

Vapour-phase siliconizing of some nickel-base alloys and transition metals using Si_2Cl_6 as a source of silicon

SEIJI MOTOJIMA, MASANORI KOHNO

Department of Industrial Chemistry, Faculty of Engineering, Gifu University, Gifu 501-11, Japan

TATSUHIKO HATTORI

Research Laboratory, Toagosei Chemical Industry Co. Ltd, 1-1 Funami-cho, Minato-ku, Nagoya 455, Japan

Some nickel-base alloys and transition metals were siliconized using hexachlorodisilane (Si_2Cl_6 , b.p. 144°C) in the temperature range 500 to 1000°C , and subsequently their corrosion stabilities were examined. Using hexachlorodisilane as a silicon source, the siliconizing temperature could be lowered by 150°C for Monel, 200°C for Inconel (No. 600), 50°C for titanium and 150°C for molybdenum in comparison with that using silicon tetrachloride. The corrosion stability of Inconel plate against $1\text{N H}_2\text{SO}_4$ and 1N HNO_3 were improved considerably by the siliconizing of the surface. On the other hand, that of Monel against $1\text{N H}_2\text{SO}_4$ was improved outstandingly by the siliconizing of the surface, but not improved against 1N HNO_3 .

1. Introduction

The diffusion coating of metals or alloys with silicon has come to be used fairly widely in recent years to improve their physical and chemical properties, or to protect them against high-temperature oxidation and hot corrosion.

We have developed in recent years the commercial production process of hexachlorodisilane (Si_2Cl_6 , b.p. 144°C). This new reagent has many advantages as the source of chemical vapour diffusion (CVD) or silicon diffusion. We have found that the siliconizing temperature of nickel metal could be lowered by 200 to 300°C using Si_2Cl_6 in place of SiCl_4 as a silicon source [1].

The nickel silicide layers have been most frequently formed on a silicon wafer by the deposition of nickel thin films on silicon followed by the thermal or ion-beam annealing and interdiffusion of nickel and silicon (two-step processes) [2-7].

In this work, we have examined the siliconizing conditions of nickel base-alloys (Inconel No. 600 and Monel) and some of the transition metals (titanium, niobium, tantalum, molybdenum and tungsten) using hexachlorodisilane as a silicon diffusion source, and subsequently their acid corrosion stabilities were examined.

2. Experimental procedures

Metal or alloy plates ($5\text{ mm} \times 5\text{ mm} \times 0.2\text{ mm}$) to be siliconized was set horizontally on a quartz boat which was located in the central part of the horizontal diffusion reaction tube (quartz, 22 mm i.d.). Hexachlorodisilane was saturated into hydrogen and intro-

duced into the reaction zone. X-ray microanalysis was carried out on a polished cross-section of the siliconized plate using an X-ray dispersive microanalyser. The siliconized metal or alloy plates were immersed for 30 min in a 1 N sulphuric acid or 1 N nitric acid solution maintained at 100°C , and the weight decrease was measured.

In these experiments, the reaction conditions were fixed as follows unless otherwise described: reaction time 60 min , total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} , and Si_2Cl_6 flow rate 0.026 ml sec^{-1} (or SiCl_4 flow rate 0.052 ml sec^{-1}).

3. Results and discussion

3.1. Reaction (siliconizing) temperature

Nickel-base alloys (Inconel No. 600 and Monel) were siliconized using Si_2Cl_6 (or SiCl_4) as a silicon source. The relationship between the reaction (siliconizing) temperature and the weight gain obtained is shown in Fig. 1. Using Si_2Cl_6 as a silicon source, a noticeable weight gain of the nickel-base alloy plates (Inconel and Monel) were observed commonly at a temperature about 500°C , and the weight increased with increasing reaction temperature, with a similar rate of increase. On the other hand, using SiCl_4 , which has been commonly used as a silicon source in the vapour-phase siliconizing or in the CVD process, a noticeable weight gain was observed at a temperature as high as 700°C for Inconel and 650°C for Monel. It may be considered that the weight gain is not affected by the different silicon source at a temperature above 800°C and that the same weight gain is attained. It is very useful that the reaction (siliconizing) temperature of

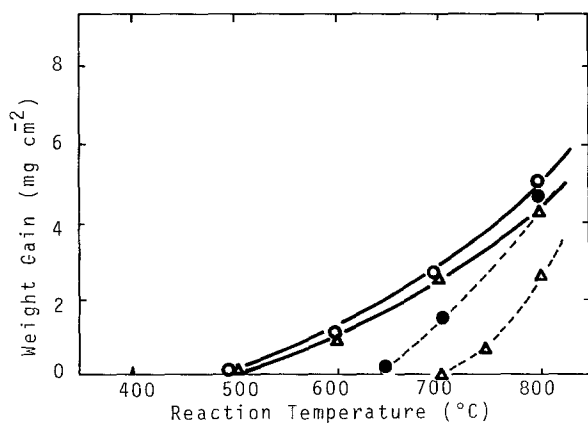


Figure 1 Effect of the reaction (siliconizing) temperature on the weight gain of nickel-base alloys. Reaction time 60 min, total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} . (○) Monel, Si_2Cl_6 flow rate $0.026 \text{ ml sec}^{-1}$; (△) Inconel (No. 600), Si_2Cl_6 flow rate $0.026 \text{ ml sec}^{-1}$; (●) Monel, SiCl_4 flow rate $0.052 \text{ ml sec}^{-1}$; (▲) Inconel (No. 600), SiCl_4 flow rate $0.052 \text{ ml sec}^{-1}$.

the nickel-base alloys is lowered by 150 to 200°C using Si_2Cl_6 in place of SiCl_4 as a silicon source.

At low temperatures, it may be considered that the siliconizing of metals or alloys is rate-determined mainly by the reaction on the substrate surface, i.e. by the deposition of silicon metal on to the surface by the decomposition and/or hydrogen reduction of the silicon source. Thus, it may reasonably be considered that this outstanding decrease effect of Si_2Cl_6 on the siliconizing temperature is probably attributable to its high reaction activity, leading to an abundant formation of active species at lower temperatures.

Relationships between the reaction (siliconizing) temperature of titanium and molybdenum plates and the weight gain by siliconizing are shown in Fig. 2. Using Si_2Cl_6 as a silicon source, a noticeable weight gain of metal plates was observed at a temperature above 500°C for titanium and above 750°C for molybdenum, and the weight increased steeply with increasing reaction temperature. On the other hand, using SiCl_4 , the weight gain was observed above

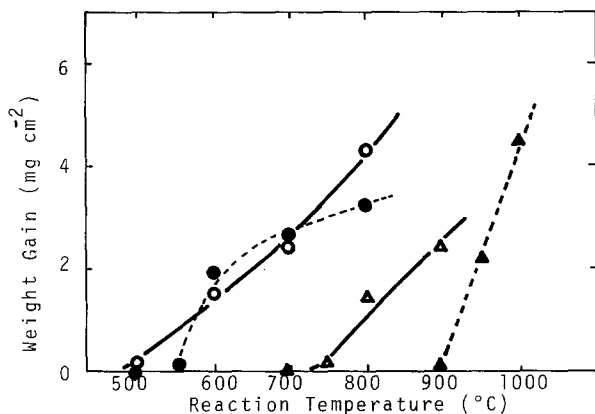


Figure 2 Effect of the reaction (siliconizing) temperature on the weight gain of titanium and molybdenum plates. Reaction time 60 min, total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} . (○) Titanium plate, Si_2Cl_6 flow rate $0.026 \text{ ml sec}^{-1}$; (△) molybdenum plate, Si_2Cl_6 flow rate $0.026 \text{ ml sec}^{-1}$; (●) titanium plate, SiCl_4 flow rate $0.052 \text{ ml sec}^{-1}$; (▲) molybdenum plate, SiCl_4 flow rate $0.052 \text{ ml sec}^{-1}$.

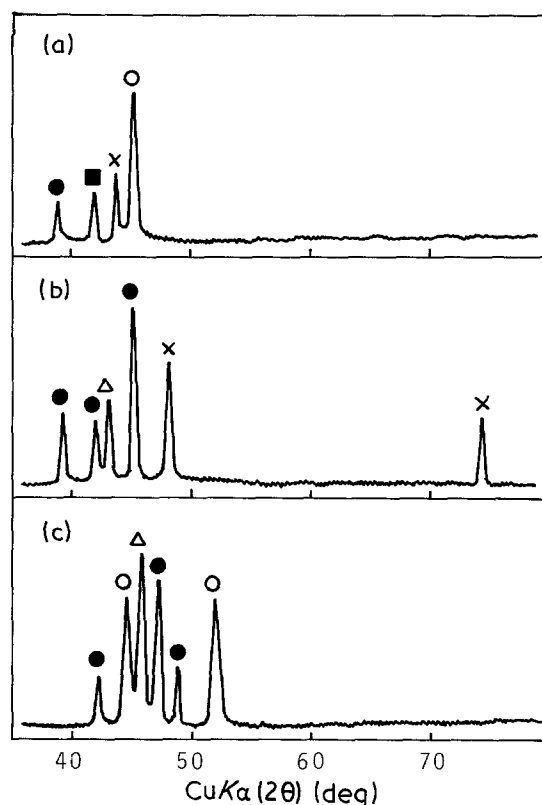


Figure 3 X-ray diffraction patterns of the surface of siliconized Inconel (No. 600) plate. Reaction time: (a) 7.5 min, (b) 15 min, (c) 30 min. Total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} , Si_2Cl_6 flow rate $0.026 \text{ ml sec}^{-1}$. (○) Ni_3Si_2 (ASTM No. 14-429), (●) $\epsilon\text{-Ni}_3\text{Si}_2$ (3-1057), (△) $\sigma\text{-Ni}_2\text{Si}$, (■) $\text{Ni}_{16}\text{Cr}_7$, (x) Inconel.

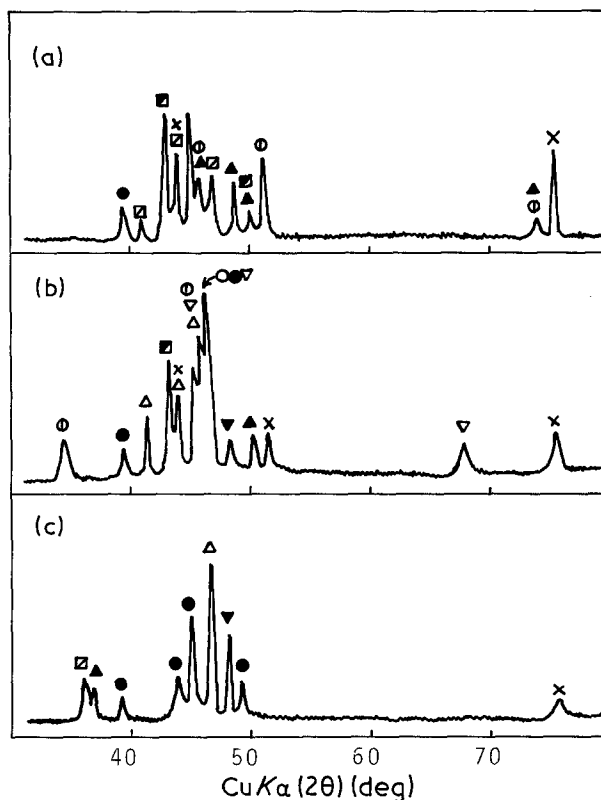


Figure 4 X-ray diffraction patterns of the surface of siliconized Monel plate. Reaction time: (a) 7.5 min, (b) 15 min, (c) 30 min. Total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} , Si_2Cl_6 flow rate $0.026 \text{ ml sec}^{-1}$. (○) Ni_3Si_2 (ASTM No. 14-429), (●) $\epsilon\text{-Ni}_3\text{Si}_2$ (3-1057), (△) $\sigma\text{-Ni}_2\text{Si}$, (▲) $\eta\text{-NiSi}$ (3-1085), (▼) $\gamma\text{-Cu}_5\text{Si}$ (4-0841), (⊙) $\epsilon\text{-Cu}_{15}\text{Si}_4$ (4-0840), (■) Cu_4Si (3-0990), (⊚) Cu-Ni-Si , (▽) $\zeta\text{-NiSi}_3$ (3-1094), (x) Monel metal.

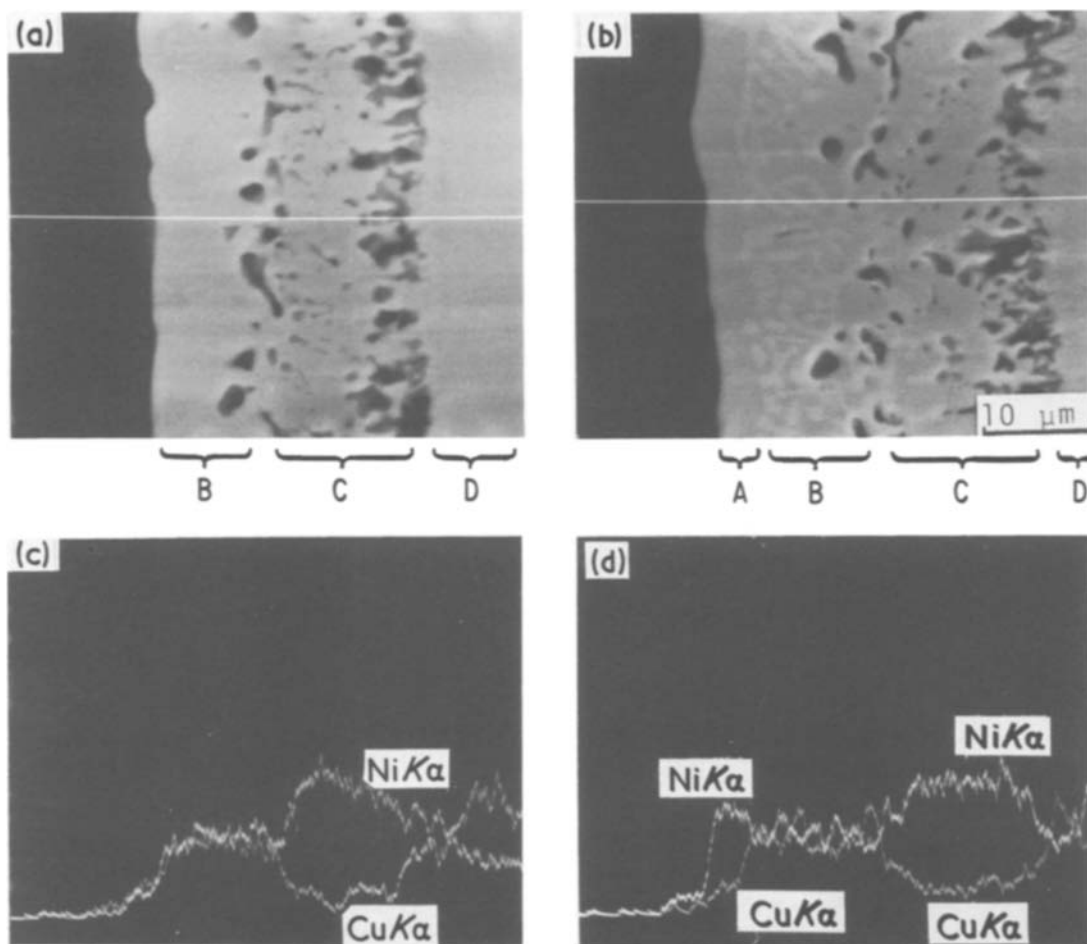


Figure 5 Cross-section of siliconized Monel plate and its X-ray microanalysis. Reaction temperature 900°C , total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} , Si_2Cl_6 flow rate 0.026 ml sec^{-1} . (a): reaction time 7.5 min; (B) outer silicide layer, (C) inner silicide layer, (D) Monel layer. (b): reaction time 15 min; (A) outermost silicide layer, (B) intermediate silicide layer, (C) innermost silicide layer, (D) Monel layer. (c): X-ray microanalysis on Fig. 5a. (d): X-ray microanalysis on Fig. 5b.

550°C for titanium and 900°C for molybdenum. It can be seen that a large effect of Si_2Cl_6 on the lowering of the reaction (siliconizing) temperature was obtained also in the case of molybdenum. But, in other transition metals, such as tantalum, niobium and tungsten, the weight gain was not observed at a temperature below 1150°C in both silicon sources of Si_2Cl_6 and SiCl_4 .

3.2. Composition of the silicide layers

Representative X-ray diffraction patterns on the surface of the Inconel (No. 600) siliconized at a reaction temperature of 900°C for various reaction times are shown in Fig. 3. The compositions of the siliconized layers were almost the same as that of the siliconized nickel plate, except for the presence of an $\text{Ni}_{16}\text{CrSi}_7$ phase at the initial stage of the siliconizing (Fig. 3a). The composition (wt %) of the Inconel (No. 600) is Ni 75, Cr 15 and Fe 10. Among these elements, nickel is the most likely to siliconize at lower temperatures, and thus it resulted in the formation of silicide layers composed mainly of Ni_3Si_2 and $\epsilon\text{-Ni}_3\text{Si}_2$.

In case of Monel, considerable amounts of copper silicides (Cu_4Si , Cu_3Si , $\text{Cu}_{15}\text{Si}_4$) and copper alloys (Cu–Ni–Si) were formed in addition to the nickel silicides in the initial stage of the siliconizing, as can be seen in Fig. 4a. At increasing reaction time, the peaks

of the copper silicides began to disappear, and almost all the peaks for 30 min reaction time were assigned to nickel silicides, except for the presence of the small peaks of Cu–Ni–Si alloy (Fig. 4c). Monel metal contains (Ni + Co) 65%, Cu 33% and Fe 2%. The copper siliconizes easily at lower temperature than the nickel metal.

Cross-sections of the Monel plate siliconized at 900°C using Si_2Cl_6 and its X-ray microanalysis are shown in Fig. 5. Many voids or cavities of various sizes and forms, for example, 0.3 to $1.5\ \mu\text{m}$ diameter or 1 to $3\ \mu\text{m}$ long, can be seen in the silicide layers, especially in the part close to the boundary between the silicide layers and the Monel layer. These observations are very similar to that of siliconized nickel plate [1] or phosphidized nickel plate [8]. It can be seen in Fig. 5 that siliconized layers of the Monel plate are composed of two layers for 7.5 min reaction time (Fig. 5a) and three layers for 15 min (Fig. 5b). The same peak height of $\text{NiK}\alpha$ and $\text{CuK}\alpha$ can be seen in the outer silicide layer of Fig. 5a (B) and in the intermediate layer of Fig. 5b (B) (Figs 5c and d). On the other hand, the peak high of $\text{CuK}\alpha$ in the outermost silicide layer (Fig. 5b (A)) is considerably low in comparison with that of $\text{SiK}\alpha$ (Fig. 5d).

These results are in good agreement with those from the X-ray diffraction patterns from the surface of the

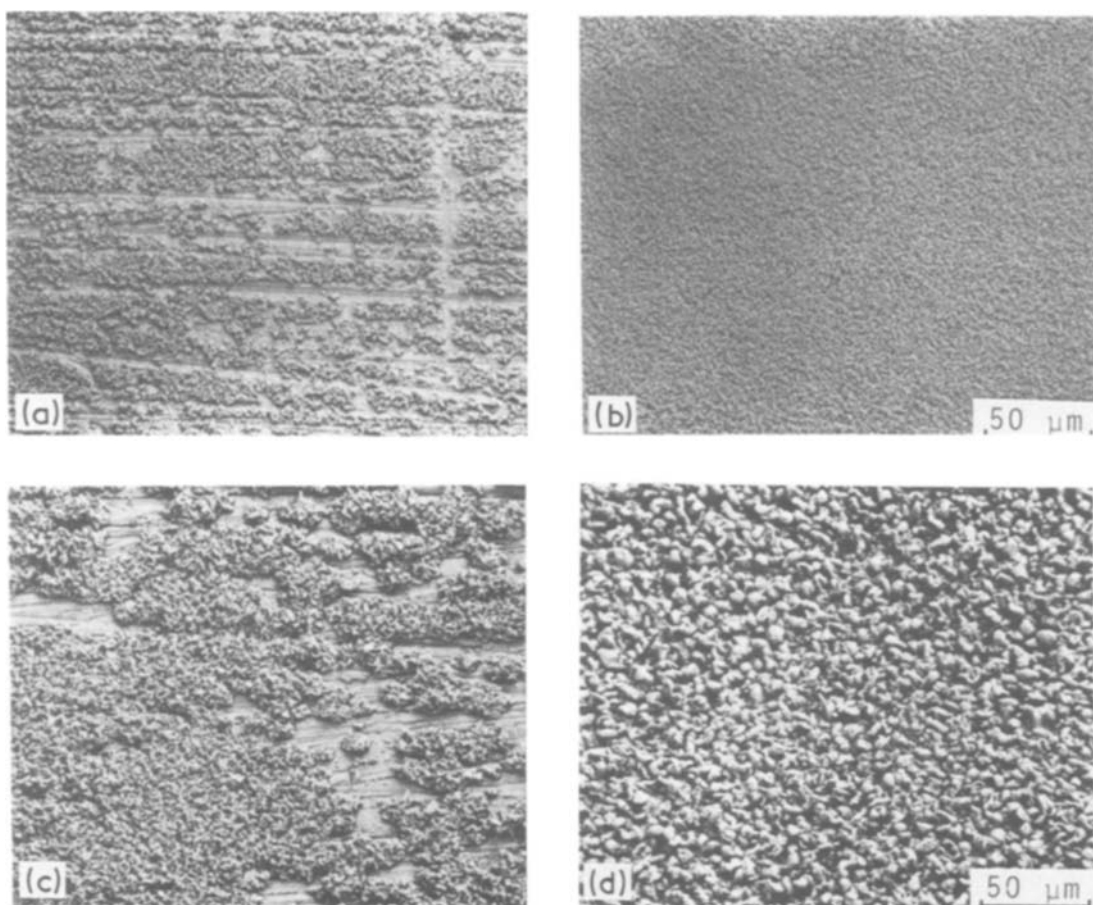


Figure 6 Appearances of the surface of siliconized Inconel (No. 600) plate. Reaction temperature 900°C , reaction time: (a) and (c) 7.5 min, (b) and (d) 15 min. Total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} , Si_2Cl_6 flow rate: (a) and (b) 0.026 ml sec^{-1} , SiCl_4 flow rate: (c) and (d) 0.052 ml sec^{-1} .

silicide layers. Therefore, it may be reasonably considered that the siliconizing of the Monel plate proceeds as follows: (i) the copper is siliconized predominantly in the first place, followed by the siliconizing of the nickel to form mixed phases of copper silicides and nickel silicides; (ii) with increasing thickness of the silicide layer, its outermost layer becomes enriched with nickel silicides, probably caused by the faster in-solid diffusion velocity of the nickel atom compared with that of the copper atom; (iii) the outermost silicide layer, which is mainly composed of nickel silicides, is formed in the final stage of the siliconizing.

3.3. Morphologies of the silicide layers

The surface morphologies of Inconel plate siliconized using Si_2Cl_6 as a silicon source are shown in Figs 6a and b, in which the reaction temperature was fixed at 900°C . It was observed that the siliconizing of Inconel proceeded predominantly at the corners and the part adjacent to the abrasive scars, and small granules of the silicides projected here and there. These projections spread horizontally with increasing reaction time, followed by covering all over the surface of the Inconel plate as can be seen in Fig. 6b. Using SiCl_4 as a silicon source, the sizes of projecting granules were

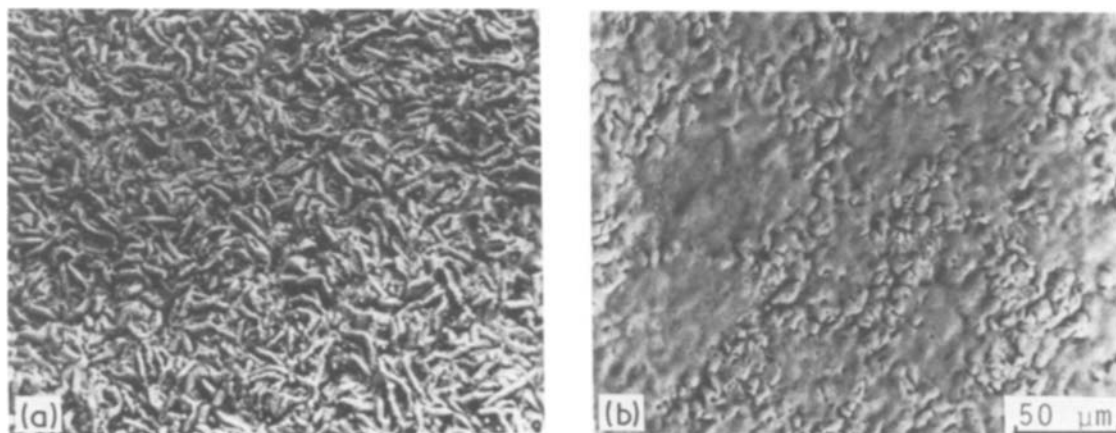


Figure 7 Appearances of the surface of siliconized Monel plate using Si_2Cl_6 as a silicon source. Reaction temperature 900°C , reaction time: (a) 7.5 min, (b) 15 min. Total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} , Si_2Cl_6 flow rate 0.026 ml sec^{-1} .

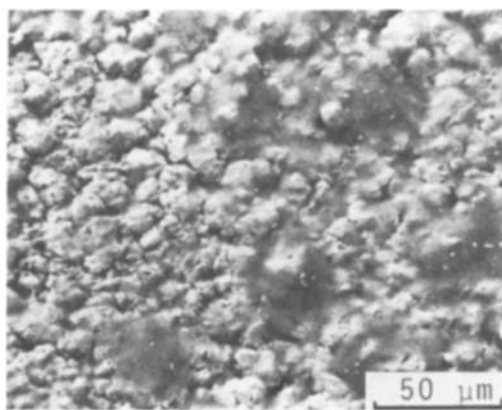


Figure 8 Appearance of the surface of siliconized Monel plate using SiCl_4 as a silicon source. Reaction time 15 min, SiCl_4 flow rate $0.052 \text{ ml sec}^{-1}$. Other siliconizing conditions are the same as for Fig. 7.

in general considerably larger than those obtained using Si_2Cl_6 , as can be seen in Fig. 6d.

In case of the Monel plates siliconized using Si_2Cl_6 , the surface was covered all over with wrinkled silicide layers after 7.5 min reaction time, followed by the deposition of silicide granules as shown in Fig. 7. It may be considered that the wrinkled deposits are silicide layers containing considerable amounts of copper silicides, as shown by the X-ray diffraction and X-ray microanalysis. Using SiCl_4 as a silicon source, the grain size of the silicide layers formed at 15 min reaction time was considerably larger than that obtained using Si_2Cl_6 as shown in Fig. 8.

3.4. Corrosion stability against 1N acid solutions

The weight decreases of siliconized Inconel plate when immersed in 1N nitric acid and 1N sulphuric acid are

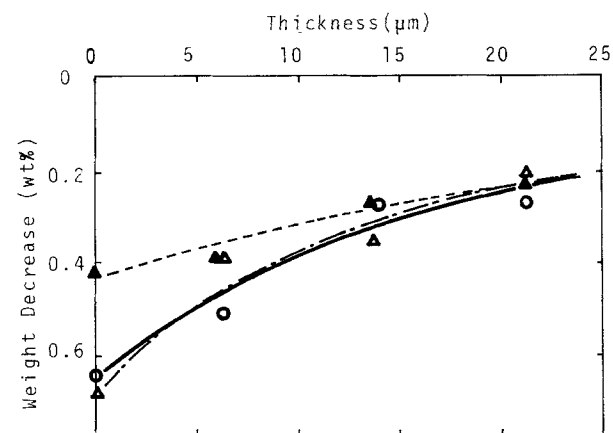


Figure 9 Corrosion stability of siliconized Inconel (No. 600) plate against 1N HNO_3 and 1N H_2SO_4 . Reaction temperature 900°C , total gas flow rate 2.6 ml sec^{-1} , H_2 flow rate 0.65 ml sec^{-1} . Si_2Cl_6 flow rate: (O) $0.026 \text{ ml sec}^{-1}$, SiCl_4 flow rate: (Δ) and (▲) $0.052 \text{ ml sec}^{-1}$. Immersion time in acid solution 30 min, temperature of acid solution 100°C . (▲) Weight decrease of the sample against 1N H_2SO_4 , (O) and (Δ) against 1N HNO_3 .

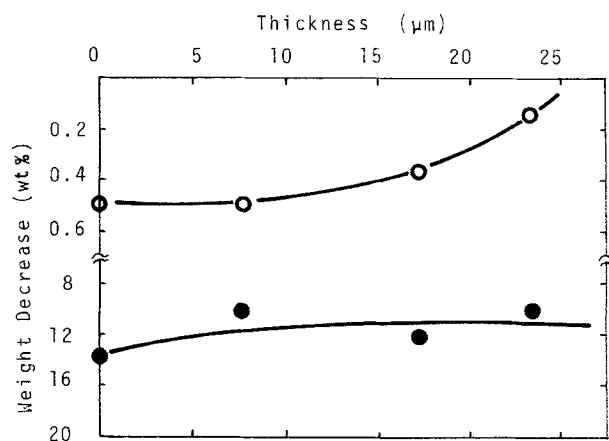


Figure 10 Corrosion stability of siliconized Monel plate against 1N HNO_3 and 1N H_2SO_4 . Reaction conditions and corrosion measurements were the same as for Fig. 9, except that only Si_2Cl_6 was used as a silicon source. (●) Weight decrease of the sample against 1N HNO_3 , (O) against 1N H_2SO_4 .

shown in Fig. 9, in which the siliconizing temperature was fixed at 900°C . The weight decrease of the siliconized Inconel plate when immersed in 1N nitric acid reduced monotonically with increasing thickness of the silicide layers, and was half that of the bare Inconel plate for $15 \mu\text{m}$ thickness. A similar reduction of the weight decrease was observed against 1N sulphuric acid.

The weight decreases of siliconized Monel plate when immersed in 1N acid solutions are shown in Fig. 10. It can be seen that the stability of Monel plate against 1N sulphuric acid was improved by the siliconizing, and the weight decrease of the siliconized Monel plate with about $25 \mu\text{m}$ thickness of silicide layers was a fifth of that of the bare Monel plate. On the other hand, the stability of the Monel plate against 1N nitric acid was not improved by the siliconizing of the surface.

References

1. S. MOTOJIMA, M. KOHNO and T. HATTORI, *J. Mater. Sci.* **22** (1987) 547.
2. K. N. TU, E. I. ALESSAUDRINI, W. K. CHU, H. KROÛLE and J. W. MAYER, *Jpn. J. Appl. Phys.* **13** Suppl. 2, Part 1 (1974) 669.
3. T. G. FINSTAD, J. W. MAYER and M-A. NICOLET, *Thin Solid Films* **51** (1978) 391.
4. R. PRETORIUS, C. L. RAMITTER, S. S. LAU and M-A. NICOLET, *Appl. Phys. Lett.* **30** (1977) 501.
5. J. E. E. BAYLIN, H. A. ATWATER, D. GUPTA and F. M. D'HEURLE, *Thin Solid Films* **93** (1982) 255.
6. A. I. RODIONOV and V. A. USKOV, *Izv. Vyssh. Uchebn. Zaved. Fiz.* **28** (1985) 78 (*Chem. Abstr.* **102** (1985) 226315t).
7. B. L. MEILER, *Poverkhnost* **4** (1985) 67 (*Chem. Abstr.* **102** (1985) 195982b).
8. S. MOTOJIMA, M. NAITO and M. HAYASHI, *J. Cryst. Growth* **73** (1985) 111.

Received 18 March
and accepted 2 June 1986