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Analysis of electrochemically deposited chromium films

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Chromium films are deposited on mild steel substrates using chromic acid bath with formic acid as an additive. The effect of air annealing on the films has been investigated using hardness tests, grazing angle X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy. It is observed that hardness of the chromium films goes on increasing from 1100 to 1500 VHN with annealing temperature till 500° C, which can be explained by formation of chromium carbide on the surface. The hardness of the films decreases with further annealing due to strong oxide formation as well as films cracking.

1. Introduction

Chromium plating is a widely used technology in various industries as it offers high corrosion and wear resistant as well as decorative coatings. Amongst the various methods, the process developed by Sargent [1] and Fink [2] employing chromic acid bath with sulphate catalyst is extensively used for hard chrome plating. However, these coatings exhibit a large pinhole density. Besides, the hardness also falls off rapidly with increasing temperature. In recent years it has been observed [3, 4] that the addition of organic chemicals containing –CHO and –COOH group to the chrome plating bath not only increases the plating efficiency but also reduces the pinhole density. Moreover, the hardness of such coatings increases with annealing temperature, going through a maximum at 500° C. Hoshino *et al.* [5] have attributed the increase in the hardenss of these coatings to the formation and growth of chromium crystallites up to 500° C, and reduction thereafter to chromium carbide formation. In this paper we report our results on similar coatings.

It has been observed that the properties of the chrome platings are essentially similar to those of Hishino *et al.*, however, the use of glancing angle X-ray diffraction analysis throws more light on the nature of these films. Chromium carbide is observed on the surface of annealed samples which explains increases in hardness with annealing, as discussed below,

2. Experimental procedure

The chromium deposits were obtained on mild steel substrates by the method described by Hoshino *et al.* The optimized set of deposition conditions is summarized in Table I. The depositions have been repeated several times and are found to have very good reproducibility as far as rate of deposition, brightness, structure and hardnesss are concerned. The samples were air annealed at various temperatures from 100° C to 800° C for one hour each.

X-ray diffraction analysis was carried out using Seeman Bohlin Geometry. CuK$_\alpha$ radiation (0.15418 nm) from a rotating anode target was used as the source. The angle of incident radiation was varied from 0.5 to 10° in order to detect the depthwise phase variation in the films.

The chemical analysis of the coatings was carried out using X-ray photoelectron spectroscopy (XPS). ESCALAB MKII system supplied by VG Scientific, U.K. was employed. AlK$_\alpha$ radiation (1486.6 eV) served as the source of X-rays and Au 4f$_{7/2}$ spectral line at 84.0 $\pm$ 0.1 eV as the reference. Depth profiling was carried out using argon ion gun operated at $\sim$5 KV and 10 μA current.

Surface morphology was investigated under Spectroscan 120 scanning electron microscope (SEM) supplied by Cambridge Instruments, U.K.

3. Results and discussion

The deposits obtained were shining white in colour. The coatings were subjected to hardness test before and after air annealing at various temperatures. As shown in Fig. 1 the hardness of these coatings increases with increase in annealing temperature up to 500° C and then starts decreasing. The hardness, in no case, was less than 1 100 VHN. This behaviour of these coatings is in agreement with that reported earlier for chrome deposits [5].

The X-ray diffraction pattern obtained from the films at various angle for different annealing temperatures is given in Fig. 2. The earlier reports on similarly deposited films point out that these deposited films are amorphous in nature. With annealing up to 500° C a crystalline chromium phase

TABLE I Deposition conditions

Cr_2O_3	100 g l^{-1}
H_2SO_4	5 ml l^{-1}
HCOOH	20 ml l^{-1}
Current density	0.4 A cm^{-2}

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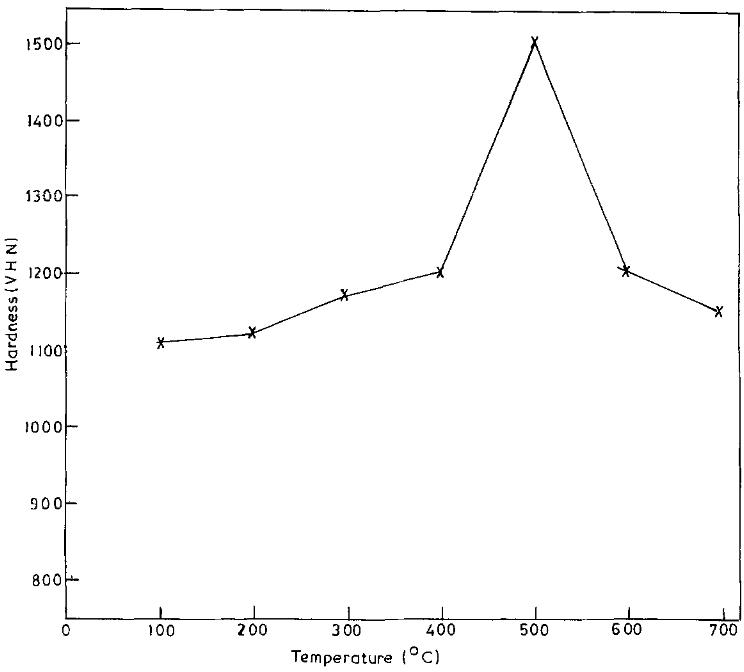


Figure 1 Hardness behaviour of chromium films with temperature.

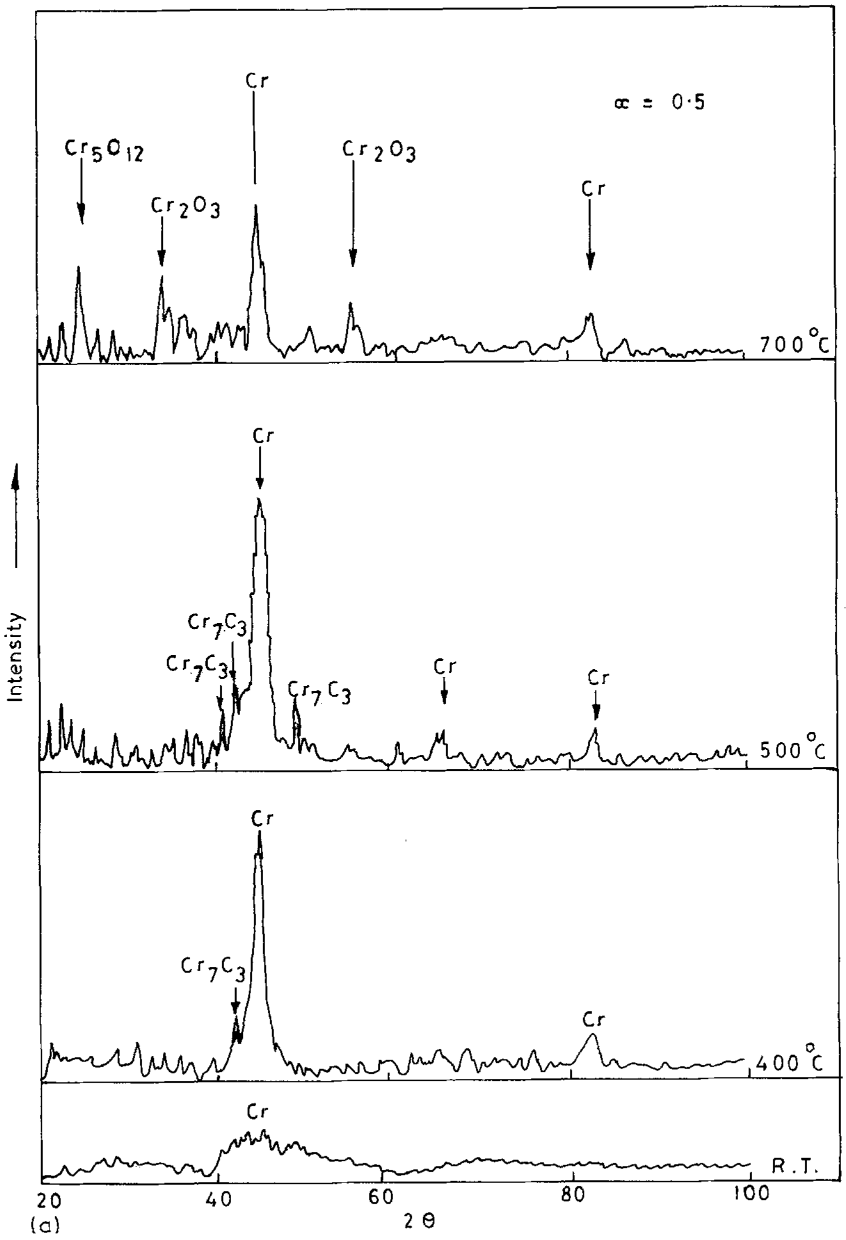


Figure 2 XRD pattern of films at different temperatures (a) grazing angle with respect to sample (α) = 0.5°, (b) α = 2°, (c) α = 10°.

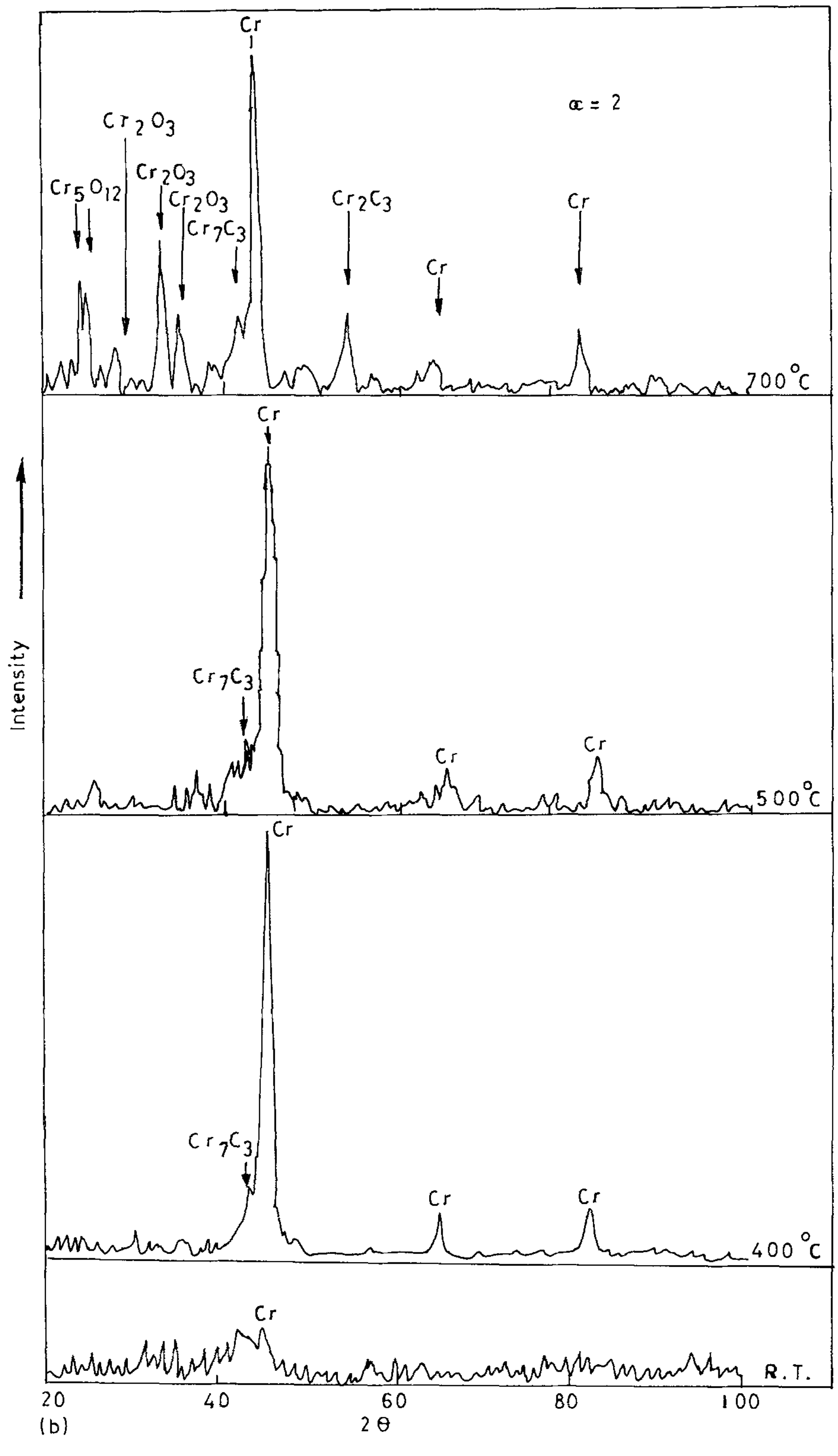


Figure 2 Continued

appears, after which Cr_7C_3 phase is detected. The increase in hardness of the chrome deposits was attributed to crystalline chromium and decrease in hardness to Cr_7C_3 phase. Use of glancing angle X-ray diffraction reveals different facts about these deposits. By varying the angle of incidence of X-rays, different depths of the sample can be probed from surface. If α is the angle of incidence with respect to the surface, the penetration depth t is given by [6]

$$t = 2\alpha u_l^{-1}$$

where u_l = linear absorption coefficient

Thus, using u_l to be 1445.5 for chromium [7], the probed depths are 1200A, for $\alpha = 0.5°$, 4800A for $\alpha = 2°$ and 2.4 μm for $\alpha = 10°$.

In agreement with earlier reports, there is a single, broad hump at $2\theta = 44°$ for as deposited films at all values of α investigated here. Annealing to 400° C converts the amorphous coating into crystalline film as is evident from sharp peaks (Fig. 2). In the surface region i.e. at $\alpha = 0.5°$ and $\alpha = 2°$, in addition to chromium, peaks corresponding to Cr_7C_3 are also present. At $\alpha = 10°$, only chromium phase dominates. For coatings annealed at 500° C this particular trend is predominant. At $\alpha = 10°$, only chromium phase is identified. Thus, at depth of 2.4 μm, which can

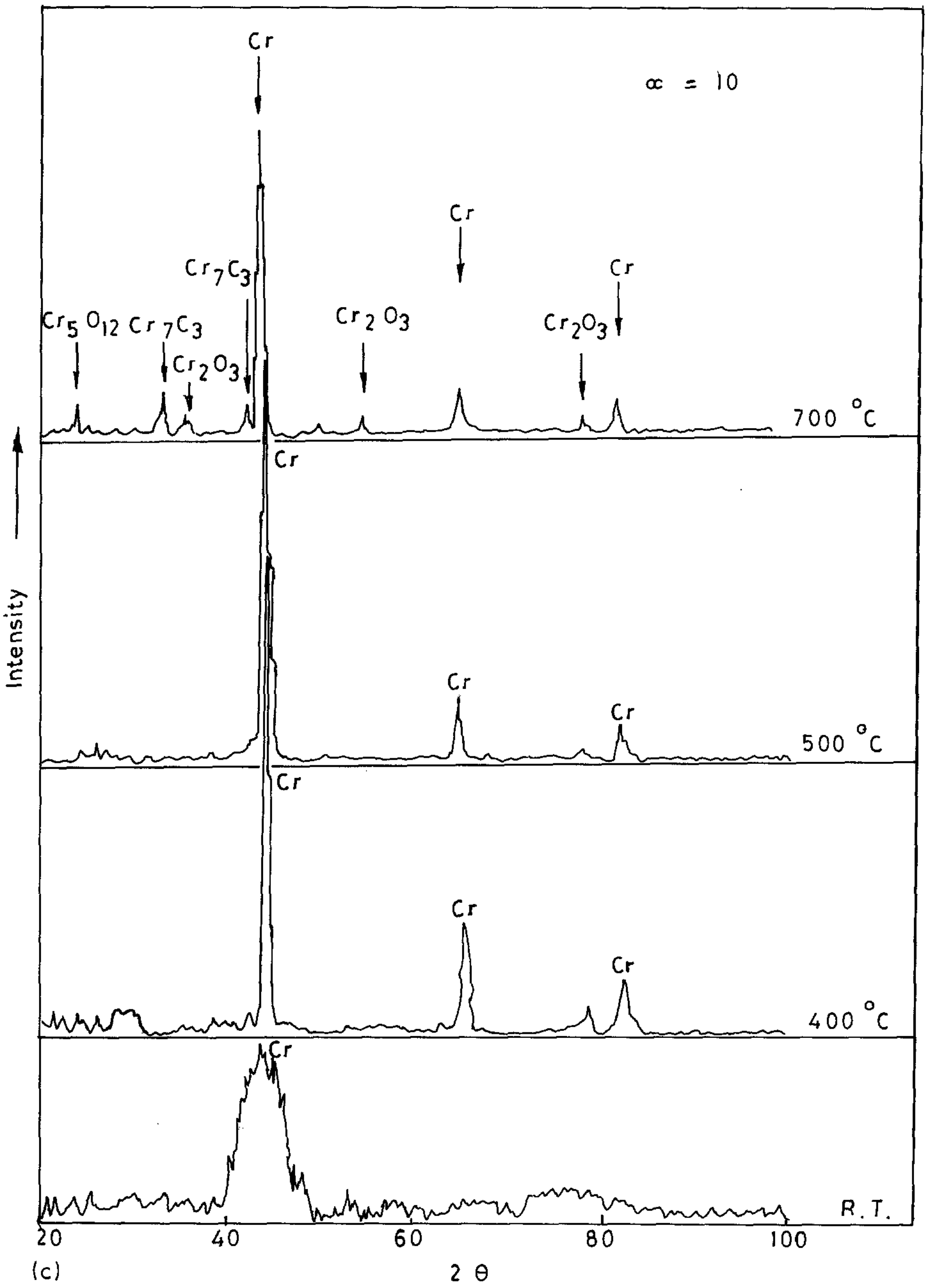


Figure 2 Continued

be treated as bulk, only chromium is present in agreement with earlier reports [5]. Hardness of the material depends to a large extent on the surface conditions. In Table II the hardness values of the chromium carbides along with the chromium metal are summarized. It is quite evident that the chromium carbide Cr_7C_3 is the hardest of all chromium carbides as well as chromium metal. The hardness of the annealed films can therefore be attributed to the presence of Cr_7C_3 phase rather than just crystalline chromium. Cr_7C_3 phase exists even at 700° as observed from Fig. 2. However the oxide phase dominates rather than the carbide one at this temperature, specially in surface region, and as discussed below, also appear cracks in the film causing reduction in hardness.

In order to shed further light on the behaviour of the films we have carried out SEM analysis of these films. The unannealed films show uniformity and are without any islands or pinholes, as shown in Fig. 3. Annealing introduces cluster formation and their size is found to increase with annealing temperature. At 400° C the islands are 1.4 μm in diameter and at 500° C they become 2.6 μm in diameter. The density of these islands also seems to have increased. These islands could be of Cr_7C_3 phase. At 700° C, cracking of the films starts which could be the reason for reduced hardness.

In order to obtain the chemical information about the surface of these air annealed films, XPS analysis is carried out. XPS and glancing angle XRD results cannot be directly correlated since the probing depths are different. XPS gives chemical state of the elements present up to about 5.0 nm. Figure 4 shows survey scan of the a deposited film. It can be observed that besides chromium, carbon, oxygen and small amounts of sulphur and nitrogen are also present.

TABLE II Reported hardness values

Material	Hardness (VHN)
$Cr_{23}C_6$	1300
Cr_7C_3	1600
Cr_3C_2	1000
Cr metal	800

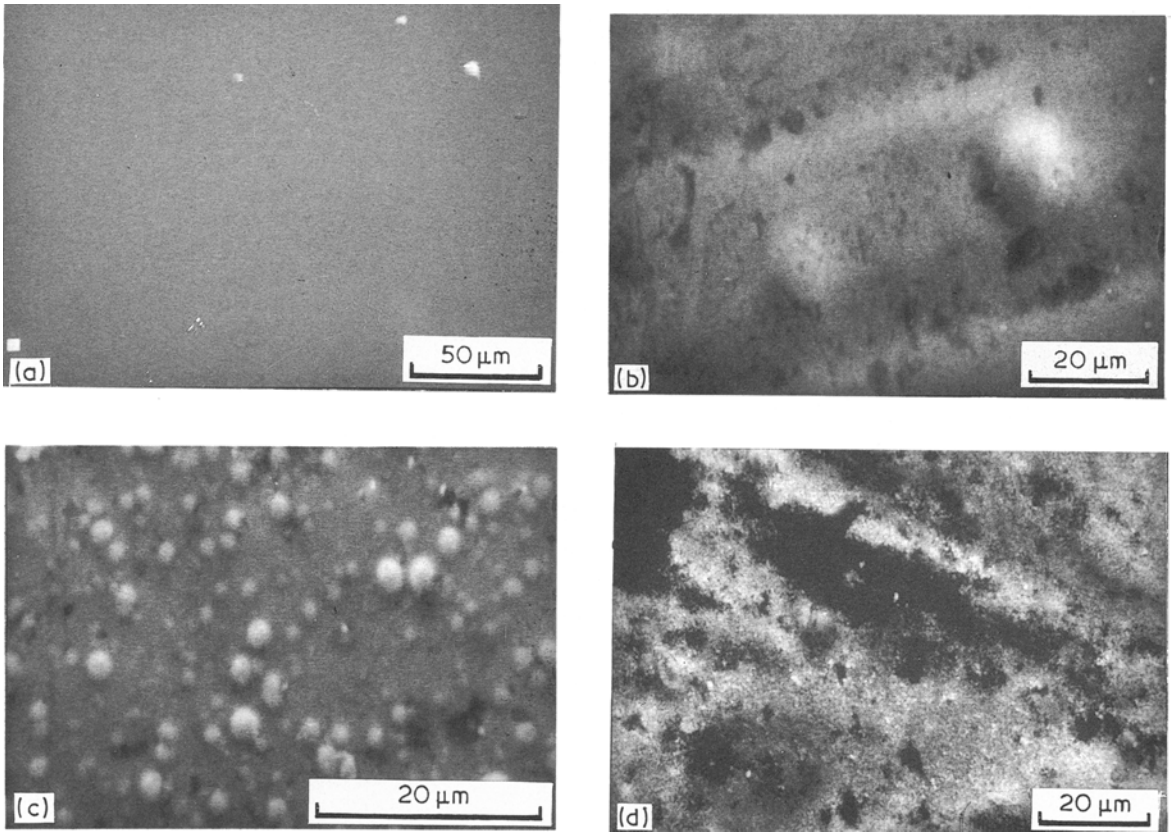


Figure 3 Scanning electron micrographs of samples (a) room temperature, (b) 400° C, (c) 500° C, (d) 700° C.

The detailed analysis indicates that for non-annealed films, Cr 2p spectrum shows two components namely, chromium (574.0 eV) and chromium oxide (576.0 eV) as shown in Fig. 5a and b. Chromium carbide peak cannot be observed distinctly as the binding energies for metallic chromium and chromium carbide are very close to each other [8]. Argon ion bombardment for 30 min removed the oxide component and left only chromium component. The samples annealed at 400° C and 500° C, show a broad peak of chromium oxide component only. Argon ion bombardment removed oxide component and only metallic chromium component is observed. Samples annealed at 700° C show only chromium oxide peak even after argon ion bombardment indicating heavy oxidation. Thus, for non-annealed as well as samples annealed at

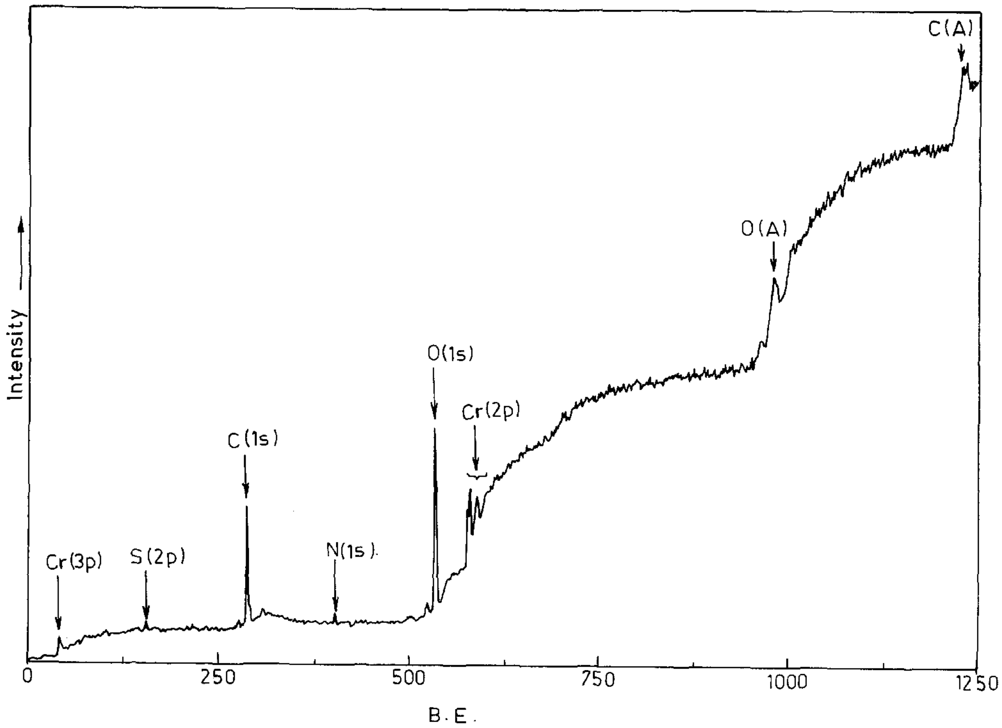


Figure 4 Survey scan of as deposited film.

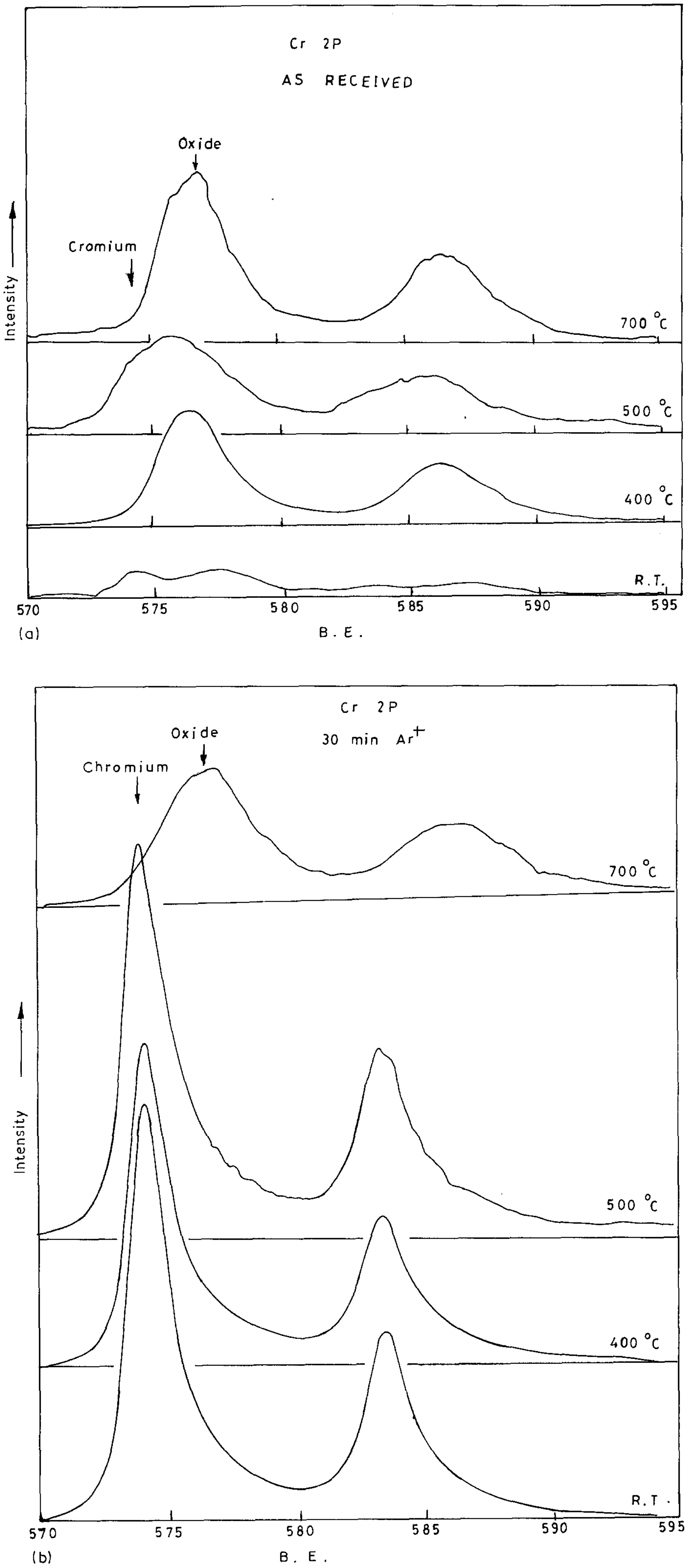
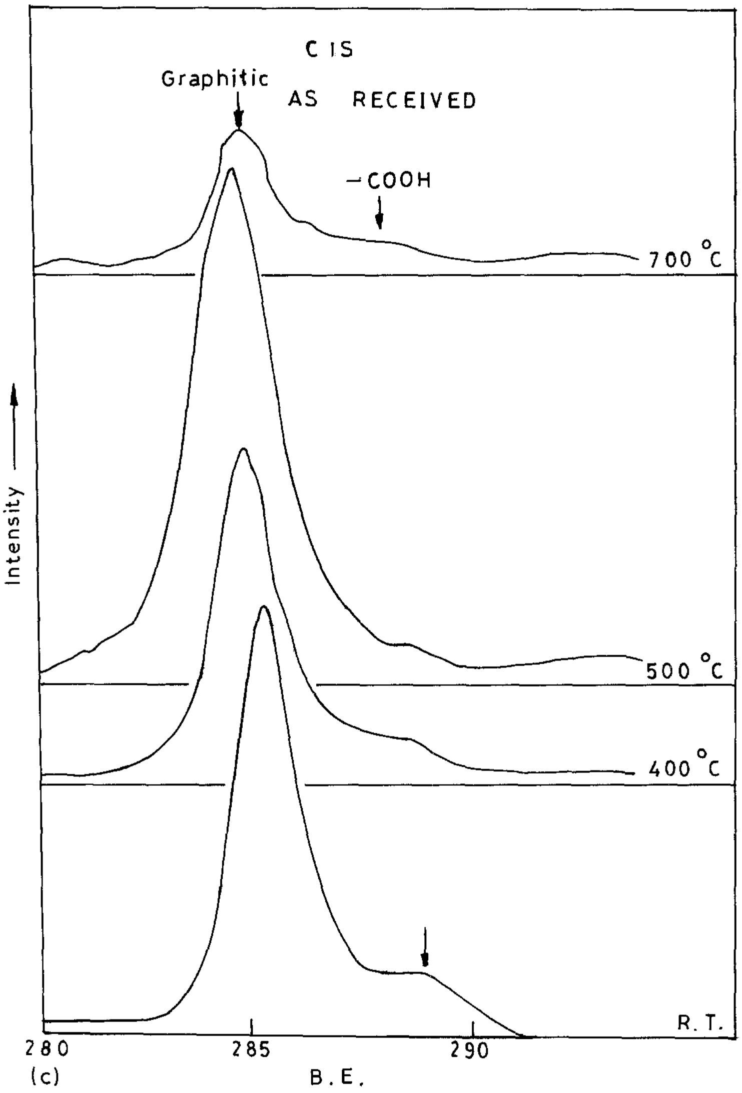
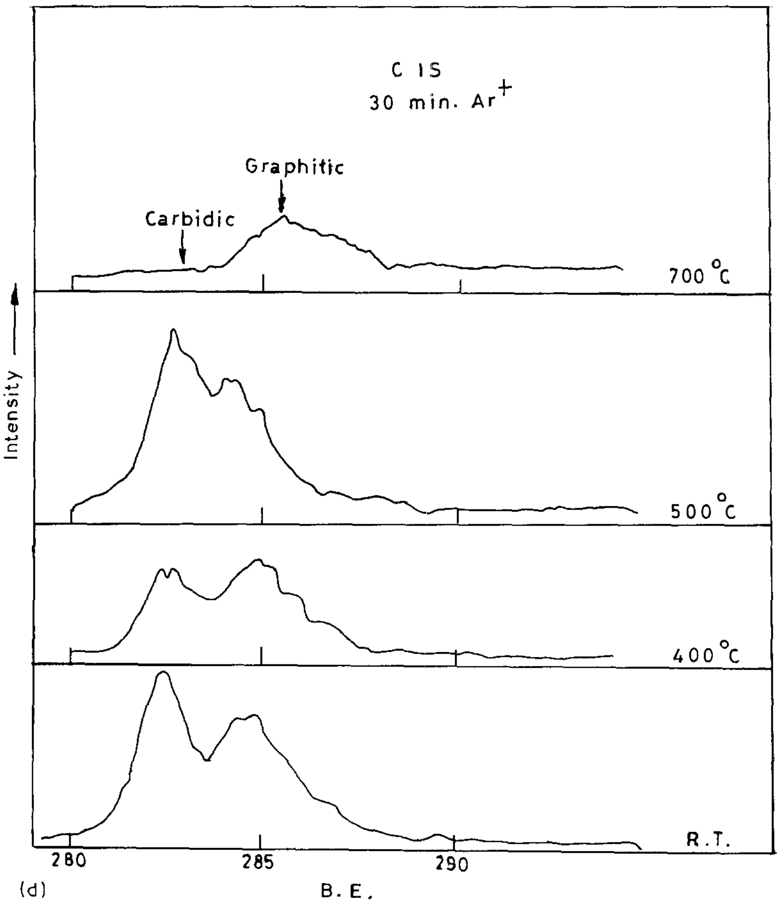


Figure 5 X-ray photoelectron spectra, (a) Cr 2p as received, (b) Cr 2p 30 min. Ar^+, (c) C ls as received, (d) C ls 30 min. Ar^+, (e) 0 ls as received, (f) 0 ls 30 min. Ar^+.

Figure 5 Continued





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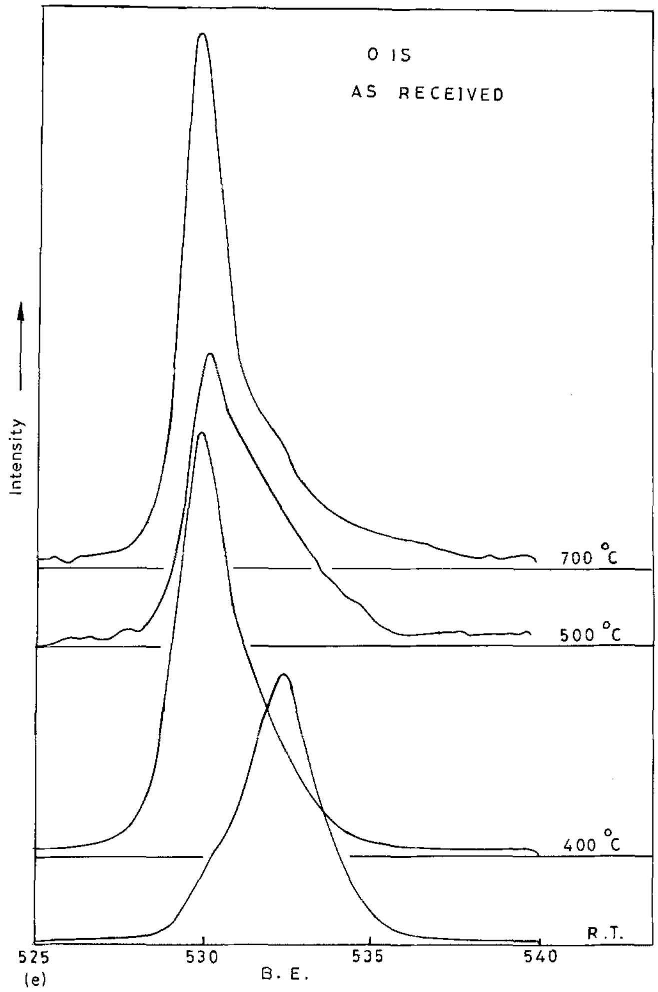

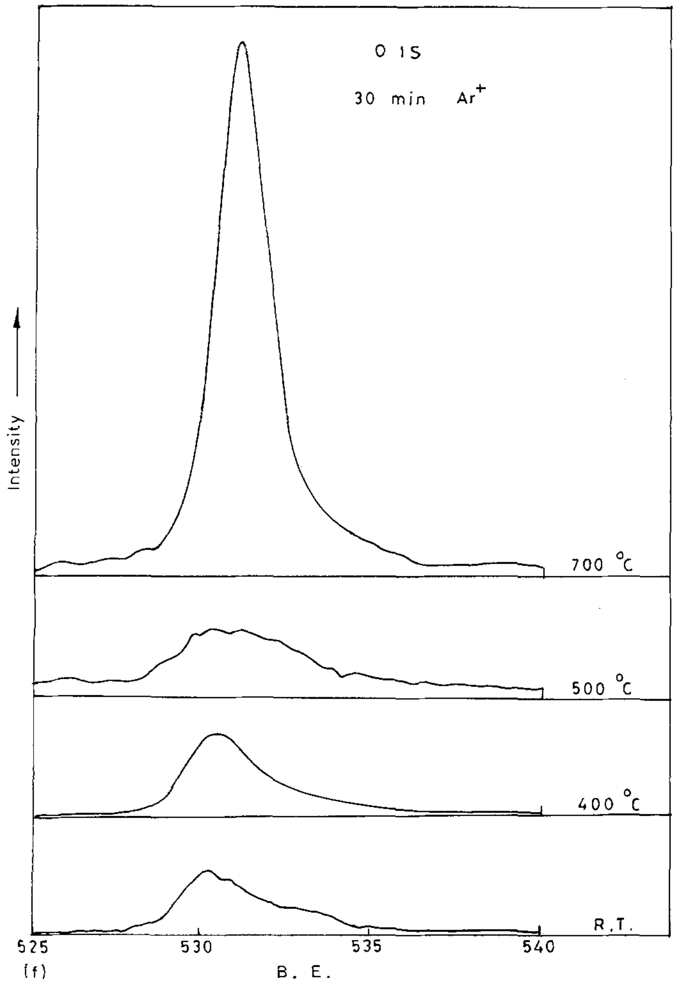

400° C and 500° C, oxide forms only on surface and decreases after argon ion bombardment whereas for sample annealed at 700° C, oxide peak intensity remains high indicating deep oxidation.

The C ls spectrum for as deposited sample shows –COOH and graphitic carbon (binding energies 289.0 eV and 285.0 eV respectively) on surface. After argon ion bombardment, carbidic and graphitic components can be observed as shown in Fig. 5c and d. Samples annealed at 400° C and 500° C also show removal of –COOH component and presence of graphitic and carbidic carbon after argon ion etching. Only graphitic carbon is observed for films annealed at 700° C.

From XRD and XPS observations it can be concluded that in non-annealed samples, chromium carbide is not ordered and after annealing, it becomes crystalline. Thus, carbide is present in surface region for non-annealed samples and crystalline carbide is present in surface region for samples annealed at 400° C and 500° C, with more percentage or carbide at less depth for 500° C, thereby increasing hardness of samples at those temperatures. At 700° C, oxide is dominant in surface region and only chromium oxide is present till depth of 120 nm. Thus oxide formation on surface together with development of cracks at 700° C explains reduction in hardness.

4. Summary

Chromium films were deposited electrochemically with an organic additive in sulphate bath. Hardness of these films goes on increasing with annealing temperature till 500° C and then decreases. Increases in hardness of the chromium films with annealing temperature with a maximum at 500° C can be explained from the fact that the hardest phase of chromium carbide (Cr_7C_3) is present to a large extent in the surface region at this temperature and hardness decreases after increasing annealing temperature to 700° C due to formation of chromium oxide and development of cracks in the film.

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