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Stable and metastable phases in the vacuum arc deposited Co thin films

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Abstract

The Co coatings were produced with the aid of the vacuum arc deposition and studied by transmission electron microscopy and electron back-scattering diffraction. At large distances from the cathode, the deposition rate R_d of Co is comparable with R_d values for vacuum arc deposited Mo and Ni–Ti alloys and exceeds R_d obtained in magnetron sputter deposition. The vacuum arc deposited coatings are formed from the 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 (5 nm) grains. The Co microparticles solidified after collision with a substrate have a metastable face centered cubic structure. © 1998 Published by Elsevier Science S.A.

Keywords: Vacuum arc deposition; Co; Microparticles; Grain structure

1. Introduction

Deposition of ferromagnetic coatings is technologically very important, for example, for the manufacturing of magnetic sensors, magnetic and magneto–optical recording media, etc. [1,2]. Magnetron sputter deposition being generally the most powerful coating method has an important disadvantage in this application field because a ferromagnetic cathode makes ineffective the magnetic stabilisation system for magnetron discharge [3]. As a result, the ferromagnetic films can only be deposited very slow in comparison with non-ferromagnetic materials [1,2]. The physical processes in a vacuum arc discharge differ principally from those in a magnetron discharge [4]. This difference permits employment of a non-magnetic stabilization of discharge system and, therefore, the deposition rates of ferromagnetic metals comparable with those of non-ferromagnetic metals can be obtained. The goal of this work was to study the vacuum arc deposition of such a strong ferromagnetic material like Co. Together with titanium, Co is one of the best biocompatible materials [5]. Development of the high-rate deposition method can open the way for production of Co-based coatings for implants and surgery. Co can exist in two allotropic modifications, namely, face-centered cubic (fcc) above 422°C and hexagonal close-packed (hcp) below 422°C [6]. Manufacturing of Co products in a non-equilibrium conditions can easily shift this allotropic transition. For example, the ball milling of Co allows to produce a mixture of the nanoparticles with the variable content of fcc and hcp phases at room temperature [7]. Therefore, another goal of this work was to study the phase constitution of Co coatings created in a non-equilibrium process of the vacuum arc deposition.

2. Experimental

The vacuum arc apparatus used in this work consists of vacuum chamber having the form of a horizontal cylinder of 700 mm diameter and 700 mm length [8]. 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 6×10^{-5} Pa was achieved before deposition. The pressure during deposition was 8×10^{-4} Pa. On the end of this cylinder, the vacuum arc apparatus with the system for spot stabilization and the Co cathode are placed. The cathode of diameter $D = 60$ mm was made from Co of 99.95% purity. The facilities for magnetic filtering of the macroparticles 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 a distance $L = 425$ mm from the surface of the cathode. The surface of the substrates was perpendicular to the surface of the cathode.

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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) equipped with an EDX system (Noran Instrument). The interplanar spacings were calculated from the measured diameter of the diffraction rings, using gold thin films as the 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 macroparticles formed in the Co coating. The EBSD method permits 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 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 semi-automated fit procedure for indexing of the EBSD patterns. The thickness of a Co film deposited on the Si wafer was measured in the SEM mode at the edge of a fractured coated Si substrate.

3. Results and discussion

Fig. 1 displays the microstructure of the Co coating for $L = 425$ mm deposited onto Si substrate. During the vacuum arc deposition the flux of material coming from the cathode to the substrate contains multiply-charged ions and microdroplets [4]. Both droplets and the homogeneous film formed by deposition of individual ions are clearly seen in the TEM micrograph (Fig. 1). Due to the rather short deposition time $t = 200$ s and the long distance from the cathode ($L/D = 7$), the film between particles is thin ($d = 100$ nm), and the particles are clearly visible. If the deposition time increases, the ionic component of flux covers the particles gradually and they incorporate into the growing film [9]. The substrate was positioned perpendicular to the cathode surface, therefore, the particles are elongated in the direction parallel to axis of the vacuum chamber. If the cathode and substrate are parallel, the particles have a circular form [9].

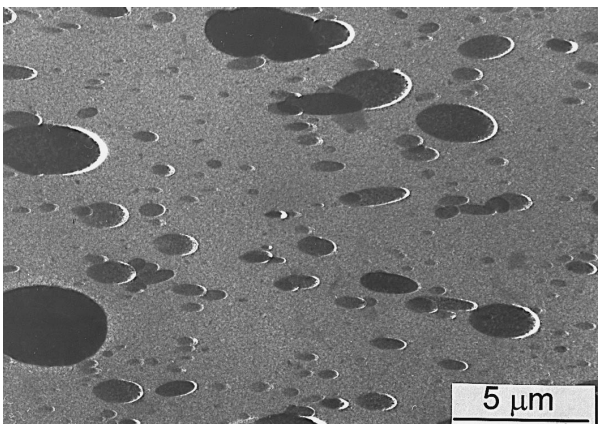

Fig. 1. TEM bright field image of Co coating deposited at cathode to substrate distance of $L = 425$ mm. Both homogeneous film and microparticles are visible.

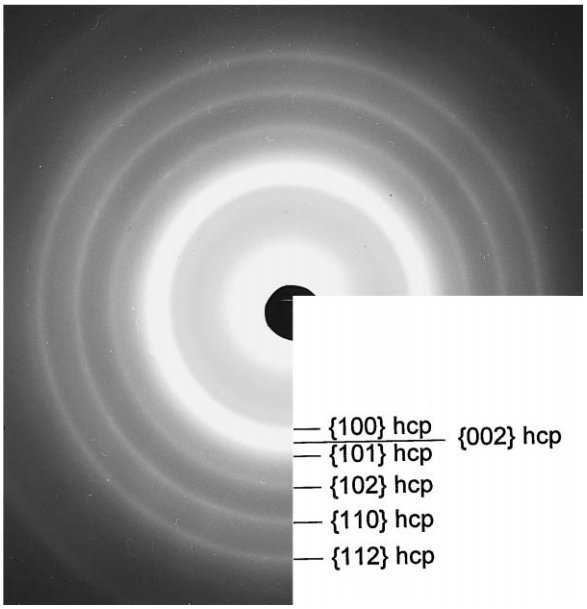

Fig. 2. Electron diffraction pattern from Co film between microparticles.

The deposition rate R_d for Co film is about 0.5 nm/s at $L = 425$ mm ($L/D = 7$) and deposition power $P = 2$ kW. The vacuum arc deposition rate of ferromagnetic Co at high L/D is much higher than R_d for the magnetron sputter deposited non-ferromagnetic materials [3,10,11]. High deposition rate at the large distances from a cathode is a very important advantage of a vacuum arc deposition.

The electron diffraction pattern (EDP) from the film between particles is shown in the Fig. 2. The film is crystalline. The data for the interplanar spacings d measured from EDP are given in Table 1 together with the tabular data for fcc (d_{fcc}) and hcp (d_{hcp}) phases of Co. The comparison shows that all diffraction rings present in a pattern can be identified as a result of diffraction from a hcp phase. Some of the rings can result both from fcc and hcp phase, but no rings coming only from fcc phase are present. Therefore, the deposition of individual Co ions on the substrate kept at the room temperature leads to the formation of a film having an hcp structure which is thermodynamically stable below 422°C. The high magnification bright field TEM micrograph (Fig. 3) reveals that the film between particles is dense and uniformly thick. The grain structure is uniform and the mean grain size is

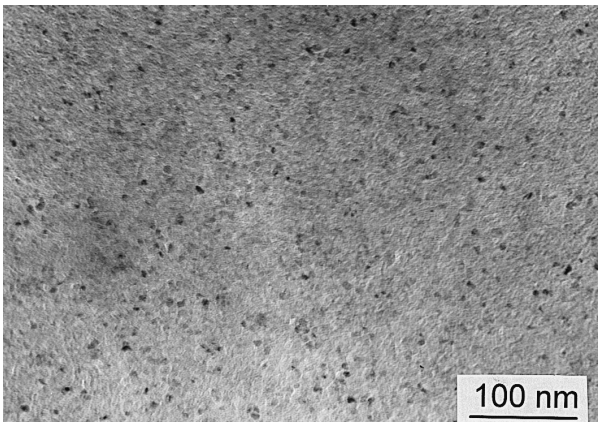

Fig. 3. Grain structure of homogeneous film between microparticles (Co coating, cathode to substrate distance 425 mm, TEM bright field image).

Table 1
Interplanar spacings d in homogeneous Co film measured with the aid of electron diffraction patterns (Fig. 2) in comparison with tabular data for fcc (d_{fcc}, spacing $a = 3.5443$ Å) and hcp (d_{hcp}, spacings $a = 2.505$ Å and $c = 4.089$ Å) phases of Co

Co (hcp lattice)		Co film (d, Å)	Co (fcc lattice)	
{hkl}	d_{hcp}, Å		d_{fcc}, Å	{hkl}
{100}	2.169	2.17		
{002}	2.040	2.05	2.046	{111}
{101}	1.916	1.92	1.772	{200}
{102}	1.488	1.51		
{110}	1.252	1.31	1.253	{220}
{112}	1.068	1.07	1.069	{311}

very small, about 5 nm. We should mention that two different substrates were used (NaCl for TEM and Si for SEM samples), and some differences in the film growth can occur. The Co coatings created by the thermal evaporation method also have the hcp structure. But they are strongly textured, not dense and possess the grain size of about 100 nm [12]. Magnetron sputter deposited Co films have hcp structure and grain size between 100 and 500 nm [11]. Therefore, the vacuum arc deposition permits to achieve the higher quality of Co coatings.

The film between particles is formed by the condensation of individual ions from the plasma phase bypassing the liquid state. The microdroplets form in the arc spot which melts locally the surface of the cathode. The droplets fly towards the substrate being liquid. They solidify after the collision with the substrate in a process analogous to a splat cooling. It is evident from the elongated and flattened form of droplets (Fig. 1). The crystallographic and grain structure of particles were analysed with the aid of EBSD method. The grains in the most particles are very fine, below the spatial resolution of the instrument (100 nm).

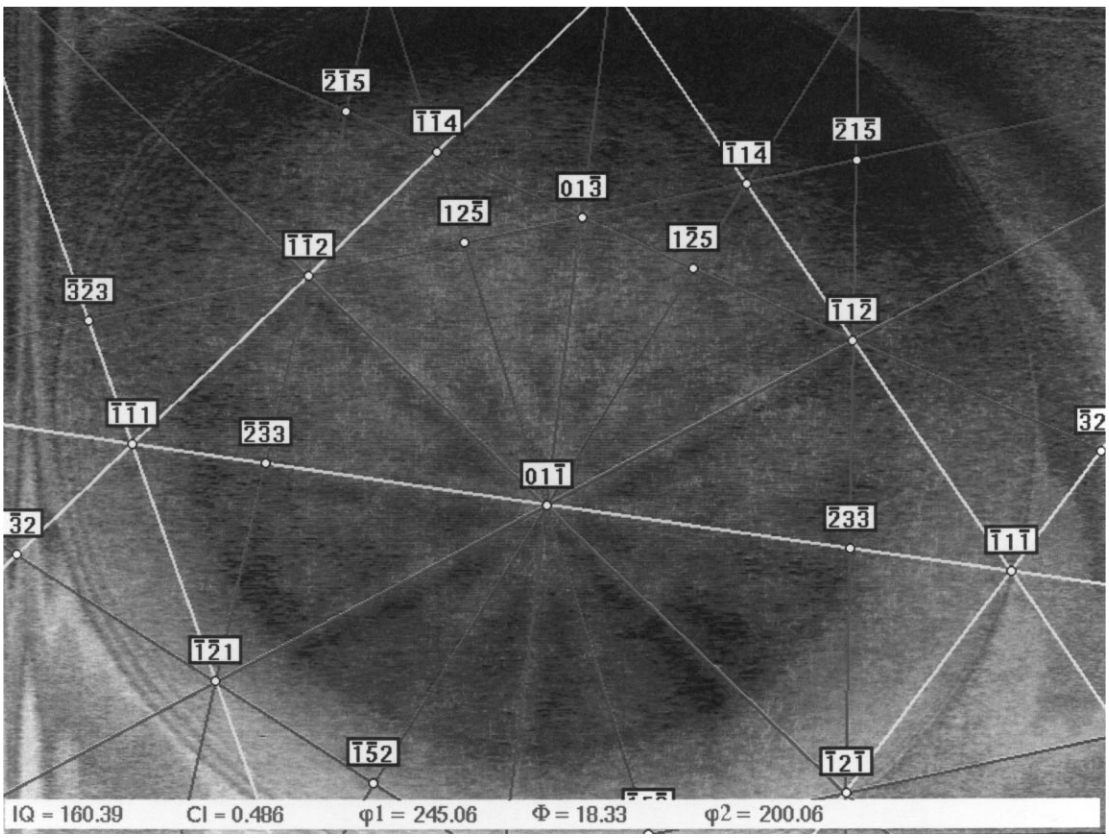

Fig. 4. EBSD pattern from the microparticle (Co/Si, cathode to substrate distance 425 mm). The results of the fitting for the fcc-lattice are shown.

Only in the largest particles with diameter > 10 μm it was possible to resolve the individual grains. They have circular form resulting from the splat cooling solidification mode of a particle. Typical EBSD pattern is shown in the Fig. 4 together with the results of the fitting procedure for the fcc structure. Therefore, the big particles have the fcc structure which is thermodynamically stable above 422°C. The particles conserve the high-temperature structure formed just after solidification due to the high cooling rate on the cold substrate. It is known that the fcc to hcp transition in Co proceeds very slowly, and the fcc phase can be stable at the room temperature as a consequence of stacking faults [5]. The allotropic transformation in Co can proceed under the influence of mechanical deformations. The mixture of the nanoparticles with variable content of fcc and hcp phases can be produced by the ball milling [7]. The Co coatings produced in this work also contain a mixture of fcc and hcp allotropes of Co.

4. Conclusion

Vacuum arc deposition permits to produce dense Co coatings containing a film with uniform nanosized grain structure and solidified droplets.

High deposition rate opens a way to application of the vacuum arc deposited Co films as biomaterials for coating of implants and surgical instruments.

Co coatings contain a mixture of fcc and hcp phases. The crystallographic structure depends on the condensation route.

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References

[1] J. Nishimaki, K. Hono, N. Hasegawa, T. Sakurai, Appl. Phys. Lett. 69 (1996) 3095–3097.
[2] R.J. Highmore, W.C. Shih, R.E. Somekh, J.E. Evetts, J. Vac. Sci. Technol. A 9 (1991) 2123–2127.
[3] B.S. Danilin, V.K. Syrchin, Magnetron Sputtering Systems, Radio i Svjas' Publishers, Moscow, 1982, p. 41 (in Russian).
[4] R.L. Boxman, P.J. Martin, D.M. Sanders (Eds.), Handbook of Vacuum Arc Science and Technology, Noyes Publications, Park Ridge, NJ, 1995, pp. 367–550.
[5] A.M. Beltram, in: M.B. Bever (Ed.), Encyclopedia of Materials Science and Engineering, Pergamon, Oxford, 1986, pp. 686–690.
[6] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1995, pp. 12–10.
[7] J.Y. Huang, Y.K. Wu, H.Q. Ye, Acta Mater. 44 (1996) 1201–1209.
[8] N. Vershinin, B.B. Straumal, W. Gust, J. Vac. Sci. Technol. A 14 (1996) 3252–3255.
[9] B.B. Straumal, W. Gust, N.F. Vershinin, V.G. Glebovsky, H. Brongersma, R. Faulkner, Nucl. Instr. Meth. Phys. Res. B 122 (1997) 594–597.
[10] C.S. Lim, H. Nickel, A. Naoumidis, E. Gyarmati, L. Mat. Sci. 30 (1995) 3874–3882.
[11] T. van Vorous, Solid State Technol. 19 (1976) 62–66.
[12] K. hara, K. Itoh, M. Kamiya, H. Fujiwara, K. Okamoto, T. Hashimoto, Jpn. J. Appl. Phys. 33 (1994) 3448–3452.