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The Grain Structure of Vacuum Arc Deposited Co Thin Films

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ABSTRACT

Co layers on Si and NaCl substrates were produced with the aid of vacuum arc deposition and studied by transmission electron microscopy and electron back-scattering diffraction (EBSD). The vacuum arc deposited coatings are formed from a multiply charged ion flux and microparticles. The Co film formed from ions consists of a hexagonal close-packed phase and possesses a dense microstructure with uniform and extremely small grains (5 nm). The Co microparticles, which solidified after collision of liquid Co droplets with the substrate, have a metastable face-centred cubic structure. The EBSD method allowed one to resolve the thin semicircular grains having a size about 100 nm in the largest droplets.

INTRODUCTION

Vacuum arc deposition technology is important for the production of materials for construction and decoration. Vacuum arc deposited coatings possess high hardness and high wear and corrosion resistance. These properties depend critically on the phase and grain structure of the coating. In this process the vacuum arc discharges in the vapour of the cathode material [1]. A flux of the multiply charged ions and microdroplets form simultaneously. Both ions and microdroplets fly with a supersonic velocity towards the substrate forming the coating layer [2]. As a result, the conditions for the formation of the microstructure of vacuum arc deposited coatings are rather complicated. Even by magnetic filtering with the aid of a quarter-torus the microdroplets cannot be eliminated completely from the flux [3]. Usually, the presence of solidified microdroplets in the deposited film is not desired. However, for some applications the presence of microparticles can be useful, increasing the deposition rate and allowing one to produce the coatings of a controllable roughness [4]. One of the most important questions in the vacuum arc deposition technology is how the difference in the condensation conditions for individual ions and liquid droplets influences the phase and grain structure of the coating. In order to answer this question we investigated the microstructure of vacuum arc deposited Co layers. Co has two allotropic modifications. Above 422°C the face-centred cubic (fcc) structure is stable. Below 422°C Co has a hexagonal close-packed (hcp) structure [5]. During solidification from the melt it is easy to undercool bulk samples of Co and Co alloys such that the fcc phase is stable at room temperature.

Therefore, we can expect that the different condensation conditions for ions and liquid droplets can result in a mixed phase structure in the coating.

EXPERIMENTAL

The vacuum arc apparatus used in this work consists of a vacuum chamber having the form of a horizontal cylinder of 700 mm diameter and 700 mm length [6]. Its pumping system consists of a Balzers turbomolecular pump with a capacity of 1500 ℓ/s and two rotary pumps with a total capacity of 40 ℓ/s. A base pressure of $6\cdot10^{-5}$ Pa was achieved before deposition. The pressure during deposition was $8\cdot10^{-4}$ Pa. The vacuum arc apparatus with the system for spot stabilization and the Co cathode are placed on the end of the cylinder, . The cathode of diameter D = 60 mm was made from Co of 99.95% purity. The facilities for magnetic filtering of the microparticles were not used in this work. The material of the anode was not consumed in the arc process. The substrates (freshly cleaved NaCl and single crystalline Si) were placed at distances of L = 175, 300 and 425 mm from the surface of the cathode. The surface of the substrates was perpendicular to the surface of the cathode. The vacuum arc source voltage was maintained constant at U = 19 V, with a discharge current I = 120 A. No bias was applied to the substrates. The coating time t was the same for all samples t = 200 s. For the transmission electron microscopy (TEM), the cobalt films were stripped from their NaCl substrates and supported on a copper grid. TEM was performed using a cold field emission instrument (HF-2000, Hitachi Ltd.) equipped with an energy dispersion X-ray analysis system (Noran Instrument Inc.). The interplanar spacings were calculated from the measured diameter of the diffraction rings, using gold thin films as a reference substance to determine the camera constant. The electron back-scattering diffraction (EBSD) method has been used by us in order to determine the orientation of individual grains in the large microparticles formed in the Co coating. The EBSD method permits one to see the microstructure of the sample and to determine the orientation of the individual grains in the same experiment. Therefore, many grains can be analysed and an overall picture of the misorientation distribution can be obtained. The EBSD patterns were measured with the aid of Hitachi S-4200 instrument. The same instrument was used for the scanning electron microscopy (SEM) of the films. The spatial resolution of this instrument in the EBSD regime is about 100 nm. We have determined the orientation of the individual grains using the integrated software package for the semi-automated fit procedure for the indexing of the EBSD patterns.

RESULTS AND DISCUSSION

Figure 1 displays the microstructure of the Co coatings for L = 175, 300 and 425 mm deposited onto Si substrate. Both droplets and the homogeneous film formed by deposition of individual ions are clearly

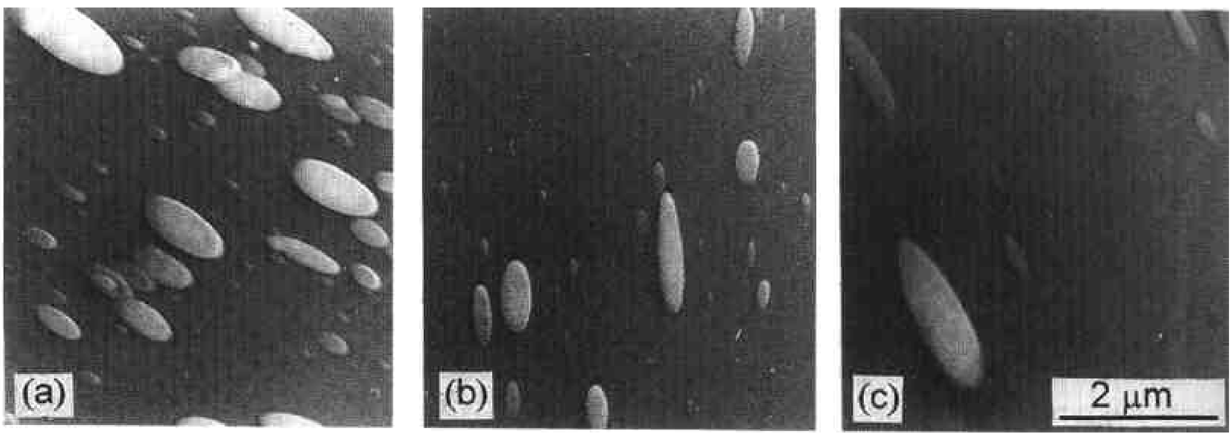

Fig. 1. SEM micrographs of the vacuum arc deposited Co layers on Si substrate at various distances L between the cathode and the substrate. I = 120 A, t = 200 s. L = 175 (**a**), 300 (**b**) and 425 mm (**c**).

seen in the micrographs. The electron diffraction patterns (EDP) from the film between particles reveal that the film is crystalline [7]. The comparison of the data for the interplanar spacings d measured from the EDPs with the tabular data for the fcc and hcp phases of Co shows that all diffraction rings present in a pattern can be identified as resulting from diffraction from the hcp phase. Some of the rings can result both from fcc and hcp phase, but no rings coming only from fcc phase are present [7]. Therefore, the deposition of individual Co ions on the substrate kept at room temperature leads to the formation of a film having a hcp structure which is thermodynamically stable below 422°C. A high magnification bright field TEM micrograph (not shown) reveals that the film between the particles is dense and uniformly thick [7]. The grain structure is uniform and the mean grain size is very small, about 5 nm.

The substrates were positioned perpendicular to the cathode surface. Therefore, the particles are elongated in the direction parallel to the axis of the vacuum chamber. The length-to-width ratio (aspect ratio) increases with increasing L from 2.2 (L = 175 mm) to 3.2 (L = 425 mm). The mean length a increases from 0.88 μm (L = 175 mm) to 0.99 μm (L = 425 mm). The mean width b decreases from 0.38 μm (L = 175 mm) to 0.29 μm (L = 425 mm). The fraction of substrate area covered by particles $\Sigma S_p/S_t$ decreases with increasing L (Fig. 2). Therefore, the particles gradually disappear from the flux by flying from the cathode. By collision with the substrate, the liquid microdroplets spread over the surface and solidify in a process analogous to the "splat cooling". As a result, the solidified microparticles are rather flat. Their height can be estimated from the SEM picture (Fig. 4) made for the EBSD measurements under a low incidence angle (about 20°). The EBSD pattern for the individual grain in a flat solidified Co droplet is shown in Fig. 3 together with the results of the identification of the crystallographic orientation. It was possible to resolve the individual grains with the aid of EBSD only for the biggest droplets, having a length and width about 10 to 20 times larger than the coresponding mean values a and b . Figure 4 represents such a droplet. The cross marks the position for the pattern represented in Fig. 3. Figure 5 displays the grain chart constructed with the aid of the EBSD data. The area represented in Fig. 5 is marked with a rectangle on the micrograph (Fig. 4). The patterns analogous to Fig. 3 were measured with a step of 100 nm. Each point in Fig. 5 represents one measurement. For each pair of neighbouring points the mutual misorientation was calculated. Two points were identified as belonging to different grains if their misorientation was above 3°. The smaller misorientation differences are represented in Fig. 5 as variations of the grey scale. The grains in the droplet have a semicircular form reproducing the outer form of the droplet. They can represent the solidification steps after the collision of the droplet with the substrate.

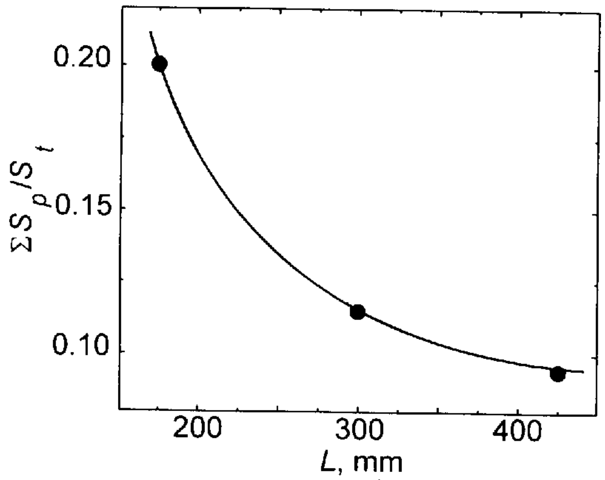

Fig. 2. The dependence of the fraction of the substrate area covered by particles $\Sigma S_p/S_t$ on L

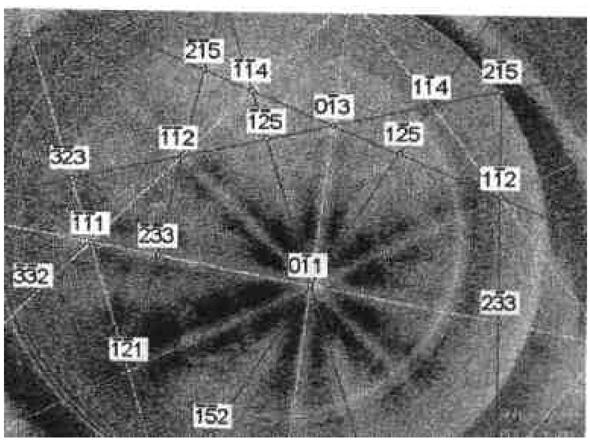

Fig. 3. EBSD pattern for the individual Co grain marked by a cross in the Fig. 4

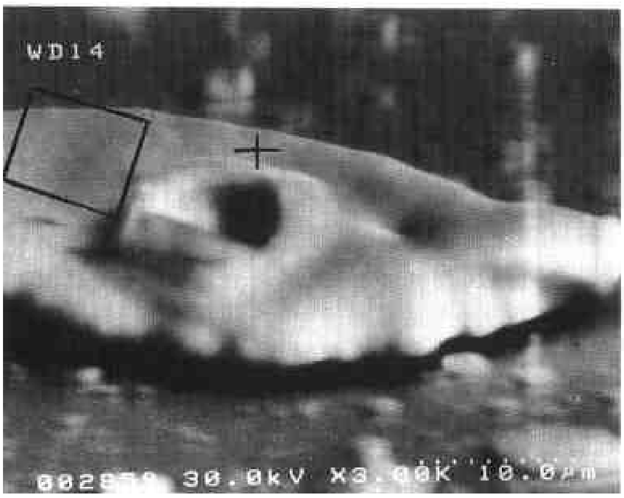

Fig. 4. SEM micrograph under a low incidence angle showing the analyzed Co microparticle

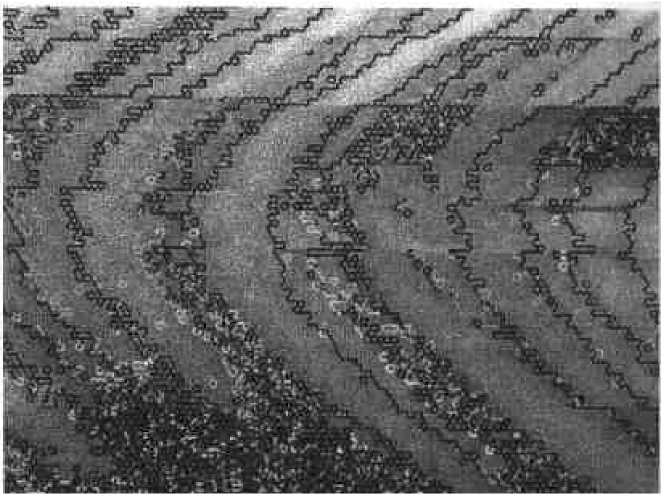

Fig. 5. Grain structure of the rectangle marked in Fig. 4 revealed with the aid of EBSD

Recently, it was shown that the smallest droplets are an integral part of a vacuum arc deposited coating having the same grain structure as the surrounding film [8]. Here another extreme case was analysed. The biggest droplets in a Co coating, possessing rather large fcc grains, are surrounded by nanosized grains of the film having a hcp structure. These data show that the question of the integrity of the grain structure of the medium-sized droplets in vacuum arc deposited coatings should be carefully studied.

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