

Characterization of Electrodeposited Iron From a Chloride Bath without Anodic Etching

By Xintan Hu & Xiaolei Xu

Samples were activated in a cold chloride plating bath with symmetrical AC rather than the anodic etching treatment traditionally used. The plating process was carried out with asymmetrical AC, which was gradually changed to DC. The microstructure and morphology of the iron deposit were examined. The results show that the columnar grain of the deposit has a (211) texture, with a secondary (110) texture. The (211) texture coefficient has the same trend as surface hardness while deposition develops, and there is a tendency for the deposit to be epitaxial with the substrate. An initial deposit with low stress was obtained that can mitigate the disruptive effect of high stress created in the DC deposit. The adherent, dense deposit demonstrates high surface hardness and has been used for restoring components such as crankshafts.

Electrodeposited iron has long been used to rebuild worn or corroded components,¹ for electroforms² and electrotypes,³ and magnetic components in electronics.⁴⁻⁶ The activation treatment traditionally used prior to iron plating is anodic etching in 30-percent sulfuric acid. The adhesion between the subsequent iron deposit and the substrate is not always good in industrial practice because the passive film formed after anodic etching cannot be stripped off completely before plating. In recent decades, a hard iron electrodeposition technique has been successfully used to restore some important components, such as marine and locomotive crankshafts. Industrial applications have proved that the iron deposit stood the test of heavy loads and high speeds.⁷ One of the main characteristics of the technique is that the activation treatment is carried out with symmetrical alternating current (SAC) directly in the plating bath, so that sulfuric anodic etching is no longer necessary. Bath temperature is kept in the range of 45-50 °C; the containment and environmental problems, therefore, are also improved to a great extent. The iron deposit is adherent, dense, and has good wear resistance and high hardness.

The mechanical properties of the iron deposit depend mainly on the microstructure and the internal stress; both of these properties are a function of the plating conditions. The microstructure refers to size, morphology and crystallographic orientation of the grains. Jiang⁸ reported that at the initial stage of the iron plating process, the internal stress is only 50 MPa, and about 100 MPa on the surface. Maximum stress appears when AC is converted to DC in the plating process. Ou *et al.*⁹ discussed the measurement of adhesion between the iron deposit and the substrate, and pointed out that the adhesion of the iron deposit could be determined by pull-out method and was approximately 350 MPa. S. Yoshimura *et al.*¹⁰ studied the relationship between microhardness and crystal

structure of iron deposits obtained from ferrous chloride solutions under various plating conditions. The results showed that the deposit had a preferred texture in the (110) plane. It seems that experimental results vary widely, and every study, referring to iron electrodeposits from the same bath with different plating conditions, come up with different conclusions.^{11,12}

The aim of this paper is the study of the characteristics of the iron deposit, the influence of SAC on the surface of the substrate before plating, the correlation between the texture and the microhardness of the iron deposit, and to discuss the adhesion between the deposit and the substrate under the experimental conditions.

Experimental Procedure

A three-phase half-wave silicon-controlled rectifier was used for the test. The cathode and anode were positioned parallel to each other, 15 cm apart, and immersed to a depth of 15 cm in 22 liters of the plating solution. The cathode was clamped midway between two anodes placed at either end of the bath. Anode and cathode materials were low-carbon steel, and the anode plates were bagged in a suitable material to collect any insoluble matter. The area ratio of cathode to anode was 1-1.5 while AC plating, and was increased to 2-4 while DC plating by increasing the number of anode plates.

The solution containing 400 g/L FeCl₂·4H₂O, 40 g/L MnCl₂·4H₂O was prepared using distilled water and reagent grade chemicals. All experiments were carried out at 45-50 °C and pH 0.6-0.9, with hydrochloric acid used to adjust pH to the desired value.

The pretreatment procedure is outlined in Table 1; the electrodeposition procedure is given in Table 2.

The microhardness of the iron deposit under a load of 100 gf was measured on the surface of the deposits and was determined by using a micro-Vickers hardness tester. Preferred orientations, expressed in terms of fiber texture coef-

Table 1
Pretreatment Procedure

1. Rust removal by grinding, then polishing with grit paper.
2. Metal detergent—soak clean at 50 °C for 5 min and rinse in water.
3. Moisten in calcium carbide liquid and rinse in water.
4. Pickle in dilute HCl (6-8%) for about 30 sec and rinse in water.
5. Activation with symmetrical AC at 6-8 A/dm² (asymmetric ratio $\beta = 1$).

Table 2
Electrodeposition Procedure

1. Asymmetric a-c initial plating (increase β value to 1.29-1.30).
2. Increase β value to 4-5 gradually.
3. AC is changed to d-c plating process.
4. Adjust current density to the desired value.

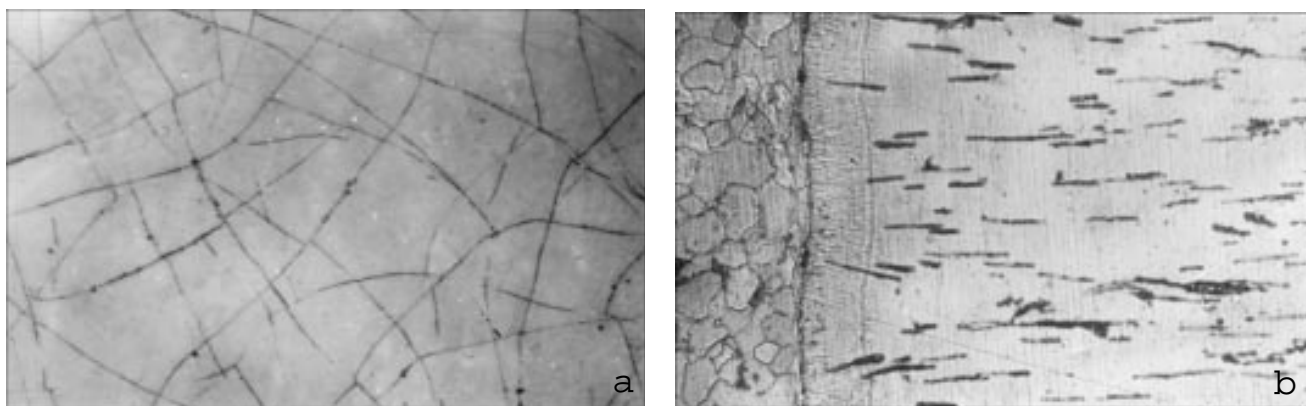


Fig. 1—Iron deposit: (a) surface appearance; (b) cross section. 160X.

ficients, were determined by X-ray diffractometer (XRD), and texture coefficients were calculated by the Willson's method.¹³ The crystalline structure of the iron deposits were also determined by XRD. The surface appearance and cross-sectional views of the deposit were examined using optical microscopy, scanning electron microscopy, and transmission electron microscopy, respectively.

Results & Discussion

Figure 1 shows the surface morphology (a) and cross section (b) of the microcracked iron deposit. Microcracks form during deposition when the tensile stress exceeds the cohesive strength of the iron. There are few microcracks in the deposit at the initial stage and transition stages of the deposition, and the number of the microcracks in the d-c deposit increases with increasing direct-current density. Although appearing to be continuous on a macro scale, microcracking is not continuous on a microscopic scale.

Scanning electron micrograph (SEM) of the typical iron deposits is shown in Fig. 2. It can be seen that in this cross section, the deposit is normally columnar in structure, and the columnar grain becomes refined gradually with the continued plating process.

Figure 3 shows the morphology of the substrate-deposit interface. It reveals that after the activation treatment, the surface microstructure of the sample has been changed to some extent. The dissolution of iron is a little greater than its deposition because anodic efficiency is higher than cathodic efficiency. While the ferrite is readily dissolved, cementite is also partly dissolved at some appropriate potential; accordingly, the carbon concentration in the tiny area where cementite is dissolved will decrease to such a low carbon equilibrium concentration that cementite will be transformed into ferrite through reconstruction of the atoms in the area, so that cementite on the surface looks discontinuous. This means that iron atoms have more opportunities to continue the crystal lattice of the ferrite on the substrate (*i.e.*, there is a tendency for the deposit to be epitaxial with the substrate), which means that the adhesion is very good.

It can be seen in Fig. 4 that current density has a significant effect on the microhardness, which varies in the range of HV 200-650, and the microhardness of the iron deposit increases with the increase of the asymmetric ratio β value. The increase of microhardness of the iron deposit, resulting from the increasing values of current density, can be attributed to the refined crystalline structure.

Figure 4 shows the texture coefficients of the deposit for

the reflection planes of the deposit obtained at different stages of the plating process. The trend of the (211) coefficient is in good agreement with that of the microhardness of the deposit while plating. The iron deposit at high current density has a primarily (211) texture with a secondary (110) texture, whereas those deposited at low current density have a fairly strong (110) texture with a secondary (211) texture, and the coefficients of the initial deposit are almost the same as for the substrate. This suggests a preferred orientation with the (110) plane parallel to the surface in the early stages, and with the (211) plane in the d-c plating. When the current density increases, the (211) peak increases in intensity, while the (110) and (200) peaks weaken, which implies that the substrate and the initial iron deposit have nearly the same structure. Analysis of the results provides valuable insight into the nature and characteristics of the iron deposited from a chloride bath.

During SAC activation treatment, the main reactions taking place alternatively on the cathodic surface are: (1) reduction of ferrous ions and hydrogen ions, and (2) dissolution of iron, as well as evolution of oxygen. All these reactions are very helpful in effectively stripping off oxides and impurities adsorbed on the surface, so that an activated film is formed. This SAC treatment makes Fe^{+2} ion dissolution a little greater than deposition in quantity, and the substrate will lose its original metallic luster. It implies that the lattice of the substrate is being exposed. According to the results, lower SAC density cannot strip off oxide film effectively, but much

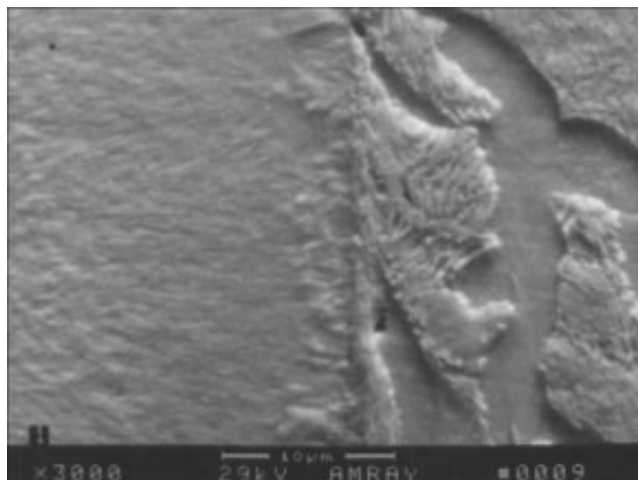


Fig. 2—SEM micrograph of iron deposit. 3000X.

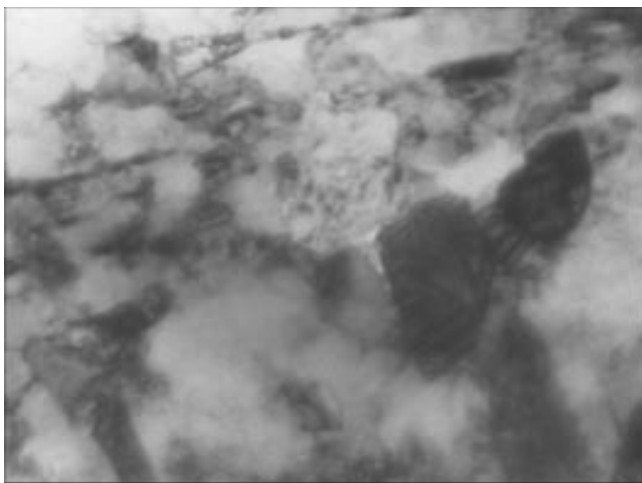


Fig. 3—TEM micrograph of iron deposit. 30,000X.

higher SAC density has an unfavorable effect on adhesion because of relatively higher hydrogen and oxygen concentration in the film. An appropriate SAC density for low-carbon steel is about 7 A/dm^2 . When the initial plating begins at a suitable current density, a large quantity of electrons is abruptly available at the cathode, making Fe^{+2} ions migrate quickly to the fixed section closest to the cathode, be discharged and be arranged in a crystal lattice. Iron atoms are most tightly held by free electrons of the substrate atoms, so a strong metallic bond between the deposit and the substrate is established.

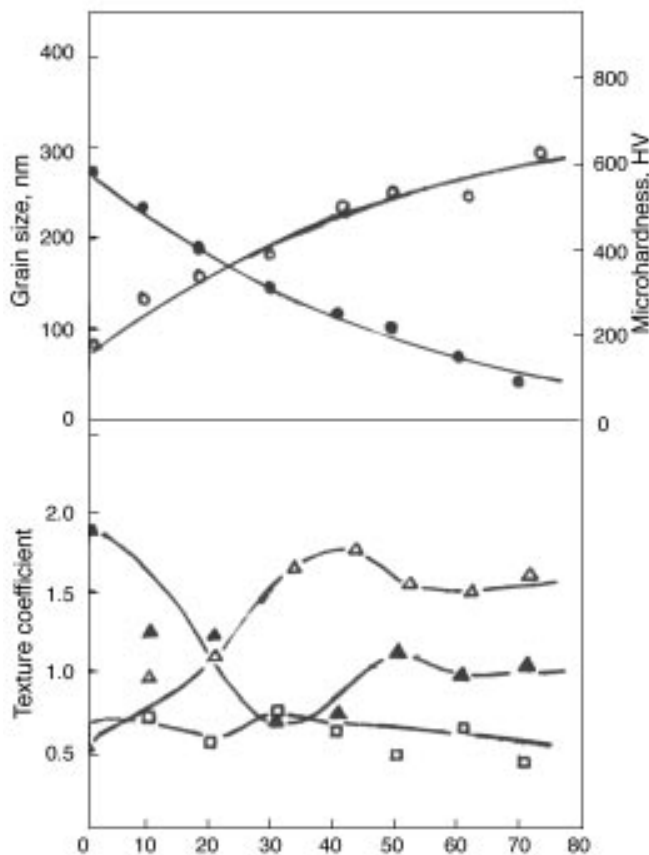


Fig. 4—Surface microhardness, ○; grain size, ●; and texture coefficients [$P_{(211)}$, ○; $P_{(110)}$, Δ; $P_{(200)}$, ▲; $P_{(100)}$, □] of reflection planes of iron deposit at different stages.

After the SAC treatment, an asymmetrical alternating current is applied to form an initial iron layer with low stress and low microhardness that acts like a buffer to mitigate effectively the disruptive effects of high stress created in the d-c deposit. The asymmetric ratio β value is adjusted gradually from 1.3 to 6, and is finally converted to d-c plating. This relatively small alternating current density results in lower cathodic polarization, making ferrous ions arrive on the surface, be reduced and form an orderly deposit layer. At the initial stage of the iron deposition, the first layer of atoms of the deposit depends on the conditions of the substrate. The normal spacings of the atoms in the crystal planes that constitute the surface are not significantly different from those of the deposit because the structure and composition of the specimen (made of low-carbon steel) are quite similar to the iron layer. The iron deposit can easily continue the crystal lattice of the substrate. Because the current density selected is optimized, grains with relatively large size are formed in the initial deposit; this plays a key role in reducing the great internal stress created in the d-c deposit, so that adhesion will not be affected.

Conclusions

Adherent, dense iron deposits with good mechanical properties can be obtained by using SAC activation treatment in concert with asymmetrical a-c initial deposition that is gradually converted to d-c plating. Because the 30-percent sulfate anodic etching activation treatment traditionally used is no longer necessary, and because bath temperature is controlled within the range $45\text{--}50^\circ\text{C}$, containment and environmental problems can be improved to a great extent.

The iron deposit has a columnar grained structure, and the average grain size decreases with increasing current density. The trend of microhardness of the deposit is in close agreement with that of the (211) texture coefficient while the process continues. The (211) preferred orientation tends to develop during the iron deposition. Consequently, this iron plating process is a practical and reliable way of applying coatings on iron and steel for dimensional restoration and wear resistance applications.

Editor's note: Manuscript received, July 1995; revision received, June 1997.

Acknowledgment

The authors appreciate the research grant from Liaoning Province Science & Technology Foundation, P.R. China.

References

1. R. Walker & S.D. Irvine, *Metal Fin.*, **74**, 39 (June 1976).
2. G.F. Bidmead & G.R. Davies, *Trans. Inst. Met. Fin.*, **56**(3), 97 (1981).
3. S.F. Harty, J.A. McGeough & R.M. Tulloh, *Surf. Technol.*, **12**(1), 39 (1981).
4. M. Bratoeva et al., *Proc. Interfinish.*, **84**, 249 (1984).
5. S. Yoshimura, et al., *J. Magn. Soc. Jap.*, **18**, 281 (1994).
6. P. Duke et al., *Plat. and Surf. Fin.*, **69**, 61 (1982).
7. Dong Yuhua et al., *Electroplat. & Pollut. Control* (Chinese), **6**(4), 6 (1986).
8. Jiang Chenghai, *Met. Ph. Exam. & Test* (Chinese), **Sum 60**(6), 37 (1992).

continued on page 78