Creating Functionally Graded Microstructures by Electrodeposition & Diffusion Annealing

By F. Czerwinski

Fe-14%Ni alloy coatings were electrodeposited onto 0.9 percent carbon steel substrate, then subjected to thermal and thermochemical treatments. The diffusion of carbon between the substrate, carburizing environment and the coating, led to formation of graded microstructures with various microhardness profiles. A difference in phase transformation temperature between the steel substrate and the coating was a key factor in creating the graded microstructures.

Functionally graded materials offer new strategies for the implementation of high-performance structures in engineering components. They comprise continuous or discontinuous varying composition and/or microstructure over definable geometric orientations or distances. As a result, they exhibit some unique properties beneficial for realistic application environments. For example, the use of functionally graded systems in high-temperature components can enhance the adhesion and thermomechanical response of ceramic coatings deposited on metallic substrates.¹

In general, many existing technologies are readily adaptable for the manufacture of functionally graded materials. These techniques range from gas phase processing, including plasma spraying, ion plating and chemical vapor deposition through liquid phase processing, which involves eutectic reactions, electrodeposition and thermal spraying.^{2,3} Another viable method is solid phase processing by applying powder metallurgy and self-propagating synthesis.^{4,5}

This study explored another concept of creating functionally graded microstructures by a combination of electrodeposition and diffusion annealing. As an example, the Fe-Ni alloy coating is first deposited onto a carbon steel substrate that is subsequently subjected to thermal or thermochemical treatments. In this concept, a difference in phase transformation temperature between the substrate and the coating is of essential importance for the formation of graded microstructures.

Experimental Procedure

High-speed electrodeposition of Fe-Ni alloy coatings was performed from an electrolyte composed of nickel chloride and ferrous chloride with concentrations of 200 and 300 g/ dm³, respectively. The process was conducted galvanostatically at a current density of 250 mA/cm², a pH of 1.5 and an electrolyte temperature of 85 °C. Pure iron was used as an anode. The coatings were deposited onto steel containing 0.9 percent C and impurities at a level of 0.06 percent Ni, 0.04 percent Cr, 0.20 percent Si, 0.28 percent Mn, 0.014 percent P and 0.015 percent S (all are wt pct). The steel surface was prepared by mechanical polishing up to 800-grit SiC paper, followed by chemical polishing in 10percent hydrochloric acid. The coating, with a thickness of approximately 400 μ m, contained 14 percent Ni and a low level of impurities (*e.g.*, 0.062% Si, 0.022% P, 0.014% S and 0.032% Cr).

Diffusion annealing was conducted at temperatures up to 1,000 °C in a flowing argon atmosphere. The specimens $(10 \times 10 \times 5 \text{ mm})$ were cooled from an annealing temperature in air. The carburizing was performed at 710 and 920 °C in a solid mixture containing 90 percent charcoal and 10 percent Na₂CO₃. The microstructure on the cross-sectional and planar specimens was examined using optical- and transmission-electron microscopy. Samples for optical microscopy were etched in a 3-percent solution of nitric acid in ethanol. Hardness measurements were performed on polished cross sections at different distances from the substrate/deposit interface, using a Vickers microhardness tester with a pyramidal indenter. A load of 100 g was applied and the final value quoted is the average of at least five measurements.

Results & Discussion

In an as-deposited state, the coatings were composed of columnar grains with the longitudinal axis parallel to the growth direction and normal to the substrate surface. Many of the grains had a columnar length almost equal to the thickness of the coating. For an average content of 14 percent Ni, the phase analysis detected only the presence of the α phase.⁶ The purpose of the post-deposition heat treatment was to modify the chemical composition and the microstructure of the coating as well as the surface region of the substrate. The major change in chemistry after annealing was an enrichment



Fig. 1—Differences in phase transformation temperatures between the Fe-14% Ni coating and Fe-0.9% C steel substrate & schematics of the carbon redistribution within the substrate & the coating following annealing at temperatures indicated.



Fig. 2—Graded microstructures produced after thermal & thermochemical treatments: (a) 650 °C, 0.5 hr; (b) 710 °C, 0.5 hr; (c,d) 1000 °C, 0.5 hr.

of the coating in carbon, diffusing from the substrate. At higher temperatures, inward diffusion of Ni to the substrate made a noticeable contribution. Moreover, the possibility of increasing the carbon content in the coating was tested by applying an external source of carbon through the carburization process.

The difference in phase transformation temperatures between the steel substrate and the Fe-Ni deposit is an important factor of the thermal treatment proposed (Fig. 1). At temperatures below 727 °C, the steel containing 0.9 percent C is composed essentially of pearlite (*i.e.*, α + Fe₃C). Such a rough eutectoidal composition was deliberately selected to trace easily the diffusion of carbon on the basis of microstructural observations. To simplify the analysis, the presence of some traces of secondary Fe₃C was neglected. At the same time, the temperature of the α - γ transformation of the coating is approximately 680 °C.7 By selecting the temperature between 680 and 727 °C, the thermal treatment can be conducted at the coexistence temperature of an α (substrate) - γ (coating) diffusion couple. By contrast, during annealing at a temperature above 727 °C, both the steel substrate and the coating were composed exclusively of austenite (γ). The coexistence of the α - γ or the γ - γ diffusion couples leads to essentially a different redistribution of carbon across the coating thickness and the surface region of the substrate, as shown in Fig. 1.

Thermal Treatment at Coexistence of the α - γ Diffusion Couple

During annealing at temperatures below the α - γ transformation of the steel substrate, the coating already contained a significant amount of the γ phase, which is the solid solution of Ni in γ Fe (fcc). It is clear that the substrate during annealing remained fully pearlitic. Thus at a high temperature, cementite coagulated, dissolved and acted as a source of carbon, diffusing toward the coating. Assuming that the diffusion coefficient of carbon in ferrite D_{C}^{α} at 710 °C is 6.8 × 10⁻¹¹ m²/ sec,⁸ the mean square root displacement for carbon in ferrite is 350 µm after 30 min. This means that carbon was easily supplied to the substrate-coating interface. Because of a relatively low temperature, the transport of large amounts of carbon for long distances within the coating was difficult. After 30 min of annealing at 710 °C, the mean square root displacement of the carbon in austenite is 32 µm. The calculation was performed assuming a diffusion coefficient of carbon in austenite of D_{C}^{γ} at 710 °C being equal to 5.5×10^{-10} 13 m²/sec. 8 The influence of the carbon and nickel content on carbon diffusion was here neglected. It is well established, however, that D_{C}^{γ} increases by increasing the atomic ratio of C/Fe.9 Moreover, in austenites containing as much as 25 percent Ni, the diffusivity of carbon increases with increasing nickel content.¹⁰ There is also preferential diffusion of carbon along the austenite-ferrite grain boundaries and the $D_{c}^{\gamma}(gb)\delta/\delta$ D_{C}^{γ} (vol) ratio is about 2 at 800 °C, where D_{C}^{γ} (gb) and D_{C}^{γ} (vol) are diffusion coefficients along the interface and in the bulk, and δ is the width of the grain boundary. 11 The exact diffusion range is therefore larger than that estimated above.

The carbon concentration gradient within the coating caused differences in the microstructures formed after cooling from annealing temperatures. An exemplary cross sectional image of the microstructure formed after cooling from the two phase ($\alpha - \gamma$) range of the coating, is shown in Fig. 2a. The ferrite, which did not transform, is seen as a white phase, while the

products of austenite transformation are dark. It is clear that by increasing the distance from the substrate-deposit interface, the volume fraction of the remaining ferrite increases. The coating cooled from the one-phase region (γ) comprises also continuously graded microstructures caused primarily by the carbon content. According to the TEM microscopic observation, this changes from bainite, in the near-substrate region, to an acicular ferrite located close to the coating surface. The heat treatment not only influenced the microstructure of the coating but also the microstructure of the substrate. As a result of outward diffusion of carbon, a thin layer of pure ferrite was formed at the substrate-coating interface. At the temperature and for the time shown above, the ferrite layer reached a thickness of approximately 10 µm (Fig. 2b).

An effective way to increase the amount of carbon transported to the coating is by using its external source. Because the coating is transformed to austenite at approximately 680 °C, carburizing can also be conducted at a temperature below the α - γ transformation temperature of the substrate. It should be emphasized that at the high temperatures of carburizing, the substrate also acted as a source of carbon and, in fact, carbon diffused simultaneously from two interfaces: the substrate-coating and the gas-coating.

Thermal Treatment at a Coexistence

of the γ - γ Diffusion Couple

Significantly different changes in coating microstructure were observed after annealing at temperatures higher than the α - γ transformation of the steel substrate. For example, at 1,000 °C, the diffusion coefficient of carbon in austenite $D_{\rm C}{}^{\gamma}$ is equal to 2.5×10^{-11} m²sec.⁸ The calculated root mean square displacement for carbon after 30 min is 268 μ m, which means that carbon can almost penetrate the entire coating thickness.

At temperatures above 727 °C, diffusion of the carbon within the substrate, toward the substrate-coating interface, took place in the austenite. As a result, the distribution of carbon in the substrate after cooling had a character signifi-



Fig. 3—Hardness of the coating & surface layer of the steel substrate after thermal and thermochemical treatments at temperatures indicated. Times of diffusion annealing and carburizing were 30 & 90 min, respectively.

cantly different from that described in the previous section. In general, the substrate did not show a ferritic layer but a continuously graded microstructure composed of ferrite and pearlite with an increasing contribution of pearlite while moving inward from the substrate-coating interface. After 30 min annealing at 1,000 °C, the ferritic and pearlitic region was approximately 400 μ m thick (Fig. 2c).

Because of a high flux of carbon diffusing from the substrate, the coating exhibited, after cooling, a microstructure composed of martensite and retained austenite (Fig. 2d). Again, the microstructure changed gradually across the coating thickness. The high enrichment of coating in carbon, especially in the regions located close to the substrate-coating interface, accompanied by a content of 14 percent Ni, led to a significant volume fraction of retained austenite.

Carburizing at temperatures above 727 °C allowed a higher enrichment of the coating in carbon, which influenced the coating microstructure. While the coating carburized at 710 °C had a microstructure of acicular ferrite and bainite, the coating carburized at 920 °C was composed of martensite and retained austenite.

The Hardness Profile Across the Graded Microstructure The changes in the composition and microstructure of the coatings and the surface regions of the substrates were accompanied by significant variations in their hardness (Fig. 3). It should be mentioned that the Fe-14% Ni coating deposited on pure iron (0.003% C) had, after annealing at 920 °C, a hardness of about 200 HV. This finding supports the critical role of carbon in controlling the coating hardness. The hardness profiles, shown in Fig. 3, can easily be explained on the basis of the microstructural observations. The maximum hardness of 600-700 HV was achieved after carburizing at 920 °C because of the formation of martensite. The reduced hardness in the regions close to the substrate and the outer surface was caused by a higher volume fraction of the retained austenite (areas marked 1 and 2 in Fig. 2c).

The mixture of hard martensite with an austenitic matrix is a microstructure that has good wear behavior. By selecting the appropriate volume fractions of both phases, the required hardness can be obtained. The ferritic layer, formed at the coating-substrate interface, is also beneficial in some applications. Such a thin ferritic layer has the function of arresting microcracks that may nucleate during the service of the coating and prevent crack propagation toward the coated element.¹² In layered material, strong adhesion is usually obtained when an alloy formation occurs as a result of diffusion between the substrate and the coating.¹³ An observation of the substrate-coating interface indicates that in addition to the carbon diffusion towards the coating, there is also nickel diffusion toward the substrate. The diffusion range of nickel is seen as a thin film within the ferritic layer (Fig. 2b), and as a brighter contrast at grain boundaries of the former austenite (Fig. 2d). Here the distinct interface, present after deposition, is replaced by the continuously graded diffusion region, considered beneficial for coating adhesion.

Finally, thermal treatment affects the internal stress in the coating. As reported previously,^{6,14} the Fe-Ni coatings after deposition are under tensile stress, reaching a level of approximately 800 MPa in the near-substrate region, then decreasing to 300 MPa close to the outer surface. It is clearly established that tensile stresses enhance the nucleation of microcracks and reduce the fatigue life of a coated part.¹³ The

stresses and cracks limit the application of hard coatings in an as-deposited state on the engineering components subjected to fatigue.^{15,16} The annealing primarily relieves the tensile stress. The bainitic or martensitic transformations, which take place during subsequent cooling, generally lead to an increase in the coating volume and to the origin of compressive stress, which is beneficial for fatigue life. It indicates that the two-step surface treatment described here may be an effective way of manufacturing hard coatings without risk of reducing the fatigue life of a coated part.

Conclusions

The experiments of this study reveal that the combination of electrodeposition with thermal or thermochemical treatments is an effective way of fabricating functionally graded materials. The annealing of the Fe-Ni coating on the steel substrate leads to the diffusion of carbon from the substrate to the coating. The depletion of the substrate and the enrichment of the coating in carbon depend on the phases coexisting at the reaction temperatures. It is expected that the electrolytic coatings with a microstructure modified by the post-deposition treatment described and accompanied by chemical and microstructural changes in the substrate, will exhibit superior properties for some applications in terms of adhesion, wear resistance, corrosion resistance and fatigue life.

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