ-Cr is dominant.

A remarkable difference was observed between electron diffraction patterns of chromium films made at large angles and small angles of incidence. Figures 2(b) and 3(b) are the electron diffraction patterns corresponding to Figs. 2(a) and 3(a), respectively. Figure 2(b) ($\theta = 0°$) consists solely of the b.c.c. pattern consistent with α-Cr and Fig. 3(b) ($\theta = 80°$) shows many Debye rings consistent with δ-Cr. When the mean thickness of a film was between 20 and 70 Å approximately, the intensity of the Debye rings due to δ-Cr increased with respect to the intensity of the rings from α-Cr as the incident angle θ was increased, *i.e.* among films of equal thickness those films prepared with $\theta = 80°$ always gave the strongest intensity due to δ-Cr. On the other hand, the films prepared at normal incidence gave, in almost all cases, only the b.c.c. Debye pattern consistent with α-Cr. When the mean thickness of the films exceeded about 70 Å, however, the above-mentioned tendency began to be less evident (see Fig. 4) and those films whose mean



(a) (b)

Fig. 4. (a) Electron micrograph and (b) diffraction pattern from a Cr film of 90 Å mean thickness, oblique incidence ($\theta = 80°$).

thickness exceeded about 100 Å, even if they were prepared with $\theta = 80°$, showed only a Debye pattern consistent with α-Cr.

When the mean thickness of the films decreased to the order of 10 Å, those prepared at normal incidence still showed a flat surface although the contrast of the micrographs was very low. The films made at oblique incidence, however, did not have a flat surface but consisted of island grains whose mean size was less than a few tens of ångströms. These particles aligned themselves in a chain-like structure perpendicular to the direction of the vapour stream. An example is shown in Fig. 5. A shadow cast by a dirt particle shows the direction of the vapour stream.

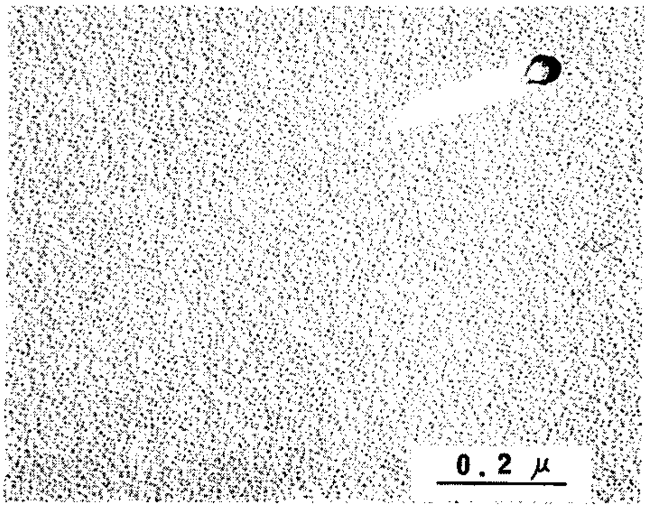


Fig. 5. Cr film of 10 Å mean thickness; oblique incidence ($\theta = 80°$). Alignment of island grains can be seen if one observes the micrograph at grazing angle in the direction normal to the shadow of the vapour stream.

These features of the alignment of the particles in a chain-like structure and the correlation between the direction of the vapour stream and the chain are in accord with the observations made by Smith *et al.*[10] in the case of permalloy films prepared by oblique incidence in vacuum.

Electron diffraction patterns from the present thin films of chromium showed diffuse halo rings in almost all cases, irrespective of the incidence angles and the appearance of the corresponding micrographs; however, some films made at an incidence angle of 80° occasionally gave a weak Debye pattern which could be identified as due to δ-Cr. The origin of the halo pattern is still unknown at present. Figure 6 shows very roughly the regions in which each of the three types of diffraction patterns was observed; the ordinate gives the mean thickness of the film and the abscissa the incidence angle.

3.2. *Effect of the substrate*

The results described so far are mainly based upon observations on chromium films deposited on amorphous substrates, *i.e.* carbon and Formvar films. Thin flakes of single crystal graphite and NaCl and KCl crystals cleaved in air were also used to study the effect of the substrates on the crystal structure of chromium films. Various kinds of substrates were juxtaposed on each step of the supporting

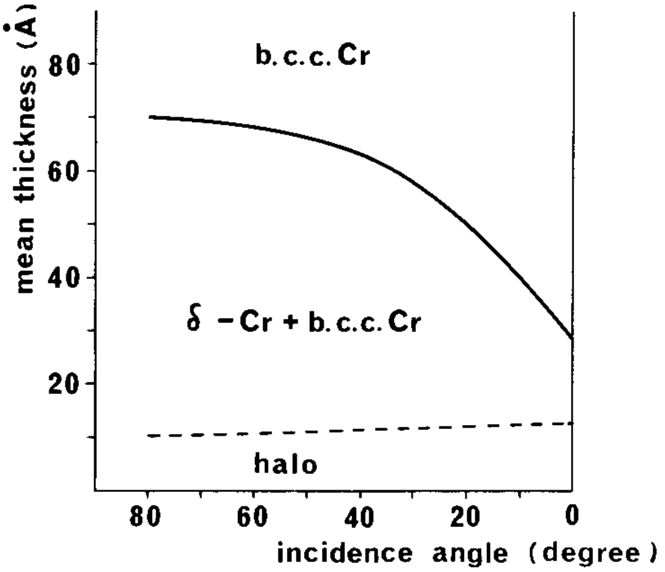
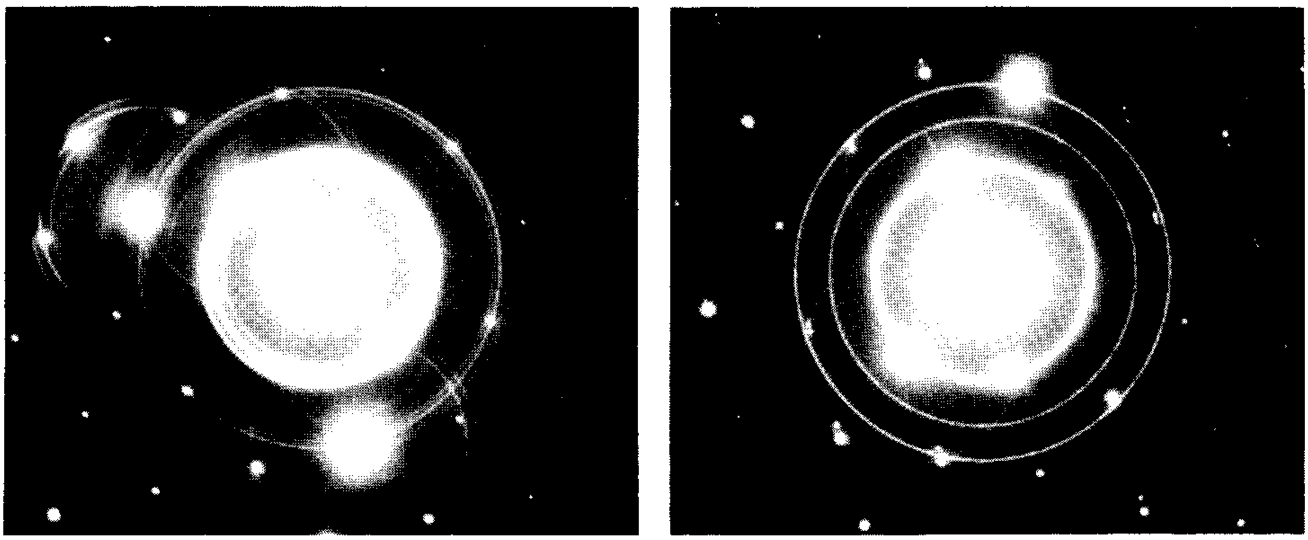


Fig. 6. Regions in which each of the three types of diffraction patterns was observed.

frame and condensation of chromium was carried out under various conditions at room temperature. No definite effect of the substrate on the occurrence of δ-Cr could be perceived. The photographs shown in Fig. 7 were taken from chromium films on graphite flakes.



(a) (b)

Fig. 7. Electron diffraction patterns from a Cr film of thickness 50 Å on graphite: (a) oblique incidence ($\theta = 80°$); (b) normal incidence ($\theta = 0°$).

3.3. Rate of condensation

To study the effect of the rate of condensation, it was changed from 0.05 Å/s to 5 Å/s in the case of a film of 60 Å in mean thickness. No effect could be observed either on electron micrographs of the films or on the occurrence of δ-Cr.

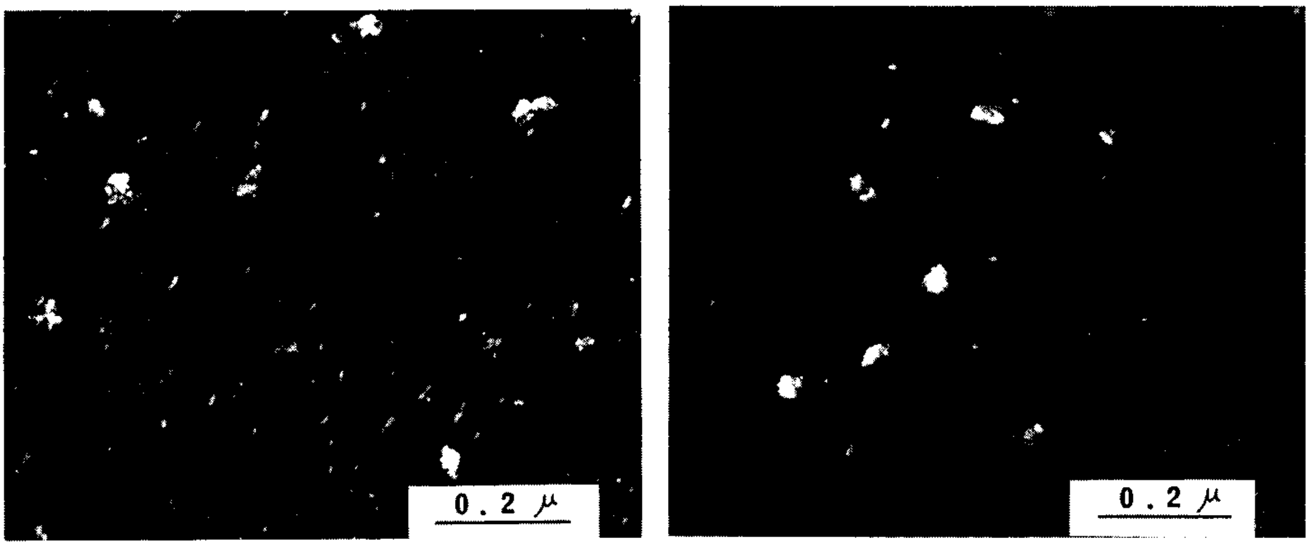
3.4. Degree of vacuum

Improvement of the vacuum to about 1×10^{-7} torr from about 1×10^{-5} torr, which was the pressure of the vacuum ordinarily used during evaporation, had no effect on the results.

3.5. Comparison of the particle sizes of δ-Cr and α-Cr

The particle sizes of δ-Cr and α-Cr were compared in order to check the possibility that the grain size of the particles may have had an influence on the occurrence of δ-Cr. Dark field microscopy was most appropriate for the purpose.

An aperture of 5 μm was used with a film of 50 Å mean thickness prepared at an incidence angle $\theta = 80°$. Figure 8 shows the results. Figure 8(a) is a dark



(a) (b)

Fig. 8. (a) Dark field electron micrograph from the assembly of four Debye rings: (200), (210) and (211) reflections of δ-Cr and (110) reflections of α-Cr. (b) Dark field electron micrograph from (200) reflections of α-Cr (see also Fig. 3(b)).

field micrograph from four reflections, *i.e.* the (200), (210) and (211) reflections of δ-Cr and the (110) reflections of α-Cr, where the (210) reflections of δ-Cr almost coincide with the (110) reflections of α-Cr (see Fig. 3(b)). Figure 8(b) is one from the (200) reflections only of α-Cr in the same film. Figure 8(a), which was obtained from the mixture of δ-Cr and α-Cr, consists of two kinds of crystals: one has a crystal size which is smaller than 100 Å and the other has a crystal size of approximately several hundred ångströms. Figure 8(b), which was due to α-Cr only, consists of grains whose size is approximately equal to that of the larger crystals in Fig. 8(a). This result suggests that the small crystals in Fig. 8(a) are δ-Cr and the larger ones α-Cr. Two other films were also used for the same test. Both were films of 60 Å mean thickness prepared simultaneously, one at 80° incidence angle and the other at normal incidence ($\theta = 0°$). The latter film consisted solely of b.c.c. α-Cr. The same procedures were carried out for these films as in the previous test and the results obtained were also the same, *i.e.* the dark field micrographs obtained from the film of 80° incidence consisted of two kinds of crystals, smaller and larger ones; the size of the smaller crystals was about 100 Å or less and that of the larger crystals was several hundred ångströms. On the other hand, the crystal size observed in the film of normal incidence was several hundred ångströms only and crystals considerably smaller than this size were not observed.

These observations suggest again that the size of the crystals in δ-Cr is much smaller than in α-Cr.

4. DISCUSSION

δ-Cr was first found in the fine particles of chromium produced by evaporation and condensation of pure chromium in pure argon at low pressures. Forssell and Persson found that this phase of chromium also existed in very thin films of chromium made by condensation in vacuum on cleaved NaCl and KCl crystals and that it could be observed only in the coalescence stage of the film formation and ceased to be observed when the film became thick enough to be continuous.

In the present study, it was found that the incidence angle of the vapour stream of chromium had a strong influence on the occurrence of δ-Cr, *i.e.* normal incidence was the least favourable. By using oblique incidence it has been possible to extend considerably the range of thickness of the films in which δ-Cr may be observed from the very narrow range designated by Forssell and Persson to the point where the films are thick enough to be continuous. The existence of δ-Cr, however, has still been confined within very thin films, *i.e.* δ-Cr could not be observed when the film thickness exceeded about 100 Å even when the films were prepared with an incidence angle of about 80°.

Even though the physical significance of oblique incidence in vacuum deposition is not clear at present, almost all the literature agrees that oblique incidence in vacuum deposition causes columnar structure in metallic films; in other words, oblique incidence has the effect of hindering the normal growth of crystal grains in the deposition metal films. As shown in the micrographs obtained by the dark field method, the size of the particles of δ-Cr was clearly smaller than that of the particles of α-Cr and it is suggested that in chromium films produced by evaporation in vacuum the smallness of the crystals is probably a necessary condition for the formation of δ-Cr.

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