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Vacuum arc deposition of Ni-Ti gradient coatings

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Abstract

The vacuum arc discharges in the vapour of the cathode material. When several cathodes are used, the possibility exists to control each discharge independently from the others because no reactive gas is needed which can lead to interaction among the discharges of individual cathodes. The deposition rate of each component can be changed during the deposition process in situ. It permits gradient coatings to be produced. In this work, Ti and Ni were deposited onto silica glass substrates in a chamber having two separated vacuum arc sources. The discharge power P for both cathodes was gradually changed during the deposition process. Depth profiling of the coatings produced was made with the aid of secondary ion mass spectroscopy. The concentration of Ni is maximal close to the substrate and decreases gradually towards the surface of the coating. The concentration of Ti is least at the substrate and maximal on the surface. The slope of the concentration profiles depends on the distance L between the substrate and cathodes. The concentration gradient can be controlled both by changing P and L. © 1998 Elsevier Science S.A.

Keywords: Gradient coatings; Vacuum arc deposition; Deposition rate; Ni; Ti

1. Introduction

Functionally gradient coatings form a new class of structures in which the microstructure and properties vary gradually from the surface to the interior of the material. In a number of applications, including the use of coatings for thermal, wear or corrosion resistance, joining of structural components, and microelectronics, the mismatch in properties at the interface between a coating and a substrate can cause stress concentrations to develop during fabrication or while in service that result in failure of the interface. Functionally gradient coatings offer a potential solution to this problem [1]. The possibility to produce the coatings where the composition changes gradually from the substrate to surface of a film can also be useful in many other applications such as coatings for turbine blades [2], simultaneous protection against various corrosive media [3], biomaterials for implants [4] and for the substitution of multilayers. For example, optical films with a gradually varying refractive index in the direction normal to the

film surfaces have appeared to be of particular of interest. The almost total absence of reflections from a gradual transition between two media with different indices is promising to develop unusual properties that cannot be realized by stacks of homogenous films [5]. Therefore, the development of the reliable technologies for the controllable deposition of gradient coatings is very important. Recently, plasma spraying [4], co-evaporation [6,7], metalorganic spin-coating [8] and jet vapour deposition [9] have been used for the production of gradient coatings. The goal of this work is to demonstrate the possibility to produce the gradient coatings with the aid of a vacuum arc deposition. Vacuum arc deposition combines the advantages of evaporation and sputtering techniques [10]. The vacuum arc discharges in the vapour of the cathode material. This makes possible the simultaneous use of several sources because no reactive gas is needed which can lead to interaction among the discharges of individual cathodes. This feature permits an easy fabrication of multicomponent coatings. When several cathodes are used, the possibility exists to control each discharge independently of the others. Furthermore, the deposition rate of each component can be changed during the

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deposition process in situ. It permits gradient coatings to be produced. Vacuum arc deposition is also suitable for coating three-dimensional parts having complex form.

2. Experimental

The vacuum arc apparatus used in this work consists of a vacuum chamber having the form of a horizontal cylinder of diameter 700 mm and length 700 mm [11]. Its pumping system consists of a Balzers turbomolecular pump with a capacity of 15001s⁻¹ and two rotary pumps with a total capacity of 40 l s⁻¹. A total pressure of 6×10^{-5} Pa may be achieved without deposition process. The pressure during deposition is $8 \times 10^{-4} \, \mathrm{Pa}$. At opposite ends of the vacuum chamber are placed two vacuum arc sources. Each source possesses the system for spot stabilization. In this work an Ni cathode was mounted in one source and a Ti cathode was mounted in the second source. Both cathodes have a diameter D = 60 mm. They were made of Ti of 99.98% and Ni of 99.93% 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 made from polished silica glass with dimensions of $20 \times 20 \text{ mm}^2$ were placed between the Ni and Ti cathodes on various distances L from the surface of the Ni cathode.

The vacuum arc source voltage was maintained constant U=20 V for Ti and 18 V for Ni. The discharge power P was changed during the deposition independently by changing the discharge current $I_{\rm d}({\rm Ni})$ and $I_{\rm d}({\rm Ti})$ of the two sources. $I_{\rm d}({\rm Ni})$ decreased stepwise from 150 to 80 A while $I_{\rm d}({\rm Ti})$ increased stepwise from 150 to 300 A (Table 1). Below $I_{\rm d}({\rm Ti})=150 \, {\rm A}$ and $I_{\rm d}({\rm Ni})=80 \, {\rm A}$, the vacuum arc discharge becomes unstable. The strength of the stabilizing magnetic field on the Ti cathode surface was 60–70 G. No bias was applied to the substrates. The coating time t was the same for all samples at $t=260 \, {\rm s}$.

The distribution of Ni and Ti in the coatings was determined using secondary ion mass spectroscopy (SIMS). An *ims 3f* secondary ion mass spectrometer (Cameca, France) has been used for in-depth analyses of the films. O_2^+ ions accelerated with energy 12.5 kV were used as primary ions. The primary ion current I_p ranged from 400 to 1000 nA. The primary ion beam

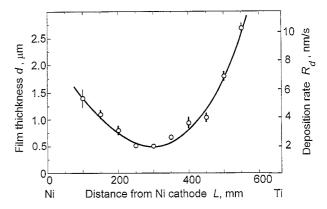


Fig. 1. Dependence of the deposition rate R_d and film thickness d on the position of the sample between the Ni and Ti cathodes.

was rastered over a square area $250 \times 250 \, \mu m$. The secondary ions, accelerated by 4.5 kV, were collected from a square area $50 \times 50 \, \mu m$ in the middle of the rastered area. The energy band pass filter for the secondary ions was $50 \, eV$, centred at the maximum energy of the secondary ions. The distributions of Ti and Ni were studied by profiling isotopes ⁵⁰Ti and ⁶²Ni, respectively. The quantification of the secondary ions was done by analysing coatings of pure titanium and nickel, deposited and analysed under the same conditions as the Ti–Ni gradient coatings. The depths of the sputtered craters were measured with a *Talysurf 10* instrument (Rank Taylor Hobson, UK). Each crater was measured several times in the central region of the crater. The deviation in the average depth ranged from 2 to 11%.

3. Results and discussion

Fig. 1 displays the dependence of deposition rate $R_{\rm d}$ and the coating thickness d on the position of the sample between the Ni and Ti cathodes. $R_{\rm d}$ and d are maximal close to the Ni and Ti cathodes and decrease with increasing distance from both cathodes. $R_{\rm d}$ and d reach a minimum at L about 300 mm (from the Ni cathode). $R_{\rm d}$ and d are about two times higher close to the Ti cathode than close to the Ni cathode owing to the higher deposition rate of Ti at the same discharge current $I_{\rm d}$. Therefore, the minimum of d(L) and $R_{\rm d}(L)$ is shifted from the middle of a chamber towards the Ni cathode. At comparable L/D ratio and discharge power P (L/D = 0.4, D is the diameter of the cathode,

Table I Variation of discharge current I_d for Ti and Ni cathodes in dependence on the deposition time t_d

t (s)	20	40	60	80	100	120	140	160	180	200	220	240	260
$I_{d}(Ni)(A)$ $I_{d}(Ti)(A)$	150	150	150	150	150	150	150	140	130	110	100	90	80
	150	150	170	200	240	260	300	300	300	300	300	300	300

 $P=3~{\rm kW}$), the $R_{\rm d}$ for Ti is about 2 to 4 times higher than $R_{\rm d}$ for magnetron sputter deposition [12,13]. Recently it was shown that $R_{\rm d}$ for vacuum arc deposition of Mo decreases with increasing L much slower than in case of magnetron sputter deposition [14]. In our case, $R_{\rm d}$ decreases with increasing distance from the Ti cathode at roughly the same rate as in case of the magnetron sputter deposition, and with increasing L from Ni cathode about 3–4 times slower [12]. Therefore, the vacuum arc deposition is generally better suited for the coating of three-dimensional parts having a complex form, in comparison with the magnetron sputter deposition.

In Fig. 2 the depth profiles of Ni–Ti coatings are displayed for the various distances L. The discharge current $I_d(Ti)$ increased and $I_d(Ni)$ decreased gradually

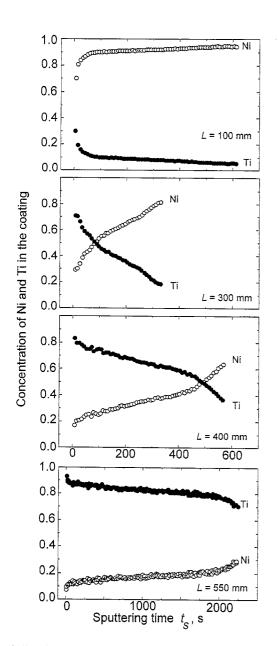


Fig. 2. Depth profiles of Ni-Ti coatings for various distances L.

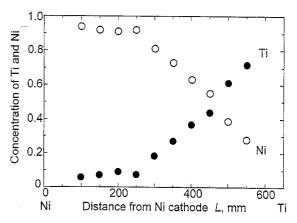


Fig. 3. Dependence of concentration of Ni and Ti in the gradient coatings close to the substrate on the distance L.

during the deposition (Table 1). In all samples the concentration of Ti increases from the substrate towards the surface of a coating, and the concentration of Ni varies conversely. Therefore, by changing I_d during the deposition, one can really control the composition of a coating and reach a gradual change of the concentration. Close to the Ni cathode (L=100 mm), the coating consists nearly of pure Ni. Only its top part contains an essential amount of Ti. Close to the Ti cathode (L=550 mm) titanium dominates in the coating. In the middle of a vacuum chamber (L=300 and 400 mm), the depth profiles of Ti and Ni intersect. The top part of these coatings consist mainly of Ti, and the bottom part mainly of Ni. The intersection point where the concentrations of Ti and Ni are equal moves from the surface of a coating towards the substrate with increasing L. The concentration steps originated from the stepwise change of discharge current, can be clearly seen in the profiles for L=300 mm. The microdroplets of Ti and Ni are present in the coatings, because the filtering facilities were not used in this work. Nevertheless, the presence of the droplets does not disturb the concentration gradient in the Ni-Ti films.

Fig. 3 displays the concentration of Ni and Ti in the coating close to the substrate for various L. Both curves intersect at L=470 mm, rather close to the Ti cathode. At the beginning of a deposition procedure, $I_{\rm d}({\rm Ni})=I_{\rm d}({\rm Ti})=150$ A. Therefore, the asymmetry of the concentration curves in Fig. 3 clearly demonstrates that the deposition rate for Ni decreases with increasing distance from the cathode slower than $R_{\rm d}$ for Ti.

4. Conclusions

(1) By changing the discharge power of two independent vacuum arc sources with Ti and Ni cathodes during the deposition process, the deposition rate of each component was changed in situ.

- (2) As a result, a gradual change of the Ni and Ti concentration in a coating was achieved.
- (3) High deposition rates $R_d(\text{Ti}) = 10.5 \text{ nm s}^{-1}$ and $R_d(\text{Ni}) = 5.5 \text{ nm s}^{-1}$ are achieved close to the Ni and Ti cathodes.
- (4) The concentration gradient depends on the distance from both cathodes.
- (5) It is possible to control the concentration gradient in a coating in situ during the vacuum arc deposition by changing the discharge power and by varying the geometry of the deposition chamber.

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