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Morphology of Mo particles and their incorporation into the growing film during vacuum arc deposition

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Abstract

Vacuum arc deposition opens the possibility to alter the surface of the substrate and growing film with the aid of a combined flux of multiply charged ions and microparticles. This plasma flux meets the substrate with a supersonic velocity. Therefore, the result of the interaction between the plasma and substrate, for instance the morphology of the microparticles sticking to the substrate, depends strongly on the angle between the substrate and cathode surfaces. Mo layers have been deposited on Cu and silica glass substrates by vacuum arc deposition. The targets of high-purity Mo have been produced by high-vacuum electron-beam multiple melting in specially designed water-cooled copper molds. The morphology of the microparticles on the film surface is investigated by means of quantitative metallography. A strong influence of the substrate position on the plasma flow is observed. The distributions of particle sizes, aspect ratios and angles between the axes of the cathode and elliptic particles have been studied as functions of the deposition time, current and distance from the cathode. While increasing the deposition time particles were continuously incorporated into the film disappearing from the surface.

1. Introduction

Studies of vacuum arc discharge were started in the 60s [1–3]. The first successful applications of vacuum arc are were developed in the 70s (e.g. titanium nitride coatings for the enhancement of the tribilogical characteristics of machining tools) [4–6]. Later the technologies for vacuum arc deposition of diamond-like coatings were developed, particularly for nuclear applications [7,8]. Vacuum arc deposition being a very promising technology evokes the growing interest of numerous researchers [9,10]. The peculiarity of vacuum arc deposition most important for its application is the possibility for changing the properties of the substrate surface and growing film with the aid of a combined flux of multiple charged ions and microparticles. It is widely believed that microparticles have a deteriorating effect on the properties of the deposited layers [8–10]. Therefore, numerous efforts have been made to develop of different methods for filtering the microparticles. However, in many applications the roughness of the film caused by the incorporated microparticles has either no effect or can be even useful. In any case the formation of microparticles and their distribution on the substrate should be studied more thoroughly.

The only work in which the geometry of the microparticles was studied is devoted to carbon coatings [11]. It was shown that the formation of microdroplets in liquid metal ion sources (LMIS) is strongly material dependent [12,13]. The same should also be true for the formation of liquid droplets in the vacuum arc spot. Therefore, the investigation of other materials, especially refractory metals, not studied in the LMIS experiments is very important. The plasma flux developed during vacuum arc deposition meets the substrate with a supersonic velocity. Therefore, the result of the interaction between the plasma flux and the substrate, for instance the morphology of the microparticles sticking to the substrate, should depend strongly on the angle between the substrate and the cathode surfaces. Only the case of normal incidence was considered in Ref. [11]. Recently we have studied the vacuum arc deposition of Mo and have observed that the deposition rate R_d depends strongly on the angle between the cathode surface and the substrate θ, the current I, and the distance between the cathode and the substrate L [14]. The droplet geometry should also depend on these parameters.

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2. Experimental

Mo coatings have been deposited onto polished copper and silica glass substrates in a vacuum arc apparatus described elsewhere [15]. 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. The pressure during deposition was 8×10^{-4} Pa. The horizontal cylindrical vacuum chamber was 700 mm in diameter and 500 mm length. On one end of this cylinder the vacuum arc apparatus with a magnetic system for spot stabilization and the Mo cathode are placed. The cathode of diameter $D = 60$ mm was made of 99.95% Mo. It was produced by high-vacuum electron-beam multiple melting in specially designed water-cooled copper molds [16]. The facilities for magnetic filtering of macroparticles were not used in this study. The polished Cu and silica glass substrates were placed at different distances L from the surface of the cathode ($L = 50$, 175, 300 and 425 mm). For each distance two substrates were positioned, one substrate parallel ($\theta = 0°$) and one perpendicular ($\theta = 90°$) to the plasma flow coming axially from the cathode (θ is the angle between the direction of plasma flow and the surface of substrate). The vacuum arc source voltage was constant ($U = 31$ V), and the discharge current I was varied from 80 to 180 A. The strength of the stabilizing magnetic field on the cathode surface ranged from 60 to 70 G. No bias was applied to the substrates. The coating time t was varied from 5 to 40 min. In order to avoid an overheating of the substrates the coating process was interrupted (in vacuum) every 2.5 min for 2.5 to 3 min. The sizes of the microparticles were measured with the aid of a scanning electron microscope (JEOL 6400) and a Zeiss Axiophot optical microscope possessing contrast accessories which allow a resolution as low as 0.2 to 0.4 μm. The area S occupied by individual particles was determined to be $S = \pi r^2$ for round particles and $S = \pi ab/4$ for elliptical particles, where a and b are the axes of the ellipse. The fractional coverage, $\Sigma S/S_t$, was determined to be the ratio of the total area of all particles counted, ΣS, to the total projected area on the substrate for all analysed rectangles S_t ($S_t = nS_c$, where S_c is the square of one counting area, typically 2444 μm^2, and n is the number of rectangles counted; n was typically about 500).

3. Results and discussion

The number, morphology and orientation of the microparticles deposited on the substrate are controlled by (a)

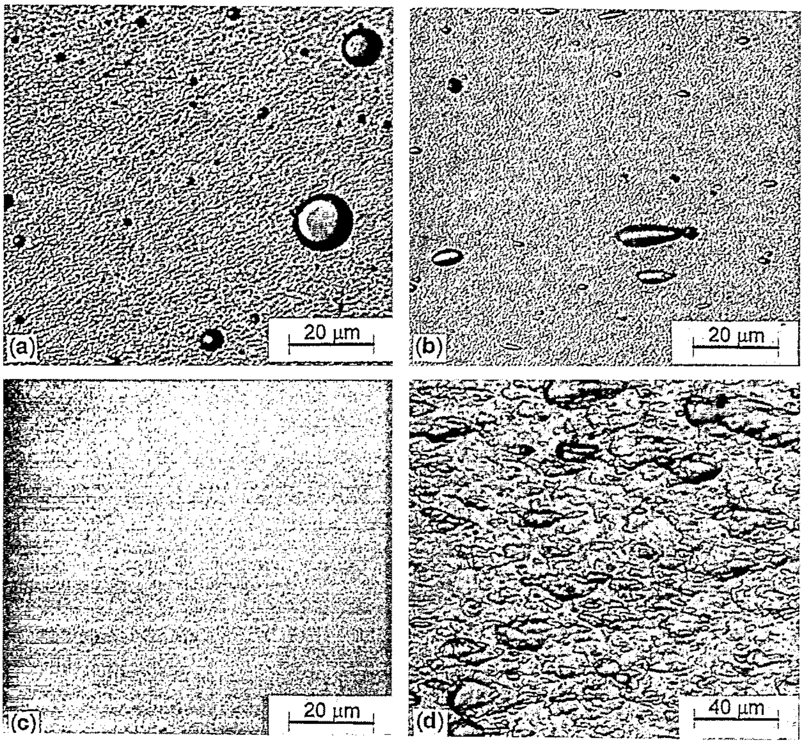

Fig. 1. Optical micrographs of the microstructure of Mo coatings. (a) Mo/glass, $\theta = 90°$, $I = 100$ A, $L = 50$ mm, $t = 5$ min, (b) Mo/glass, $\theta = 0°$, $I = 80$ A, $L = 50$ mm, $t = 5$ min, (c) Mo/glass, $\theta = 0°$, $I = 100$ A, $L = 175$ mm, $t = 5$ min, (d) Mo/Cu, $\theta = 0°$, $I = 180$ A, $L = 50$ mm, $t = 40$ min.

the processes of their formation on the cathode in the vacuum arc spot, (b) the conditions of their flight in the electromagnetic field close to the source, (c) the conditions of their flight in the supersonic plasma flow close to the substrate and the collisions with the substrate. Fig. 1a and Fig. 1b show the morphology of microdroplets on the substrates positioned perpendicular (Fig. 1a) and parallel (Fig. 1b) to the plasma flow coming from the cathode. In the first case all droplets on the substrate are round. In the second case they have the form of ellipses elongated in the direction of flight. The long axes of all droplets are nearly parallel to each other (the mean square spread is lower than 1° and is not influenced by the discharge current I). The aspect ratio $R_a = a/b$ of microparticles close to the cathode ($L = 50$ mm) is nearly independent on the discharge current and is about 2.5 (see Fig. 1b and Fig. 1d for $I = 80$ and 180 A, respectively). This relative low value of R_a is remarkable. Though the substrates are parallel to the plasma flow, the droplets collide with the substrates at rather high collision angles γ. For the substrates perpendicular to the plasma flow obviously $\gamma = 90°$ (Fig. 1a). It is interesting that with increasing distance from the cathode L the elliptical particles completely disappear (Fig. 1c). $R_a = 1$ for substrates both parallel and perpendicular to the plasma flow already at $L = 175$ mm.

Close to the cathode ($L = 50$ mm) the mean diameter, d, of round particles on the substrates positioned perpendicular to the plasma flow ($\theta = 90°$) is lower than the mean value of a for elliptical particles on the substrates positioned parallel to the plasma flow ($\theta = 0°$). At $L > 50$ mm all particles are round but in this case d for $\theta = 90°$ is also higher than for $\theta = 0°$. With increasing L the mean diameter of the particles becomes smaller. d decreases to the greatest degree between $L = 50$ and 175 mm (see Fig. 1c with Fig. 1a, Fig. 1b and Fig. 1d). The fractional coverage, $\Sigma S/S_t$, also decreases with increasing L (Fig. 2). Close to the cathode ($L = 50$ mm) $\Sigma S/S_t$ is higher for the substrates positioned perpendicular to the plasma flow. At $L > 50$ mm this difference disappears and the values of $\Sigma S/S_t$ become rather low (about 10^{-3} to 10^{-4}). The coatings at $L > 50$ mm are almost free of particles (Fig. 1c).

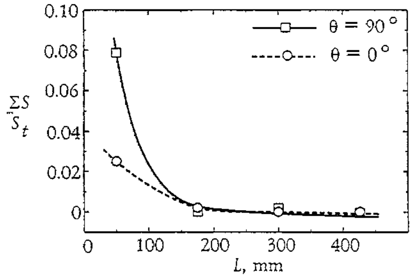

Fig. 2. Dependence of the fractional coverage, $\Sigma S/S_t$, on the distance between the cathode and substrate L for $\theta = 0°$ and 90° (Mo/glass, $I = 100$ A, $t = 5$ min).

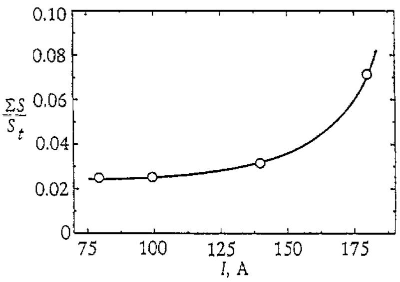

Fig. 3. Dependence of the fractional coverage, $\Sigma S/S_t$, on the discharge current I (Mo/glass, $\theta = 0°$, $L = 50$ mm, $t = 5$ min).

With increasing discharge current I the sizes of the microparticles formed (a, b and d at low L and d at high L) also increase, though R_a is nearly constant for different values of I. Therefore, the sizes of the particles are controlled by their formation process in the arc spot, while their form in the coating is controlled by the conditions in the plasma flow close to the substrate. Consequently, these conditions are nearly independent on the discharge current. $\Sigma S/S_t$ increases nonlinearly with increasing I (Fig. 3). The most important increase of $\Sigma S/S_t$ (from 0.03 to 0.07) occurs at high currents (between 140 and 180 A). At low deposition times t the particles cover only a minor part of the substrate surface (0.02 to 0.07 even at $L = 50$ mm) and do not overlap. With increasing deposition time, the particles are gradually incorporated into the coating, overlap each other and loose their "individuality", especially close to the cathode (compare Fig. 1b and Fig. 1d). Because of this, the measurement of the sizes of individual particles was possible only for $t = 5$ min. From the extrapolation the total area of the substrate can be covered with particles after about 1 h (at $I = 180$ A and $L = 50$ mm).

The size of the carbon particles in the vacuum arc deposited coatings (0.26 to 1.1 μm) obtained at $L/D = 5.9$ [11] is comparable with the results of our experiments: sizes of the Mo particles are 0.7 to 1.8 μm for $L/D = 0.83$. The number density of the Mo particles in the case of normal incidence (0.02 for $L/D = 0.83$ and 0.002 for $L/D = 6.7$) is much lower than that for carbon (0.03 to 0.08 for $L/D = 5.9$ [11]).

4. Conclusions

The important technological advantage of vacuum arc deposition in comparison to magnetron sputtering is the relatively slow decrease of the deposition rate with increasing distance between the cathode and the substrate L [14,15]. In this work, it has been shown that the coatings are almost free of microparticles even without filtering at values of L/D as low as 2.9, the ratio of the distance from the cathode to the cathode diameter. At this distance the deposition rate for vacuum arc deposition is much higher than in the case of magnetron sputtering for a comparable L/D ratio and discharge power [15]. It is also shown that the particles incorporate into the growing coating with increasing deposition time. The geometry of the particles and the total area covered by the particles can be controlled by varying deposition parameters, such as the deposition time, the discharge current, the distance from the cathode and the angle between the cathode and substrate surfaces.

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