Vacuum arc deposition of Mo films

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Mo coatings on Cu substrates were deposited with the aid of an unfiltered vacuum arc at a deposition voltage of 31 V. Dependencies of the deposition rate R_d on the discharge current I (in the interval from 80 to 180 A) and the distance L between the cathode and substrate were investigated. R_d increases monotonically with increasing I and decreases with increasing L. If the substrate is parallel to the cathode surface, R_d is much higher than it is for substrates which are perpendicular to the cathode surface. R_d values as high as 15 nm/s were reached. The reasons for this behavior are analyzed. It is also shown that Mo macroparticles are well incorporated into the coating building an integral part of it.

I. INTRODUCTION

Vacuum arc deposition begins to attract more and more attention as an effective technology for the deposition of high-quality films of metals, alloys, carbon (amorphous diamond) and compounds.[1,2] The investigations of the erosion products in vacuum arc discharge were first conducted in the 1960s by Cobine and Wanderslice[3] and Plyuto *et al.*[4] Afterwards the erosion of the copper cathode was studied by Daadler.[5] Later, technological applications of the vacuum arc deposition were developed.[6–12] The first successful technological application was the deposition of titanium nitride coatings for the enhancement of the tribilogical characteristics of machining instruments.[13–18]

The generation characteristics and deposition rate R_d of vacuum arc deposition differ from the corresponding parameters of the magnetron sputter deposition.[19–21] The reason for this is the difference in the physical processes occurring during the deposition. During the vacuum arc deposition the cathode material transforms from the solid state via liquid and dense, equilibrium nonideal plasma phases into a nonequlilibrium, expanding plasma.[22] This process (evaporation with simultaneous ionization) should not be confused with the cathode sputtering during magnetron deposition or with the simple evaporation in vapor deposition. The vacuum arc is in principle a low voltage discharge (12–40 V), whereas magnetron discharge proceeds typically at voltages of about 400–500 V. Magnetron sputtering needs the addition of a sputter gas. The vacuum arc discharge proceeds in the vapor of the cathode material itself. The addition of a reactive gas is required only in the case of the formation of nitrides, oxides, or similar coatings. The absence of a reactive gas in the chamber permits a higher purity of vacuum arc deposited coatings, in comparison with the magnetron sputter deposition under comparable conditions. The characteristics of the vacuum arc discharge during the reactive deposition depend only slightly on the composition of the reactive gas. This is another advantage of this process in comparison with the magnetron sputter deposition. During the vacuum arc deposition the cathode material is transported to a substrate in a highly ionized state.[23,24] These charged particles have high energy (some tens eV in the order of magnitude).[4] The most important disadvantage of the vacuum arc deposition is the contamination of the plasma with macroparticles. However, this problem can be avoided by using magnetic filters; therefore the vacuum arc deposition can be also applied in coatings production for optics and electronics.

Though many works were devoted to studies on the vacuum arc discharge and characteristics of the plasma, there are only a few studies on the technological parameters of the vacuum arc deposition. Due to the above noted differences between the vacuum arc deposition and the magnetron sputter deposition, in some circumstances the first method can be more effective. Therefore, its technological characteristics should be thoroughly studied, particularly the deposition rate R_d for different coatings and the dependencies of R_d on the discharge current I, the distance from the sputtering cathode L, and the orientation in respect to the cathode surface.

The properties of molybdenum, particularly its high melting temperature, low diffusivity and resistance in sulfur-containing environments,[25] determine a broad field of its potential application in form of thin films and coatings. However, the deposition of such coatings of refractory metals is a large technical problem. The most important trouble is the modest deposition rate for Mo which can be achieved with the aid of magnetron sputter or chemical vapor deposition.[26,27] On the other hand, it is known that the vacuum arc deposition permits one to achieve Mo coatings up to about 12 μm thick in a technologically allowable time.[28] Therefore the technological parameters for the

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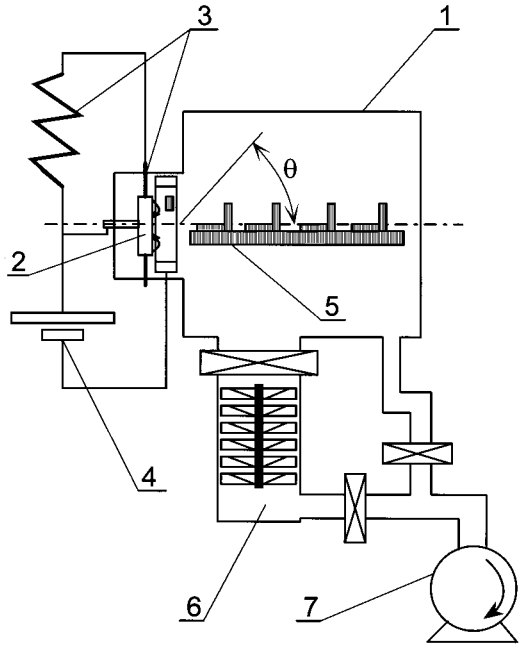

FIG. 1. Scheme of the apparatus for the vacuum arc deposition. (1) vacuum chamber, (2) cathode, (3) system for initiation of discharge, (4) power supply, (5) fixators for substrates, (6) turbomolecular pump, and (7) rotary pumps.

vacuum arc deposition of Mo coatings should be investigated.

II. EXPERIMENT

In Fig. 1 the scheme is shown of the apparatus by which Mo coatings were produced with the aid of the vacuum arc deposition. Its pumping system consists of a Balzers turbomolecular pump with a capacity of 1500 ℓ/s and two rotary pumps with at total capacity of 40 ℓ/s. A total pressure of 6×10^{-5} Pa may be achieved without deposition process. The pressure during deposition is 8×10^{-4} Pa. The vacuum chamber has the form of a horizontal cylinder of 700 mm diam and 500 mm length. The vacuum arc apparatus with the magnetic system for spot stabilization and the Mo cathodes are placed on the end of this cylinder. The cathodes of 60 mm diameter was made from Mo of 99.95% purity. The facilities for magnetic filtering of the macroparticles were not used in this work.

The polished substrates made from 99.99% Cu with dimensions of 20×20 mm^2 were placed at different distances L from the surface of the cathode ($L=50$, 175, 300, and 425 mm). At each distance, two substrates were positioned: one substrate parallel and one perpendicular to the surface of the cathode. A part of each substrate was protected with a mask. On the edge of the mask the step was formed for measurement of the coating thickness.

The vacuum arc source voltage was constant $U=31$ V and the discharge current I was changed ($I=80$, 100, 140, and 180 A). The strength of the stabilizing magnetic field on the cathode surface was 60–70 G. No bias was applied to the substrates. The coating time t was changed ($t=5$, 10, 20, and 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.

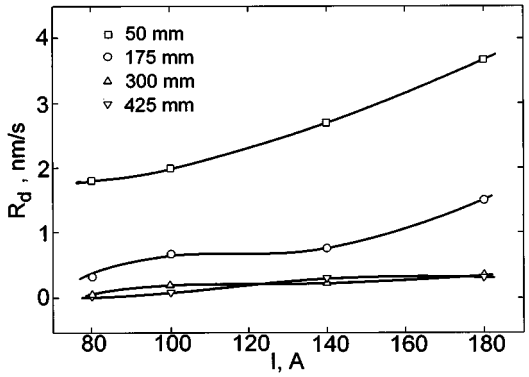

FIG. 2. Dependencies of the deposition rate R_d on the discharge current I for four different distances L for the substrates positioned perpendicular to the cathode surface.

The thickness of the coatings d was measured with the aid of a profilometer and an optical microscope. With the aid of a Polystep profilometer the height of a step was measured between the coated and protected halves of the substrate with an accuracy of 5 nm. The thickness of coatings with $d>1$ μm was additionally measured with the aid of an Axiophot optical microscope.

III. RESULTS AND DISCUSSION

Figure 2 shows the dependencies of the deposition rate R_d on the discharge current I for four different distances L of substrates positioned perpendicular to the cathode surface. The R_d values were determined for coatings in the thickness range from 50 nm to 7.5 μm. The deposition rate increases monotonically with increasing discharge current. Close to the cathode this increase is most pronounced. In Fig. 3 the dependencies are shown of the deposition rate R_d on the distance L for four different values of the discharge current I for substrates positioned perpendicular to the cathode surface. The deposition rate decreases monotonically with increasing distance from the cathode surface. This decrease is also most pronounced close to the cathode.

The data of Figs. 2 and 3 show that at the distance L close to the cathode diameter ($D=60$ mm) the deposition rate measured on the substrates positioned perpendicular to the cathode surface is close to the R_d values for the magnetron sputter deposition of Mo coatings.[19,26] In case of magnetron sputter deposition, R_d decreases very fast with increasing L. For example,[19] R_d decreases about two times by increasing L from 0.7 D to 1.5 D. In our case, R_d decreases in the same interval of L/D only at about 30%. Far from the cathode R_d decreases with increasing L even more slowly: by changing L from D to 7 D, R_d decreases only about 10 times. This makes the vacuum arc deposition very attractive for the coating of three-dimensional parts having a complex form.

In Fig. 4 the morphology of Mo film is shown deposited on the substrate perpendicular to the cathode surface ($L=50$

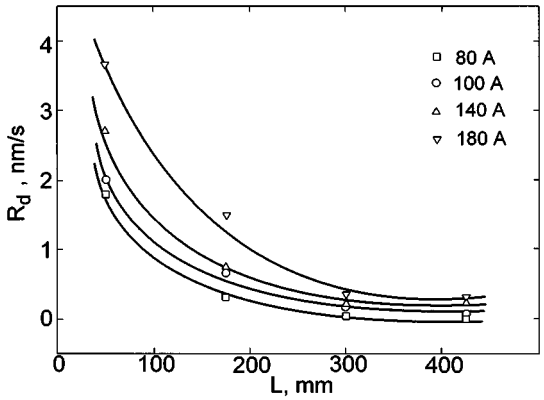

FIG. 3. Dependencies of the deposition rate R_d on the distance L for four different values of the discharge current I for substrates positioned perpendicular to the cathode surface.

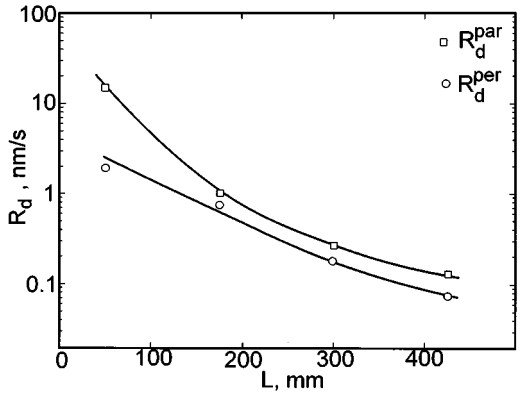

FIG. 5. Dependencies of the deposition rate R_d on distance L for $I=100$ A for the substrates positioned perpendicular and parallel to the cathode surface.

mm, $I=180$ A, deposition time 40 min). The surface of the coating is uniformly rough. It can be seen that macroparticles were gradually incorporated into the coating building an integral part of it.

Figure 5 shows the dependencies of the deposition rate R_d on the distance L for $I=100$ A for substrates positioned perpendicular and parallel to the cathode surface. At all distances R_d^{par} for substrates positioned parallel to the cathode surface is higher then R_d^{per} for perpendicular substrates. Close to the cathode ($L=50$ mm, $L/D=0.83$) the ratio $R_d^{par}/R_d^{per} \approx 6$. This difference can be understood if we consider the special features of the vacuum arc plasma. One of the important differences from the more usual gaseous plasma is that the vacuum arc plasma flow velocity ν is about 2×10^{-4} m/s and is thus supersonic with respect to the ion sound speed.[1] The average ion particle flux to the upstream substrate surface can be described as

$$J_i = n_i \nu \cos\theta, \tag{1}$$

where n_i denotes the total ion density (for all charge states) at the boundary between the plasma and ion matrix sheath built close to substrate, and θ is the angle between the plasma flow direction and the substrate surface normal (see Fig. 1).[1] Equation (1) does not describe J_i correctly for θ values close to or larger than 90°. For $\theta=90°$ (for pure deposition, e.g., without substrate bias) the ion flux is[1]

$$J_i = n_i (8kT_e/\pi m_i)^{1/2}/4Ze, \tag{2}$$

where m_i denotes the mass of ions, Z is the mean ion charge, T_e is the electron temperature in plasma, and e is the electron charge. The ratio of the deposition rates can therefore be described as

$$R_d^{par}/R_d^{per} = 4Ze\nu/[8kt_e/\pi m_i)^{1/2}]. \tag{3}$$

According to Eq. (3) the decrease of R_d^{par}/R_d^{per} with increasing L is likely to be due to the decrease of the plasma flow velocity along the axis of the vacuum chamber.

Therefore, we have shown that the deposition rate of Mo coatings with the aid of vacuum arc, can be higher than in case of magnetron sputtering and decreases slower with increasing distance from the cathode. Dense coatings of uniform roughness with well incorporated macroparticles can be produced. Due to the facts that the vacuum arc burns in the vapor of the cathode material itself, and that the reactive gas in the chamber, which is the most important source of contamination during the deposition, can be excluded, a higher purity of the vacuum arc deposited coatings in comparison with the magnetron sputter deposition can be reached.

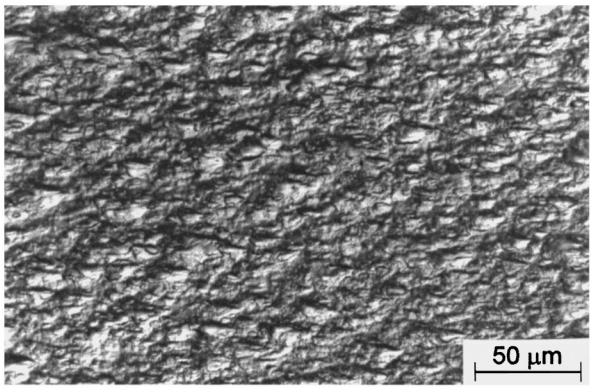

FIG. 4. Optical micrograph of the Mo film deposited on the substrate perpendicular to the cathode surface ($L=50$ mm, $I=180$ A, deposition time=40 min).

ACKNOWLEDGMENT

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