

Fe—Si Composite Coatings

J. HÍVEŠ, M. KORENKO, and P. FELLNER

*Department of Inorganic Technology, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava
e-mail: hives@chtf.stuba.sk*

Received 10 February 2000

Fe—Si composite layers on a steel substrate were prepared by codeposition of silicon powders with electrolytically deposited iron. The composite layers were thermally treated at 800 °C for 2 h and 4 h. It was found that microhardness and high temperatures oxidation resistance of the Fe—Si thermally treated composite layers are remarkably higher than those of steel substrate used. Microhardness of the composite layers has achieved up to 1000 N mm⁻².

Composite coatings consisting of a metal matrix with dispersed fine particles or fibres made of different materials have been studied extensively [1—7]. The purpose of a composite coating deposited on a metal substrate is to obtain a surface having various desired properties, such as wear resistance, high temperature corrosion protection, oxidation resistance, self-lubrication, etc. When the dispersed metallic or metalloid particles react at elevated temperatures with the metal matrix or with the metal substrate, formation of alloys and intermetallic compounds is observed. These layers might have properties different from those prepared without the heat treatment.

In this paper preparation of composite coatings made of electrodeposited iron matrix and dispersed silicon particles is described. The influence of thermal treatment on hardness of the composite layers is discussed. The main aim was to obtain layers with higher hardness and high temperature oxidation resistance in comparison with the basic steel substrate.

EXPERIMENTAL

The iron matrix was prepared from sulfate electrolyte having composition: $\rho(\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}) = 400 \text{ g dm}^{-3}$, $\rho(\text{NaCl}) = 70 \text{ g dm}^{-3}$, $\rho(\text{NaBF}_4) = 20 \text{ g dm}^{-3}$. 2 cm³ of glycerol were also added. pH of the electrolyte ranged from 2.0 to 2.5 and it was maintained by sulfuric acid. The content of silicon particles in the suspension ranged from 10 g dm⁻³ to 110 g dm⁻³. Silicon powder consisted of particles with diameter less than 10 μm (25 % of the mixture) and agglomerates with diameter less than 50 μm (75 %).

In some experiments silicon particles ground together with iron powder were used. It was expected that the surface silicon particles would be enriched in iron [8, 9] (preparation of these particles was made at the Institute of Material Research SAS, Košice). Si

powder was kept in suspension by a magnetic stirrer or in the case of magnetic particles by a single-impeller agitator.

The experimental electrolytic cell consisted of a cylindrical glass cell (diameter 70 mm, height 90 mm) with the volume of electrolyte 250 cm³. The temperature of the electrolyte was kept constant (70 ± 1) °C using an ultrathermostat. The composite layer was deposited on mild steel base of dimensions ($l \times h \times t$) 25 mm $\times$ 15 mm $\times$ 0.70 mm placed in the cell. The anode 250 mm $\times$ 70 mm $\times$ 0.70 mm was made of the same material as the cathode. It was placed in the protection cotton bag. The cathodic current density was 3 A dm⁻² and time of the electrodeposition was 60 min. These parameters and the rate of stirring were optimized in order to obtain the desired content of silicon in the composite layer [10—12]. The thickness of obtained composite layer was around 100 μm . The content of silicon in the composite layer was determined by X-ray microanalysis (Jeol JXA 840 analyzer). This value might be higher than that obtained by the chemical analysis [13].

One set of steel samples covered with the composite Fe—Si layer was heated in an argon atmosphere at 800 °C or 850 °C for 2 h and 4 h, respectively. Microhardness of the layers was measured by the microhardness tester D 32 (Zeiss, Jena) at five different places of the sample. Average values are reported. The adhesiveness of the layers to the substrate was estimated by bending the sample and by visual observation of cracks formation.

RESULTS AND DISCUSSION

In the first sets of experiments the influence of the stirring rate of the suspension of silicon particles on the content of silicon in the composite layer was investigated. This dependence is shown in Fig. 1. It can be

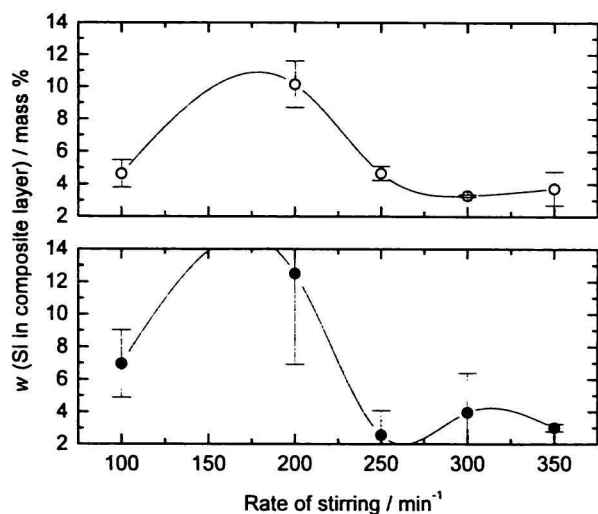


Fig. 1. Content of the silicon in iron matrix vs. rate of magnetic stirring. The concentration of the Si particles in suspension: $\circ$ 10 g dm^{-3} , $\bullet$ 110 g dm^{-3} .

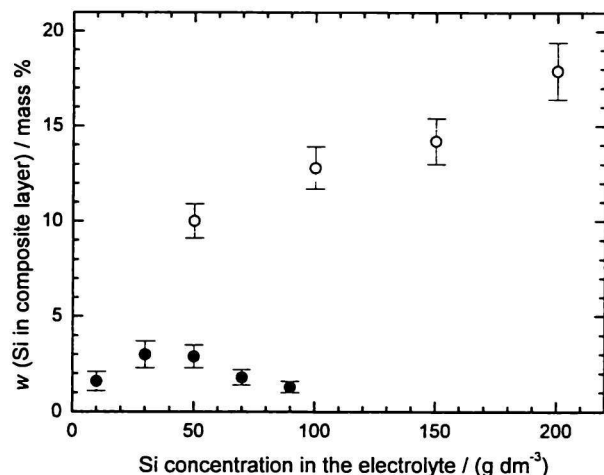


Fig. 2. The content of iron-coated silicon particles and non-coated silicon particles in the prepared composite layers, a single-impeller agitator – stirring rate 200 min^{-1} . $\circ$ Si particles, $\bullet$ Si particles covered with iron.

seen that there is an optimum rate of stirring at which a maximum content of silicon in the electrodeposited layer is achieved. This stirring rate depends neither on the concentration of particles in the suspension nor on treatment of their surface. Optimal stirring rate corresponds to the minimum rate of stirring sufficient for keeping solid particles in suspension. All results presented in this paper were obtained at this stirring rate, viz. 200 min^{-1} .

In Fig. 2, the content of silicon in the electrodeposited iron layer is plotted as a function of concentration of silicon particles in the suspension. It can be seen that pretreatment of silicon powder by grinding it with iron particles had negative influence on

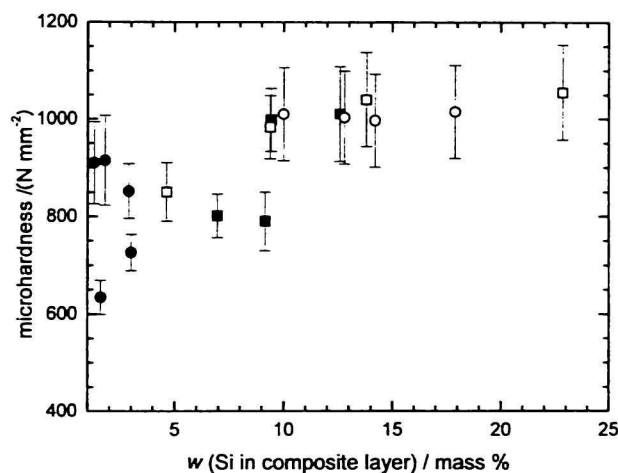


Fig. 3. Microhardness of thermally treated composite layers vs. Si concentration in the layer. $\blacksquare$ 2 h, 800°C ; $\square$ 4 h, 800°C ; $\circ$ 2 h, 850°C ; $\bullet$ 4 h, 850°C , pretreated Si.

the content of silicon in the composite layer. This is an opposite result to the one reported by *Fellner* and *Cong* [14] who covered surface of silicon particles by electroless nickel. In the cited work the increase of electrical conductivity of particles influenced positively concentration of silicon in electrodeposited nickel layer. The lower content of pretreated silicon in the electrodeposited iron layer observed in this work can be explained by rapid dissolution of iron covering silicon particles into the electrolyte. The result of this reaction are hydrogen bubbles which decrease the effective contact between the silicon particles and the cathode.

In Fig. 3, the dependence of microhardness of thermally treated composite layers on the content of silicon in the layer is shown. These results are compared with microhardness of the steel substrate and of thermally untreated composite layers. It can be seen that while microhardness HV of the steel substrate equals $(115 \pm 30) \text{ N mm}^{-2}$, microhardness of thermally untreated composite layers is in the range of $(350\text{--}600) \text{ N mm}^{-2}$ and microhardness of the thermally treated layers achieves up to 1000 N mm^{-2} . Microhardness of the electrodeposited iron layer was ca. 300 N mm^{-2} .

Microhardness of the layers thermally treated for 4 h was within the limits of error the same as of those treated for 2 h. However, longer thermal treatment (4 h) decreased adhesiveness of the composite layer to the steel substrate. This might be caused by the formation of brittle silicides on the boundary steel substrate–composite layer. However, X-ray diffraction did not give any unambiguous answer to this question. No new diffraction lines corresponding to the formation of silicides were observed. It might be suggested that under the thermal treatment only solid solutions in the system Fe–Si are formed. When the layers were thermally treated for 2 h, their adhesive-

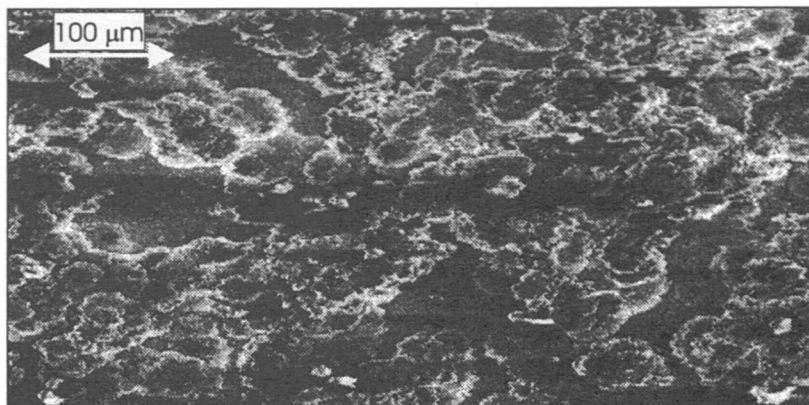


Fig. 4. Surface morphology of layers without thermal treatment.

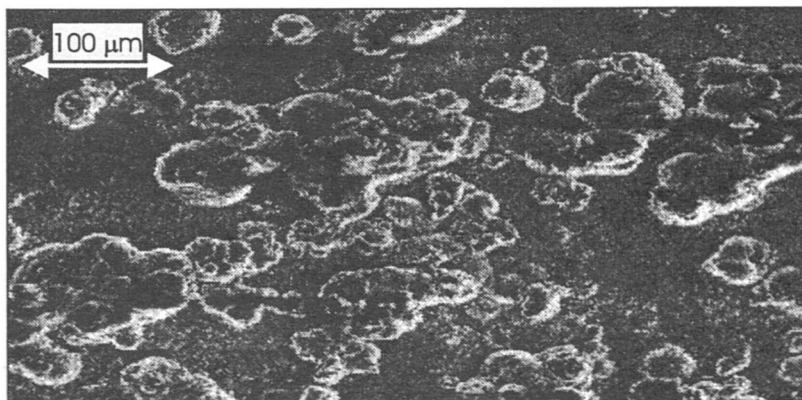


Fig. 5. Surface morphology of layers, thermal treatment at 800 °C for 2 h.



Fig. 6. Surface morphology of layers, thermal treatment at 800 °C for 4 h.

ness to steel substrate was very good. Even after fracture of the sample or after cutting steel sheet covered with composite layer in 1 mm strips, the thermally treated composite layer did not peel off.

Figs. 4–6 show the influence of heating on the surface morphology of the composite layers. It can be seen that the thermal treatment makes the surface more homogeneous.

The influence of thermal treatment on the composite layer can be also seen from the distribution of iron and silicon in the cross-section of the sample (Fig. 7) made by an X-ray microanalyzer.

The line profiles of the cross-section of the prepared

composite coatings before and after thermal treatment are presented in Figs. 8 and 9. One can see that Si peaks are less sharp and wider in the case of thermal treatment.

CONCLUSION

It is shown that composite coatings of electrolytically deposited iron with Si particles improve microhardness of the base steel material. Preparation of these composite layers is described. It is shown that covering silicon powders by electroless iron decreases the content of silicon in composite layers. The ther-

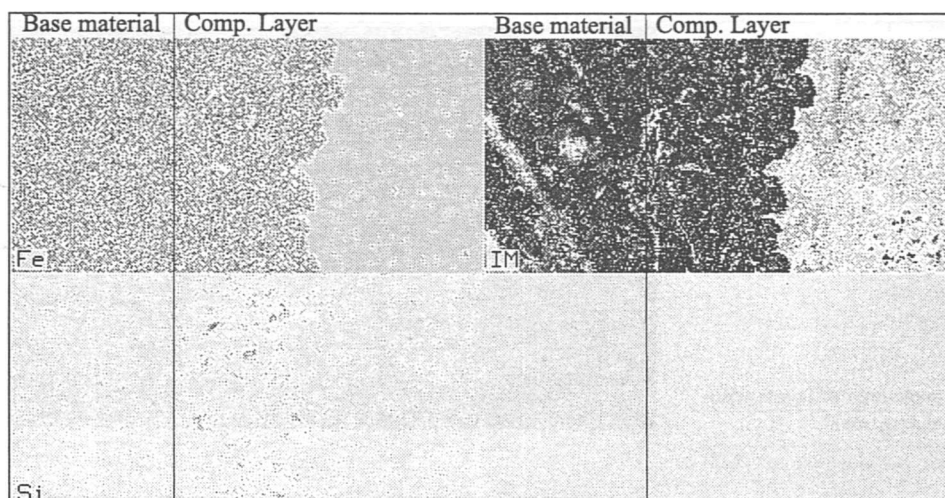


Fig. 7. Fe and Si mapping on the cross-section of the prepared composite layer. Fe mapping – upper left, Si mapping – lower left, cross-section image – upper right, blank – lower right.

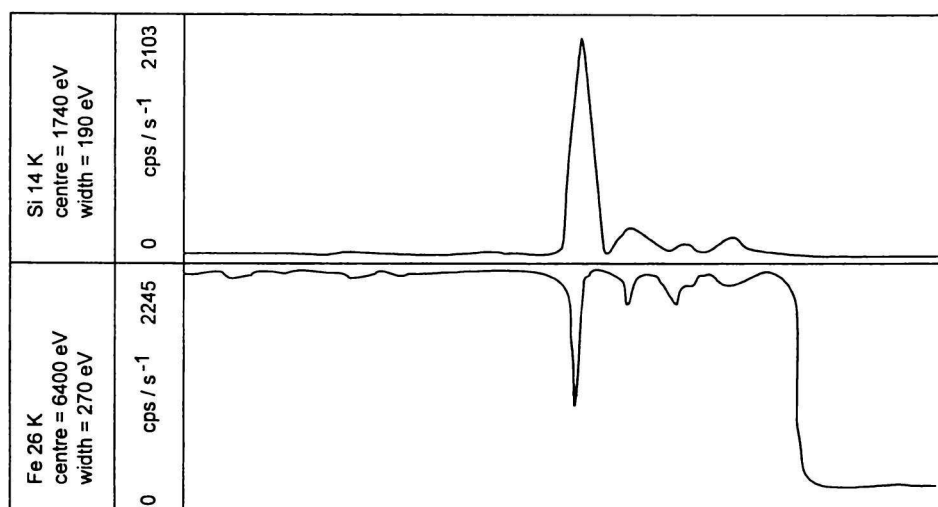


Fig. 8. Line profile of the cross-section of the prepared composite layer, before thermal treatment.

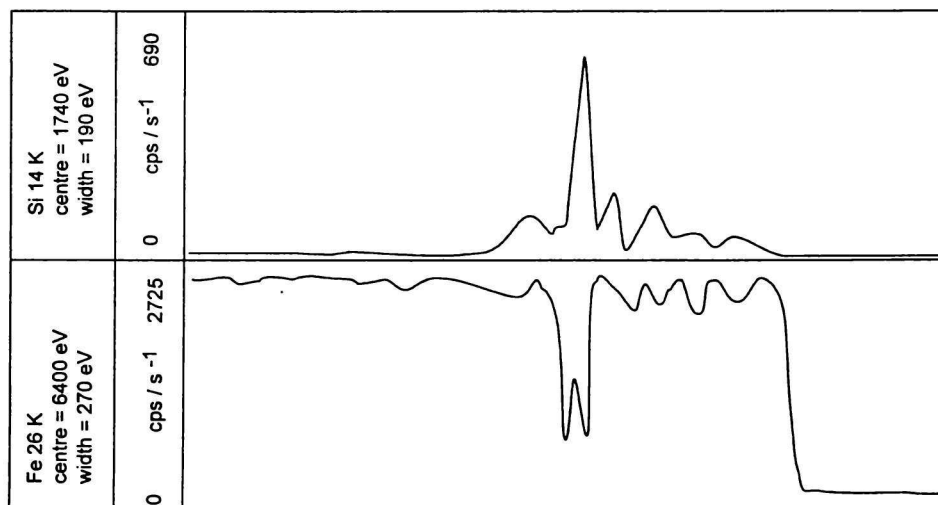


Fig. 9. Line profile of the cross-section of the prepared composite layer, after thermal treatment.

mal treatment improved adhesiveness of the deposited layers to the substrate and increased microhardness of prepared composite layers.

Acknowledgements. This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic as the grant project No. 1/6251/99.

REFERENCES

1. Greco, V. P., *Plating and Surface Finishing* 62, 1989.
2. Antropov, L. I. and Lebedinski, Yu. N., *Kompozitsionnye elektrokhimicheskie pokrytiya i materialy*. Tekhnika, Kiev, 1986.
3. Saifullin, R. S., *Neorganicheskie kompozitsionnye materialy*. Khimiya, Moscow, 1983.
4. Saifullin, R. S., *Physical Chemistry of Inorganic Polymeric and Composite Materials*. Horwood, Chichester, 1992.
5. Guglielmi, N., *J. Electrochem. Soc.* 119, 1009 (1972).
6. Celis, J. P. and Roos, J. R., *J. Electrochem. Soc.* 124, 1977 (1977).
7. Hayashi, H., Izumi, S., and Tari, I., *J. Electrochem. Soc.* 140, 362 (1993).
8. Tkáčová, K., *Mechanical Activation of Minerals*. Elsevier, New York, 1989.
9. Gálová, M., Oriňáková, R., and Lux, L., *J. Solid State Electrochem.* 2, 2 (1998).
10. Machalová, I., *Thesis*. Department of Inorganic Technology, Slovak University of Technology, Bratislava, 1991.
11. Večera, M., *Diploma work*. Department of Inorganic Technology, Slovak University of Technology, Bratislava, 1997.
12. Korenko, M., *Diploma work*. Department of Inorganic Technology, Slovak University of Technology, Bratislava, 1998.
13. Cong, P. K. and Fellner, P., *Chem. Pap.* 48, 326 (1994).
14. Fellner, P. and Cong, P. K., *Surf. Coat. Technol.* 82, 317 (1996).