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Siliconizing of molybdenum plate using Si_2Cl_6 and some of its properties

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Molybdenum plate was siliconized using Si_2Cl_6 as a silicon source, and the siliconizing conditions and some of its properties were examined. The siliconizing of the molybdenum plate began by the deposition here and there of island-like $MoSi_2$ deposits 4 to 6 μm thick in the initial stage (after 10 min induction time), and then coalescence of the deposits proceeded to form a uniform $MoSi_2$ layer all over the molybdenum plate after 30 min siliconizing time. The weight decrease of the siliconized plate by anodic dissolution in 0.2 M sulphuric acid reduced exponentially with increasing thickness of the $MoSi_2$ layer, and no weight decrease was observed at all above 16 μm thickness. The sea water corrosion and sea sand abrasion resistivities of the siliconized molybdenum plate increased with increasing siliconizing temperature and Si_2Cl_6 flow rate.

1. Introduction

Molybdenum disilicide ($MoSi_2$, melting point 1870 to 2030° C) has probably the highest oxidation stability at high temperatures among many non-oxide compounds, and has outstanding stability in a variety of chemicals. Thus, $MoSi_2$ is one of the most important compounds for use as a protective coating against oxidation at high temperature, against corrosion, or for use as a heat-resistant coating. Furthermore, $MoSi_2$ is of interest for use as the gate electrode or low-resistance interconnection in VLSI technologies.

$MoSi_2$ layers have been prepared by the reaction of a silicon substrate and molybdenum deposited on it by evaporation [1], by solution growth on a molybdenum substrate dipping into molten tin which was saturated with silicon [2], by d.c. magnetron or r.f. diode co-deposition [3–5], by r.f. plating [6], and by the CVD process [7].

We have examined the oxidation resistance and Vickers microhardness of $MoSi_2$ layers obtained by the siliconizing of the molybdenum layer using $SiCl_4$ as a silicon source [8, 9].

Vapour-phase siliconizing of metals has been commonly carried out using $SiCl_4$ (boiling point 57.6° C) as a silicon source. Hexachlorodisilane (Si_2Cl_6, boiling point 144° C) is more reactive than $SiCl_4$, and is of interest as a new CVD reagent.

In this work, we have prepared the $MoSi_2$ layers by the siliconizing of the molybdenum plate using Si_2Cl_6 as a silicon source, and examined some of its properties in relation to the deposition parameters and the thickness of the $MoSi_2$ layers.

2. Experimental procedures

The molybdenum plate (20 mm × 5 mm × 0.2 mm, abraded by emery paper No. 400) was hung by a molybdenum wire in the central part of a vertical reaction tube (quartz, 21 mm i.d. and 350 mm long), and was siliconized in a gas mixture of Si_2Cl_6 and H_2 over a temperature range from 700 to 1000° C.

The siliconized molybdenum plate was anodically dissolved into 0.2 M sulphuric acid solution for 5 min at room temperature, the sulphuric acid solution being vibrated by ultrasonics and the cathode electrode being platinum wire, and the weight change was measured. The weight decrease observed may be considered to be a measure of the number of pinholes and/or cracks which are present in the $MoSi_2$ layers and reach to the molybdenum substrate. The siliconized plate was immersed in artificial sea water at 30° C for 200 h, and the weight change was measured. Furthermore, the siliconized plate was exposed in 500 g artificial sea water into which 100 g of sea sand (20 to 30 mesh) was sunk, and stirred violently by a screw at about 360 r.p.m. for 100 h, and the weight change was measured.

The flow rates of Si_2Cl_6 and H_2 were fixed at 0.05 and 1.95 ml sec^{-1}, respectively, unless otherwise described.

3. Results and discussion

3.1. Siliconizing conditions

Using Si_2Cl_6 as a silicon source, an appreciable weight increase of the molybdenum plate was observed at a siliconizing temperature as low as about 750° C, while a weight increase was observed above 900° C when $SiCl_4$ was used as a silicon source. The effect of Si_2Cl_6 flow rate on the weight gain of the molybdenum plate is shown in Fig. 1, in which the siliconizing

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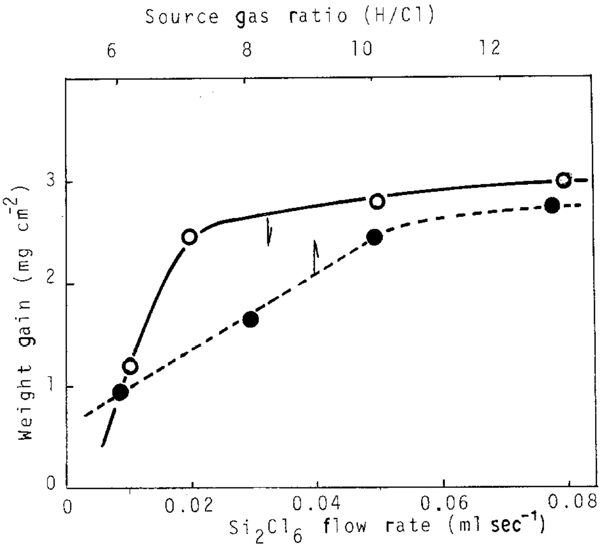

Figure 1 Effect of the (○) Si_2Cl_6 flow rate and (●) source gas flow ratio (H/Cl) on the weight gain of the molybdenum plate. Siliconizing temperature: 1000° C, siliconizing time: 30 min, total gas flow rate: 2.0 ml sec^{-1}, Si_2Cl_6 flow rate: 0.05 ml sec^{-1}, balance gas: argon.

temperature and siliconizing time were fixed at 1000° C and 30 min, respectively. The weight gain increased steeply with increasing Si_2Cl_6 flow rate and attained a constant value at about 0.02 ml sec^{-1}, in agreement roughly with that of the siliconizing of nickel or cobalt plate using Si_2Cl_6 as a silicon source. The rate-determining step of the siliconizing of the molybdenum plate may be considered to be the surface reaction and/or mass transport processes at an Si_2Cl_6 flow rate below 0.02 ml sec^{-1}, and to be a diffusion process in the solid phase at above 0.02 ml sec^{-1}. The weight gain of the molybdenum plate increased linearly with increasing source gas flow ratio (H/Cl) and attained a constant value at the ratio (H/Cl) above 10, as can be seen in the dotted line in Fig. 1. This hydrogen excess value for the following reaction,

$$Si_2Cl_6 + 3H_2 \rightarrow 2Si + 6HCl$$

is in agreement with that of the siliconizing of a nickel plate.

3.2. Initial stage of the siliconizing

It has usually been considered that very thin and uniform silicon diffusion layers were formed all over the substrate surface from the initial stage of the siliconizing. The surface and polished cross-section of the molybdenum plate at the initial stage of siliconizing are shown in Figs 2 and 3, respectively. We have observed, in this experiment, that the $MoSi_2$ phase appears here and there in island-like deposits on the surface of the molybdenum plate after an induction period of about 10 min. The number and size of these island-like $MoSi_2$ deposits increased with increasing siliconizing temperature, and was followed by the coalescence of deposits to form uniform $MoSi_2$ layers after 30 min siliconizing time. The island-like deposits or layers of $MoSi_2$ were formed on the surface of the molybdenum plate with the same thickness, about 2 to 3 μm, above and beneath the surface level. That is, the thickness of the $MoSi_2$ deposits or layers formed on the plate at the initial stage of siliconizing was about 4 to 6 μm. After the uniform $MoSi_2$ layer of 4 to 6 μm thick was formed all over the surface, thickening of the layer began with increasing siliconizing time beyond 30 min.

These results were quantitatively shown by the relationship between siliconizing time and coverage percentage, and siliconizing time and weight increase, the siliconizing temperature being 1000° C, as shown in Fig. 4. The coverage percentage refers to the percentage of the sum of the deposition area of the $MoSi_2$ deposits against that of the molybdenum plate. The coverage percentage of the $MoSi_2$ layer increased parabolically with increasing siliconizing time after an induction time of 10 min, and attained 100% at about 30 min. The weight of the molybdenum plate increased also parabolically (according to the "root law") with increasing siliconizing time. The induction time of 10 min may be considered to be the time necessary for the activation of the surface, for example, by the hydrogen reduction of the thin oxide layer present on the surface, and necessary to become a given reactive atmosphere.

The size of the island-like $MoSi_2$ deposits reduced with increasing siliconizing temperature as can be seen in Fig. 5. It may be considered that the number of the island-like $MoSi_2$ deposits formed at the initial stage of the siliconizing increased with increasing

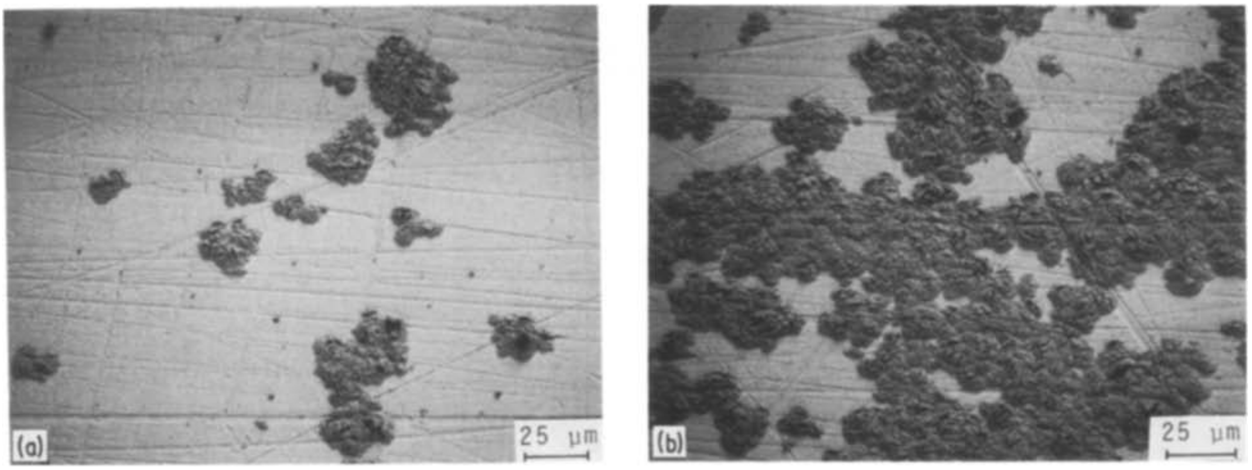

Figure 2 Surface of the molybdenum plate at the initial stage of siliconizing. Siliconizing temperature: 1000° C, siliconizing time: (a) 12 min, (b) 17 min.

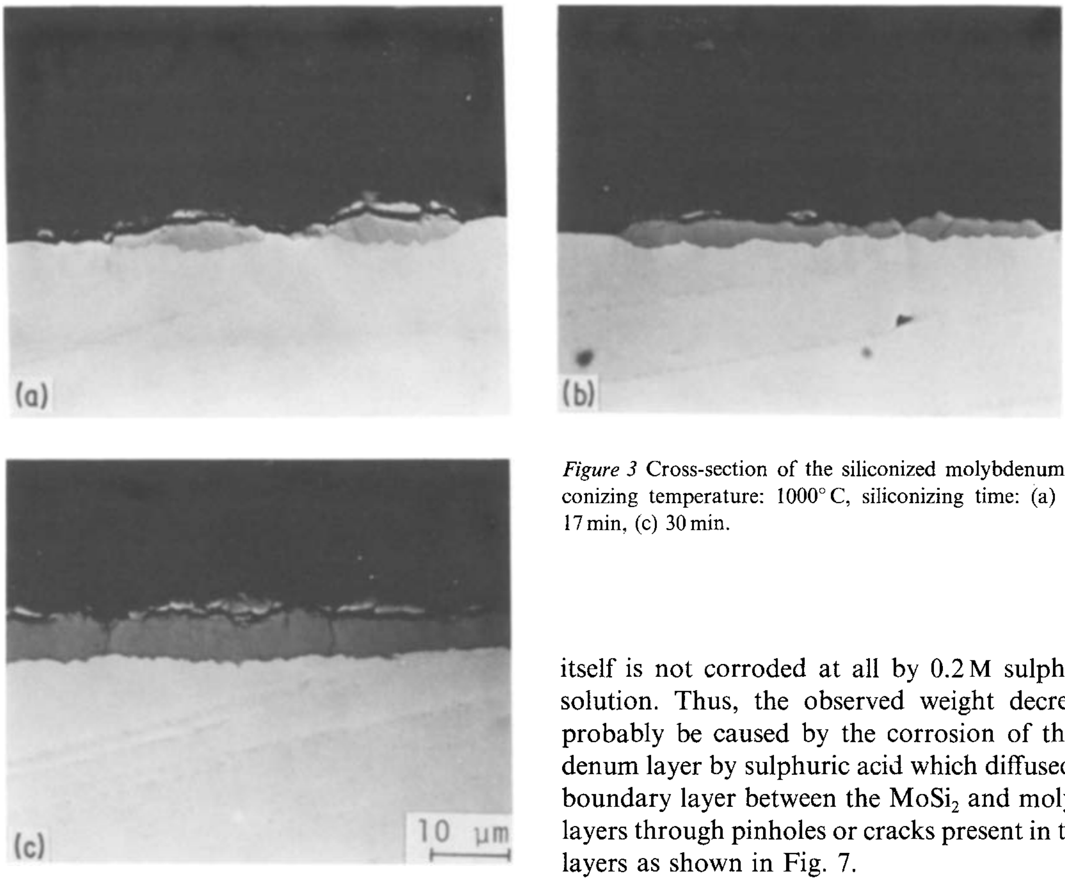

Figure 3 Cross-section of the siliconized molybdenum plate. Siliconizing temperature: 1000° C, siliconizing time: (a) 12 min, (b) 17 min, (c) 30 min.

siliconizing temperature, and thus resulted in the decreasing size. No effect of the Si_2Cl_6 flow rate on the surface appears of the $MoSi_2$ layers was observed, similar to the case using $SiCl_4$ [9].

3.3. Properties of the siliconized molybdenum plate

3.3.1. Corrision stability

The effect of the thickness of the $MoSi_2$ layers on the weight decrease of the siliconized molybdenum plate by anodic dissolution in 0.2 M sulphuric acid solution is shown in Fig. 6, the siliconizing temperature being 900° C. The weight decrease of the siliconized plate reduced outstandingly with increased thickness of the $MoSi_2$ layer, and no weight decrease at all was observed above 15 μm thickness. The $MoSi_2$ layer itself is not corroded at all by 0.2 M sulphuric acid solution. Thus, the observed weight decrease may probably be caused by the corrosion of the molybdenum layer by sulphuric acid which diffused into the boundary layer between the $MoSi_2$ and molybdenum layers through pinholes or cracks present in the $MoSi_2$ layers as shown in Fig. 7.

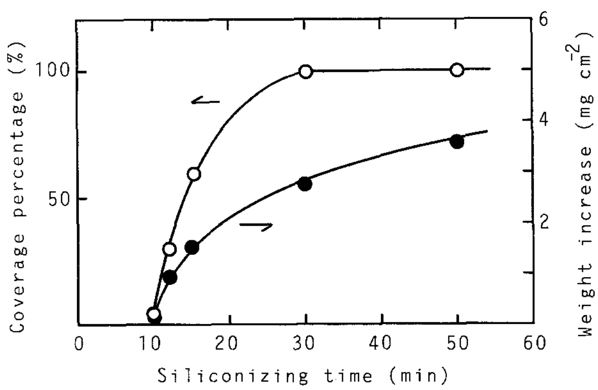

Figure 4 Effect of siliconizing time on (○) the coverage percentage and (●) the weight increase of the molybdenum plate. Siliconizing temperature: 1000° C, Si_2Cl_6 flow rate: 0.05 ml sec^{-1}, H_2 flow rate: 1.95 ml sec^{-1}.

The influence of the siliconizing temperature and Si_2Cl_6 flow rate on the corrosion stability of the siliconized molybdenum plate against sea water were examined by the weight change in the dipping test, and the result is shown in Fig. 8, in which the thickness of the $MoSi_2$ layer was fixed at 10 μm. The weight decrease of the siliconized plate reduced appreciably above 950° C siliconizing temperature, and reduced steeply with increasing Si_2Cl_6 flow rate and attained a constant value above 0.05 ml sec^{-1}. The weight of the siliconized molybdenum plate began to decrease after about 45 h immersion time, and decreased parabolically with increasing immersion time, while that of the bare molybdenum plate decreased linearly. This outstanding reducing effect of a higher Si_2Cl_6 flow rate on the weight decrease of the siliconized molybdenum plate may be attributable to a reduction of pinholes and/or cracks present in the $MoSi_2$ layer obtained at higher Si_2Cl_6 flow rate.

3.3.2. Abrasion resistivity

The weight decrease of the siliconized molybdenum plate when exposed to whirled sea sand in sea water are shown in Fig. 9, in relation to the siliconizing temperature and Si_2Cl_6 flow rate. The thickness of the $MoSi_2$ was fixed at about 10 μm. The weight decrease of the siliconized plate reduced parabolically with increasing siliconizing temperature, and reduced monotonically with increasing Si_2Cl_6 flow rate. The microhardness of the $MoSi_2$ layers increased with increasing siliconizing temperature and Si_2Cl_6 flow rate, similar to the case of using $SiCl_4$ as a silicon source [9]. Thus, it may be concluded that the higher the siliconizing temperature and Si_2Cl_6 flow rate, the higher is the stability attained against sea water corrosion and sea sand abrasion.

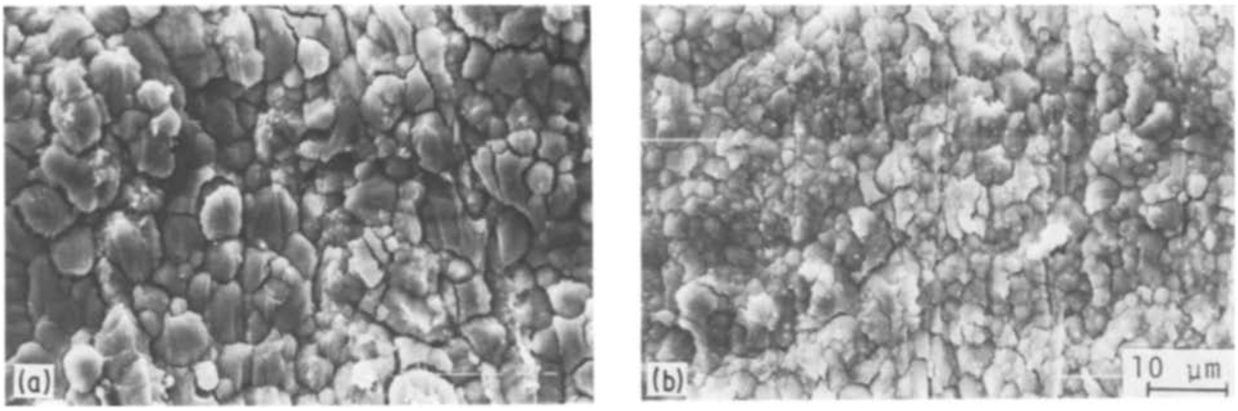

Figure 5 Surface of the siliconized molybdenum plate. Siliconizing temperature: (a) 900° C, (b) 1000° C, Si_2Cl_6 flow rate: 0.05 ml sec^{-1}, H_2 flow rate: 1.95 ml sec^{-1}.

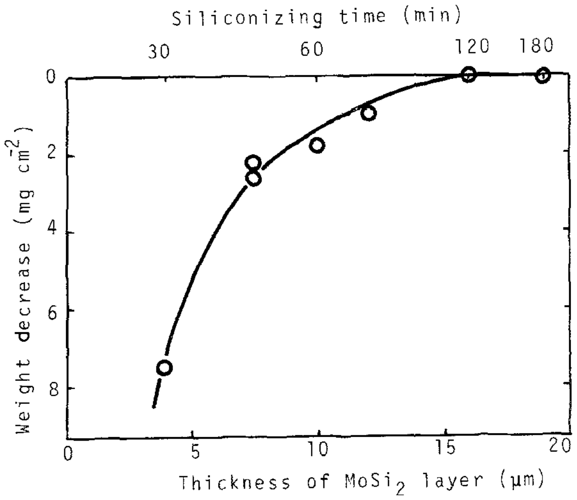

Figure 6 Effect of the thickness of the $MoSi_2$ layers on the weight decrease of the siliconized molybdenum plate by anodic dissolution in 0.2 M H_2SO_4. Siliconizing temperature: 900° C, Si_2Cl_6 flow rate: 0.05 ml sec^{-1}, H_2 flow rate: 1.95 ml sec^{-1}.

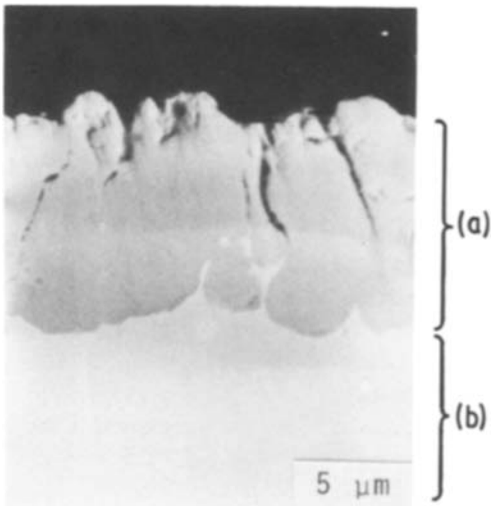

Figure 7 Enlarged view of the polished cross-section of the siliconized molybdenum plate. Siliconizing temperature: 800° C, Si_2Cl_6 flow rate: 0.05 ml sec^{-1}, H_2 flow rate: 1.95 ml sec^{-1}. (a) $MoSi_2$, (b) molybdenum.

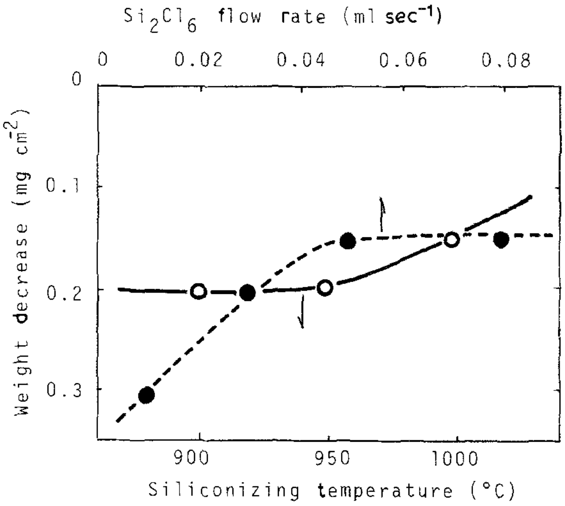

Figure 8 Effect of the (○) siliconizing temperature and (●) Si_2Cl_6 flow rate on the weight decrease by sea water corrosion. Thickness of the $MoSi_2$ layer: 10 μm, immersion time in sea water: 200 h, temperature of sea water: 30° C. (○) Si_2Cl_6 flow rate 0.05 ml sec^{-1}, H_2 flow rate: 1.95 ml sec^{-1}. (●) Siliconizing temperature: 1000° C, total gas flow rate: 2.0 ml sec^{-1}. Weight decrease of the bare molybdenum plate by sea water corrosion was 0.35 mg cm^{-2}.

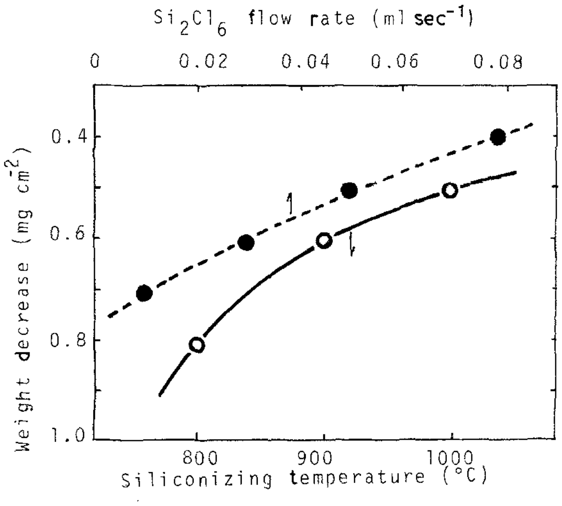

Figure 9 Effect of (○) the siliconizing temperature and (●) Si_2Cl_6 flow rate on the weight decrease by sea sand abrasion. Thickness of the $MoSi_2$ layer: 10 μm, exposure time in whirled sea sand: 100 h, temperature of sea water: 30° C. (○) Si_2Cl_6 flow rate: 0.05 ml sec^{-1}, H_2 flow rate: 1.95 ml sec^{-1}. (●) Siliconizing temperature: 1000° C, total gas flow rate: 2.0 ml sec^{-1}. Weight decrease of the bare molybdenum plate by sea sand abrasion was 0.9 mg cm^{-2}.

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