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THERMAL SHOCK RESISTANCE OF CHEMICALLY VAPOUR-DEPOSITED MOLYBDENUM COATINGS ON GRAPHITE

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Summary

Thermal shock tests were performed for chemically vapour-deposited molybdenum coatings on graphite to examine effects of thermal shock heating parameters and deposition conditions on their thermal shock resistance. The coatings, of 10 μm layer thickness, were prepared at deposition temperatures ranging from 400 to 700 °C using molybdenum hexacarbonyl, $Mo(CO)_6$, as a feed material and POCO graphite as a substrate. The thermal shock tests were performed by single-pulse electron beam heating at power densities up to 50 MW m^{-2} for pulse durations up to 2.0 s.

It was found from the tests that the surface melting limit for the coating depended on both power density and pulse duration and that the coating had a constant surface melting limit expressed as $F\tau^{1/2}$, where F was the power density that caused surface melting during a specified pulse duration τ. The tests also indicated that thermal shock resistance of the coating correlated considerably with the deposition conditions; the surface melting limit of the coating increased and the coatings showed more favourable thermal shock resistance as the deposition temperature increased from 400 to 700 °C.

1. Introduction

Refractory metal coatings are applied to improve surface properties of materials in severe environments. From this point of view, niobium, molybdenum, rhenium and tungsten coatings have been developed and characterized in our laboratory [1 - 3]. Among refractory metals, molybdenum has excellent thermophysical and mechanical properties [4]. In addition, it shows good compatibility with hydrogen isotopes at elevated temperatures [5 - 6].

In the present study molybdenum was deposited on graphite by chemical vapour deposition (CVD) to improve graphite surface characteristics such as corrosion resistance and gas permeation resistance through the

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coating. The coatings were then thermal-shock-tested to examine effects of the thermal shock heating parameters and the deposition conditions on their thermal shock resistance.

2. Experimental details

2.1. Preparation of the coatings

The chemical vapour deposition of molybdenum was carried out by a carbonyl process using molybdenum hexacarbonyl, $Mo(CO)_6$, as a feed material and DFP-3-2 POCO graphite ($10 \times 10 \times 1$ mm^3) as a substrate. The schematic diagram of the CVD apparatus is shown in Fig. 1. The deposition system consisted of a deposition chamber, a feed material supply chamber, and a pumping system. The deposition temperature was monitored with a thermocouple extending into the deposition chamber. Before the deposition, mechanically polished and ultrasonically cleaned substrates were degassed at 1400 °C for 1 h; then they were kept at deposition temperatures T_d, ranging from 400 to 700 °C in a vacuum below 10^{-5} Pa. During the deposition, the feed material was kept at 20 °C to inject its vapour into the CVD chamber. The coating layers 10 μm in thickness were adopted for all the experimental runs. The coatings thus prepared were characterized as to structural and mechanical properties such as columnar grain size, Vickers microhardness and adhesion.

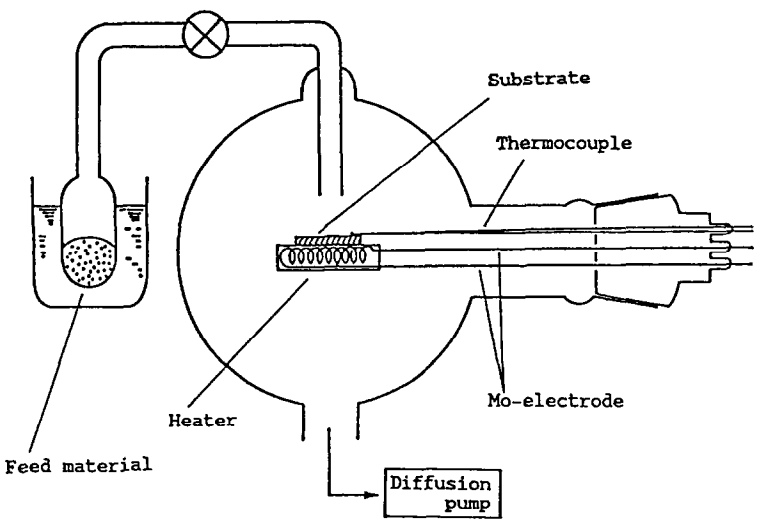

Fig. 1. Schematic diagram of the CVD apparatus.

2.2. Thermal shock tests

2.2.1. Effects of thermal shock heating parameters

To examine the effect of thermal shock heating parameters on thermal shock resistance of the coating, we heated it with a single-pulse electron

beam at various power densities (10 - 50 MW m^{-2}) and for various pulse durations (0.5–2.0 s) in a vacuum below 10^{-5} Pa. The coatings prepared at 600 °C were selected as specimens for this purpose. The apparatus consisted of a 16 keV electron beam focused to impinge onto a spot 3 mm in diameter. The specimens were placed on a water-cooled copper plate during the tests.

2.2.2. Effects of deposition conditions

In order to examine effects of deposition conditions on thermal shock resistance of the coatings, we prepared coatings at various deposition temperatures (400, 600 and 700 °C). Electron beam heating took place at power densities up to 40 MW m^{-2} for a fixed pulse duration of 1.5 s. For comparison, molybdenum sheets (10 × 10× 1 mm; purity, 99.95%) were also exposed to electron-beam heating.

Thermal failures of the coatings were examined mainly by scanning electron microscope (SEM) and optical microscope observation and surface roughness measurement.

3. Results and discussion

3.1. Preparation of the coatings

Surface and cross-sectional SEM micrographs of the as-coated specimens are shown in Fig. 2. The cross-sectional micrographs indicate that the coatings are columnar in structure. The surface micrographs indicate that the grain size increases with increasing deposition temperature and that the morphology of the coated surface varies from a domed surface to a faceted surface with an increase in deposition temperature.

The deposition parameters and fundamental properties of the coatings are summarized in Table 1. The deposition rate increases with increasing deposition temperature. This is because decomposition of the $Mo(CO)_6$ is promoted by increasing the deposition temperature in the range from 400 to 700 °C [7]. The grain size (calculated from the number count of grains in a known area of the surface) and the adhesion of the coating layer to the substrate also increase with increasing deposition temperature. Vickers

TABLE 1

Fundamental properties of the coating specimens

T_d (°C)	*Deposition rate* ($\mu m\ h^{-1}$)	*Grain size* (μm)	*Vickers microhardness* ($kg\ mm^{-1}$)	*Adhesion* ($kgw\ cm^{-2}$)
700	2.0	1.6	102	390
600	1.7	1.3	171	340
400	1.3	0.3	925	120

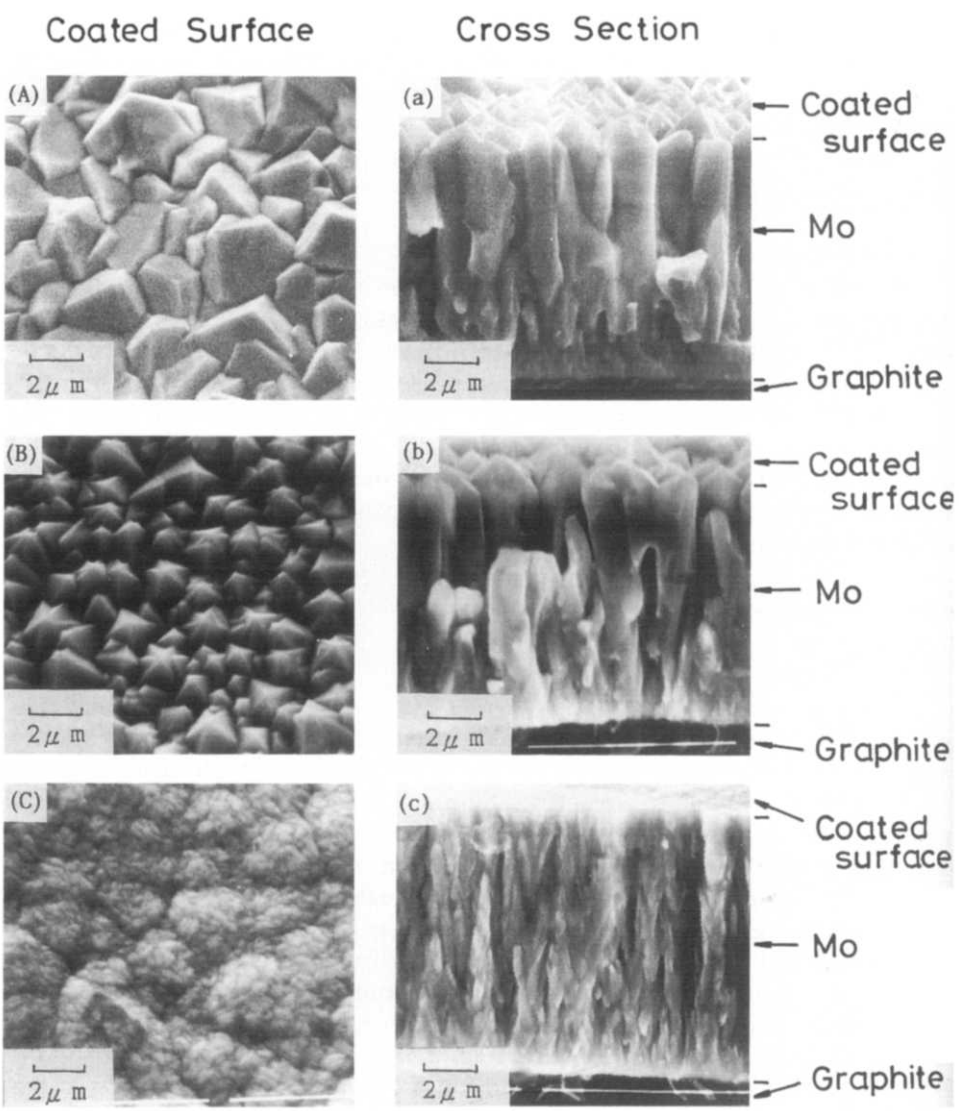

Fig. 2. Surface and cross-sectional SEM micrographs of as-coated specimens. (A), (a) T_d = 700 °C, (B), (b) T_d = 600 °C, (C), (c) T_d = 400 °C.

microhardness increases with decreasing deposition temperature owing to the carbon content in the coating [8]. Although the increase of the Vickers microhardness means an increase of the carbon content, all coatings prepared under our experimental conditions indicate only a molybdenum phase, and no molybdenum carbide was detected from X-ray diffraction measurement. Therefore the carbon content of the coatings was under the carbon solubility limit for molybdenum (about 1 at.%) [9]. Reported data about the microhardness *vs.* the carbon content in Mo–C deposits indicate that the carbon

content in a coating prepared at 400 °C is approximately 1 at.% [10]. Furthermore, the carbon content in coatings prepared at 600 °C seems to be less than 0.1–0.15 at.% from Lander and Germer's report [8].

3.2. *Thermal shock tests*

3.2.1. *Effects of thermal shock heating parameters on surface melting limit*

Assuming a semi-infinite solid and one-dimensional geometry, and neglecting surface cooling by radiation and evaporation, we can express the surface temperature T as

$$T(t) = T_0 + F_0 t^{1/2}\left(\frac{2}{(\pi\rho ck)^{1/2}}\right) \qquad (\text{for } t \leqslant \tau_0) \tag{1}$$

where T is a function of heating time t, T_0 the starting temperature, F_0 the power density, τ_0 the pulse duration, ρ the density, c the specific heat and k the thermal conductivity [11].

At this stage it would be better to introduce $F\tau^{1/2}$ as a measure of thermal load, and $F\tau^{1/2}$ can be written as

$$F\tau^{1/2} = \frac{(\pi\rho ck)^{1/2}}{2}(T_m - T_0) \tag{2}$$

where F is the power density that causes surface melting during a specified pulse duration τ and T_m is the melting point.

Figure 3 shows typical results of the thermal shock tests to examine the surface melting limit of the molybdenum coating on graphite prepared at 600 °C. Although eqn. (2) is valid for a semi-infinite solid and one-dimensional geometry, it was found from our experimental results that the surface melting limit for the coating can be also expressed using $F\tau^{1/2}$. For a coating

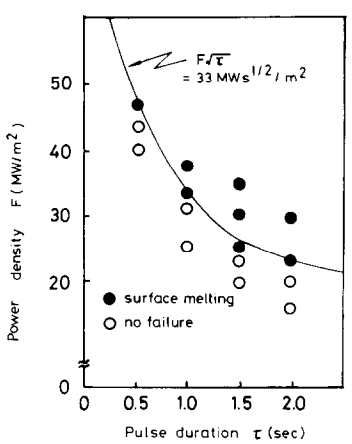

Fig. 3. Surface melting limit of the molybdenum coating on graphite prepared at 600 °C.

deposited at 600 °C, $F\tau^{1/2}$ is approximately 33 MW $s^{1/2}$ m^{-2} which is shown with a solid line in Fig. 3.

3.2.2. Effects of deposition conditions on thermal shock properties

Table 2 summarizes typical results of the thermal shock tests (pulse duration, 1.5 s) performed for coatings prepared at different deposition temperatures and bulk molybdenum sheets.

TABLE 2

Results of thermal shock tests (pulse duration 1.5 s)

Specimen	*Power density* (MW m^{-2})		
	20	30	40
Coating T_d = 700 °C		No failure	Surface melting
Coating T_d= 600 °C	No failure	Surface melting	Droplet Microcrack
Coating T_d = 400 °C	No failure	Surface melting / Blister Exfoliation	
Mo sheet		No failure	Surface melting

The surface damages observed on the specimens prepared at 400 °C are shown in Fig. 4. As seen in Fig. 4(B), the specimen indicates surface melting at the power density of 23.5 MW m^{-2}, which is the lowest surface melting limit of all the specimens. At the power density of 27.6 MW m^{-2}, blisters and their exfoliation are observed around the melted region, as shown in Fig. 4(C). These blisters and exfoliation, which are only seen for the specimens prepared at 400 °C, are probably due to release of CO gas trapped in the coating because a considerable number of CO molecules are possibly contained in the coating by the deposition from metal carbonyls when the deposition temperature is relatively low (below 400 °C) [12]. A further increase in the power density makes the blisters and the exfoliation larger as seen in Fig. 4(D). Figure 5 shows some of the exfoliations occurring from the interface when the specimen is heated at 30.0 MW m^{-2}. These exfoliations occur probably because the adhesion of the coating layer prepared at 400 °C is lower than that of other samples.

The surface damage observed on the specimens prepared at a deposition temperature of 600 °C is shown in Fig. 6. As seen in Fig. 6(B), the surface melting occurs when the specimen is heated at above 25.0 MW m^{-2}, which is a little higher than the surface melting limit for the specimen prepared at 400 °C. The specimen heated at 35.3 MW m^{-2} shows formation of droplets at the damaged region as shown in Fig. 6(C). The results of surface roughness

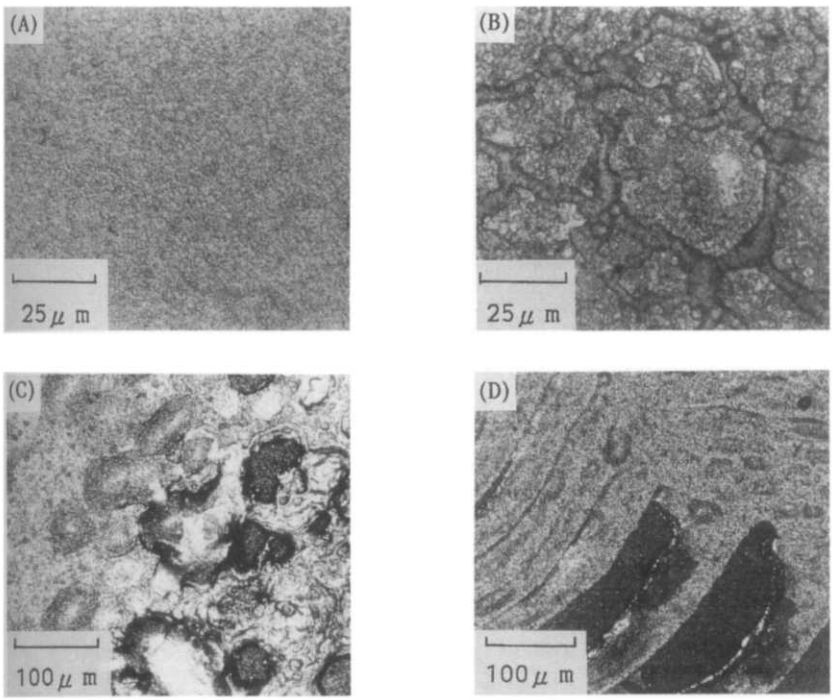

Fig. 4. Surface damage observed on the molybdenum coating on graphite (T_d = 400 °C) after the thermal shock tests: (A) as-coated, (B) 23.5 MW m^{-2}, (C) 27.6 MW m^{-2}, (D) 30.0 MW m^{-2}.

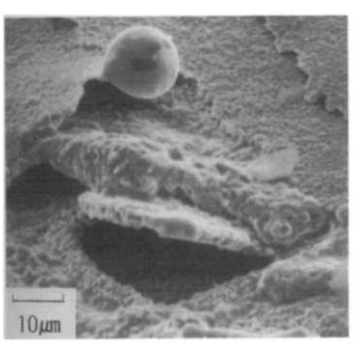

Fig. 5. Exfoliation of the coated surface after the thermal shock test at 30.0 MW m^{-2}. (T_d = 400 °C.)

measurement of these specimens are shown in Fig. 7. The surface roughness of the as-coated sample at 600 °C is about 0.7 μm. The surface roughness increases when the sample was heated at 25.0 MW m^{-2}. At the power density of 35.3 MW m^{-2}, there is almost no molybdenum layer left at the central damaged region and thickness of the edge of the damaged region increases.

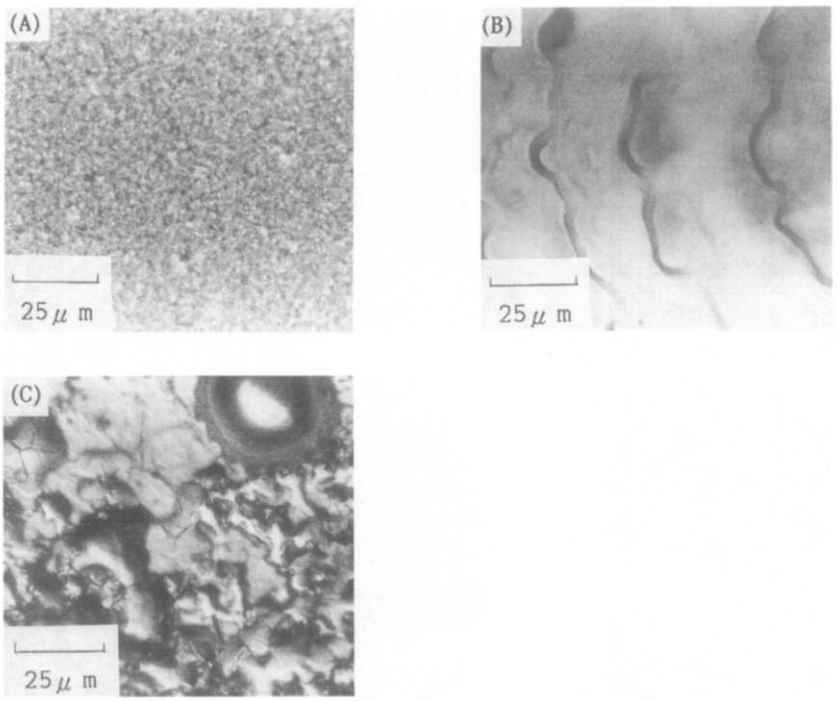

Fig. 6. Surface damage observed on the molybdenum coating on graphite (T_d = 600 °C) after the thermal shock tests. (A) As-coated, (B) 25.0 MW m^{-2}, (C) 35.3 MW m^{-2}.

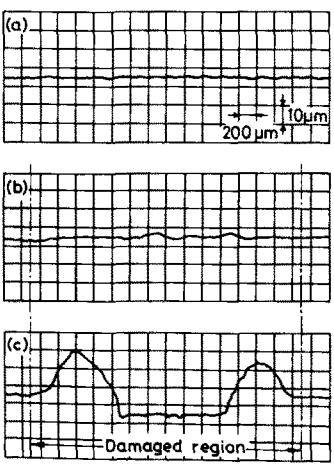

Fig. 7. Surface roughness measurement of the molybdenum coating on graphite (T_d = 600 °C) subjected to the thermal shock heatings. (a) As-coated, (b) 25.0 MW m^{-2}, (c) 35.3 MW m^{-2}.

The result of thermal shock tests conducted on the coating prepared at 700 °C are shown in Fig. 8. The surface melting limit in this case is 34.5 MW m^{-2}, which is higher than that of the coating prepared at 600 °C.

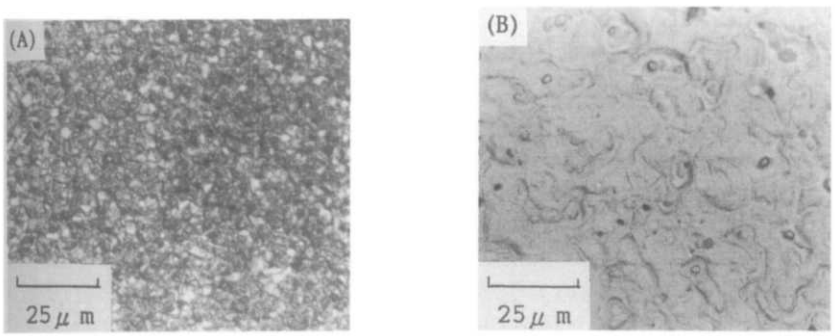

Fig. 8. Surface damage observed on the molybdenum coating on graphite (T_d = 700 °C) after the thermal shock test. (A) as-coated, (B) 35.3 MW m^{-2}).

We think that the variation of the surface melting limit for the specimens prepared at different deposition temperatures is due to the presence of carbon dissolved in the coating because, as the C–Mo phase diagram indicates, increasing the carbon content in molybdenum lowers the melting point of molybdenum [9]. As already shown in Section 3.1., the carbon content in the coating decreases with increasing the deposition temperature. Therefore, when the deposition temperature increases, an increase in the surface melting limit is observed.

The thermal shock tests performed for molybdenum sheets indicate that the surface melting and microcracking take place when the power density is more than 37.8 MW m^{-2}, as shown in Fig. 9.

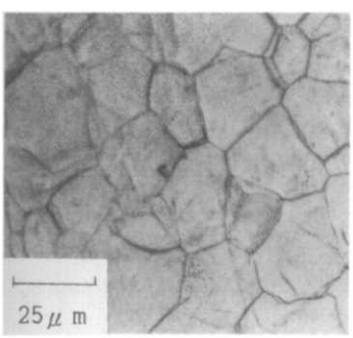

Fig. 9. Surface damage observed on the molybdenum sheet after the thermal shock test at 37.8 MW m^{-2}.

The fact that the surface melting limit of molybdenum coating on graphite is lower than that of the molybdenum sheet would be explained by the carbon content in the coating and the fact that the coating is on graphite which has lower thermal conductivity than molybdenum.

4. Conclusions

Several conclusions can be drawn from the thermal shock tests performed for chemically vapour-deposited molybdenum coatings on graphite:

(i) thermal shock resistance of the coatings depends considerably on the deposition temperature.

(ii) The coating shows a constant surface melting limit expressed as $F\tau^{1/2}$, where F is the minimum power density which causes surface melting during a specified pulse duration τ.

(iii) As the deposition temperature of the coating increases, surface melting limit of the coating increases and approaches that of molybdenum sheet.

(iv) Blisters and exfoliation are observed only for the coating prepared at the deposition temperature of 400 °C. This was probably due to release of CO gas trapped in the coating. Some of the exfoliations occurred from the interface between the layer and the substrate. It seems obvious that this arose from a decrease in adhesion corresponding to a decrease in the deposition temperature.

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References

1 M. Miyake, Y. Hirooka, R. Imoto and T. Sano, *Thin Solid Films, 63* (1979) 303.
2 M. Miyake, Y. Hirooka, T. Imoto and T. Sano, *Thin Solid Films, 79* (1981) 75.
3 S. Yamanaka, M. Tanaka, P. Son and M. Miyake, *Proc. 8th Int. Conf. on Vacuum Metallurgy, Linz, Austria, 1985*, Eisenhutte Osterreich, 1985, p. 63.
4 R. F. Mattas, B. Misra and D. L. Smith, *J. Nucl. Mater., 103/104* (1981) 217.
5 R. W. Conn, *J. Nucl. Mater., 76/77* (1978) 103.
6 A. W. Mullendore, J. B. Whitley and D. M. Mattox, *J. Nucl. Mater., 93/94* (1980) 486.
7 M. Diem, M. Fisk and J. Goldman, *Thin Solid Films, 107* (1983) 39.
8 J. J. Lander and L. H. Germer, *AIME Technical Publication No. 2259*, 1947.
9 T. Lyman, H. E. Boyer, W. J. Carnes and M. W. Chevalier, *ASM Metals Handbook* 8th edn., 1973, Vol. 8, American Society for Metals, Metals Park, OH, p. 279.
10 J. Danroc, A. Aubert and R. Gillet, *Thin Solid Films, 153* (1987) 281.
11 R. Behrisch, *J. Nucl. Mater., 93/94* (1980) 498.
12 G. J. Vogt, *J. Vac. Sci. Technol., 20 (4) (April 1982)* 1336.