United States Patent [19]

Klingenmaier et al.

[11] **3,753,664**

[45] **Aug. 21, 1973**

[54] **HARD IRON ELECTROPLATING OF SOFT SUBSTRATES AND RESULTANT PRODUCT**

[75] Inventors: **Otto J. Klingenmaier**, Warren; **John T. McWatters**, Roseville, both of Mich.

[73] Assignee: **General Motors Corporation**, Detroit, Mich.

[22] Filed: **Nov. 24, 1971**

[21] Appl. No.: **202,014**

[52] **U.S. Cl.** **29/191**, 29/196.1, 204/40, 204/48

[51] **Int. Cl.** **C23b 5/04**, C23b 5/50, B23p 3/22

[58] **Field of Search** 29/196.1, 191; 204/48, 41, 40, 48

[56] **References Cited**

UNITED STATES PATENTS

1,630,631	5/1927	Pauly	29/196.1
2,745,800	5/1956	Poor	204/48
3,528,894	9/1970	Stoddard, Jr. et al.	204/41 X

FOREIGN PATENTS OR APPLICATIONS

166,662	1/1956	Australia	204/48
568,161	3/1945	Great Britain	204/41

Primary Examiner—Allen S. Curtis
Attorney—W. S. Pettigrew and L. B. Plant

[57] **ABSTRACT**

Substrates having low surface strengths are plated with high stress iron by first depositing a layer of low stress iron on the substrate before plating the high stress iron. The low stress iron layer acts like a buffer to mitigate the surface disruptive affects of the high stress iron on the substrate.

4 Claims, No Drawings

HARD IRON ELECTROPLATING OF SOFT SUBSTRATES AND RESULTANT PRODUCT

It has been suggested to provide hard iron coatings on soft materials in order to give them wear resistance properties. To this end, thin, hard (i.e., greater than R_c20) iron coatings have been plated directly onto the soft substrates. Soft substrates which have low surface strengths can tolerate only very thin layers of hard iron (e.g., less than 0.001 inch), since thicker layers of hard iron, while adherent to the surface, nonetheless peel or spall. In this regard, it has been found that the thicker hard iron, which is highly stressed, causes the surface of the substrate to pull away from the subsurface, even though the iron strongly adheres to the surface itself. Hence, a weak bond between the surface and the subsurface of the substrate is unable to resist the influence of the tensile stress of the hard iron coating and rupture of the substrate surface occurs.

It is an object of this invention to overcome the surface disruptive affects of thick, hard iron deposits on soft substrates having low surface strengths and thereby permit the plating of thick high stress iron on these substrates without peeling or spalling of the iron deposit. This and other objects of this invention will become more apparent from the detailed discussion which follows.

This invention comprehends depositing a first layer of low tensile stress iron onto the substrate surface before plating the high tensile stress iron. The low stress iron layer acts like a buffer and mitigates the surface disruptive affects of the high stress iron layer. For purposes of this application, substrates shall be considered as having low surface strengths if they have peel strengths of less than about 200 lbs/in as determined by the modified Jacquet test described hereinafter. The aforesaid surface strength of the substrate relates to the bond between the surface which adherently receives the iron layer and the subsurface to which the surface itself is bonded. Hence the surface-subsurface bond may be a cohesive bond or an adhesive bond as will be discussed hereinafter. Likewise, the term "low stress iron" is used herein to mean iron deposits having tensile stresses lower than about 15,000 psi. Lastly, the term "high stress iron" is used herein to means as-plated iron deposits having internal tensile stresses exceeding about 30,000 psi prior to any stress relief (e.g. cracking). Hard iron deposits (i.e., greater than R_c20) fall into the high stress category, though it is not limited thereto. The aforesaid stresses are determined by the rigid plate method described by W. M. Phillips and F. L. Clifton in *The Proceedings of the American Electroplaters Society*, Vol. 34, P. 97, 1947.

The benefits of this invention may be obtained by plating the low stress iron from a first solution and the high stress iron from a second solution. In such a two solution method, the low stress iron is best deposited from an appropriately controlled, art-known ferrous chloride solution. Ferrous fluoborate or ferrous sulfamate solutions may also be used. The high stress iron is deposited from an appropriately controlled, art-known, ferrous chloride, ferrous fluoborate, ferrous sulfamate or ferrous sulfate solution. In this regard, ferrous sulfate solutions generally produce only high stress deposits at commercially practical operating temperatures and current densities and accordingly it is considered impractical for plating the low stress iron.

In a preferred form of the invention, a single plating bath is used and the low and high stress iron layers formed by varying the plating parameters of the one bath during a single immersion of the substrate. Either a ferrous chloride or ferrous fluoborate solution is used in which the ferrous ion concentration is at least about 100 grams per liter. Below this level only high stress iron is obtainable at commercially practical operating temperatures and current densities. A ferrous chloride solution having a pH of 0.2 to 0.7 and a ferrous ion concentration of about 200 grams per liter (g/l) is preferred. The substrate is immersed in the solution and is first plated under low stress producing conditions to a predetermined thickness which is determined by ghe ultimate thickness of high stress iron to be subsequently plated. This first, or low stress, layer is plated at temperatures in the range of about 140° F to about 200° F and at current densities of less than about 150 amperes per square foot (ASF). The upper level of current density suitable for low stress plating is determined by the temperature of the solution and is generally directly proportional to the temperature. In this regard, at about 160° F the current density should be less than about 25 ASF, and preferably about 20 ASF, to keep the stress below about 15,000 psi. At 190° F low stress iron can be plated at current densities as high as about 100 ASF and at 200° F as high as about 150 ASF. Lower and higher temperatures and corresponding current densities are possible, but not considered practical. Evaporation is a problem at higher temperatures and plating rates are very slow at low current densities. It is possible to obtain low stress iron from saturated solutions of ferrous sulfate above about 190° F but only at current densities of less than about 25 ASF, leaving very little flexibility as far as operating parameters are concerned. After the low stress layer is deposited and while the substrate is still immersed in the single solution, the operating parameters of the solution are changed to form high stress iron. High stress iron can be deposited by operating the bath in about the same temperature range as for low stress iron but at substantially higher current densities. In this regard, at 160° F the current density should exceed about 40 ASF to yield 30,000 psi stressed iron, and at 190° F the current density should exceed about 150 ASF to yield the high stress deposit. With higher temperatures still higher current densities must be employed to get the high stress, and accordingly it is preferred to operate nearer the lower temperatures i.e. about 160° F, in order to keep the minimum current density within practical limits.

As indicated heretofore, peeling or spalling of the plated iron is caused not by a lack of adherence of the iron to the substrate's surface but rather by a weakly bonded surface. In this regard, the bond between the substrate's surface and subsurface is not strong enough to resist the disruptive forces of the high stress iron. In the case where the substrate is cast iron, copper or other soft metal which will directly accept an iron layer, this weak bond is a cohesive bond i.e., between the cast iron of the surface and the cast iron of the subsurface or the copper of the surface and the copper of the subsurface. With other soft metals such as aluminim or magnesium which traditionally require an intermediate layer of copper or the like before iron plating, the bond between the copper surface and the aluminum subsurface is an adhesive bond. For purposes of

this description then, the term substrate is herein used to mean one which is ready to receive the electrodeposited iron and accordingly includes metals which require no special preparatory treatment as well as metals which have already been especially prepared for iron plating, as by zincate treatments, stannate treatments, copper flashes, nickel strikes or the like as is well known to those skilled in the art.

The term low surface strength has been used herein to define those substrates which have peel strengths of less than about 200 lbs/in according to a modified Jacquet test. Such metals, include, for example, 13M cast iron (*ca* 130 lbs/in), CA 110 copper (*ca* 200 lbs/in), prepared (i.e. zincate and Cu strike) 3003 aluminum (*ca* 85 lbs/in), 95-5 lead-tin (*ca* 35 lbs/in), prepared (i.e., zincate and Ni strike) aluminum as well as a number of other metals and alloys (e.g. magnesium, brass, zinc) determinable from the test described hereafter.

A modified Jacquet test was used for purposes of determining which metals fall into the low surface strength category. The basic Jacquet test for determining metal adhesion to plastic is described in the article by E. B. Saubestre et al, *Plating*, Vol. 52, P. 983, 1965. This test involves scribing a one (1) inch strip across and through the metal plated on the plastic, lifting a tab at one end of the strip, grasping the tab in an Instron machine, pulling the strip at a rate of one (1) inch per minute at an angle of 90° from the face of the test panel, and recording the amount of pull (i.e., lbs/in) required to peel the strip from the panel. In the modified form of that test used here, the following procedure is used.

1. Coat two (2) test panels, one with a nickel strike and one with a copper strike layer, using the best art-known practice for obtaining adhesion. A strike layer of at least about 0.0001 inch is necessary.

2. Plate test panels with 0.0001 inch nickel as follows:

Nickel sulfamate	325 g/l
Boric acid	37 g/l
Nickel chloride	2.4 g/l
AntiPit Agent (Barrett SNAP)	0.4 g/l
pH	3.5–4.4
Temperature	130°F
Current density	25 ASF
Time	5 MIN

3. Rinse and dry test panels.

4. Paint one (1) inch wide silver strip along one edge of panels using DuPont Silver Preparation — Electronic Grade silver paint thinned with nine (9) parts butylacetate.

5. Immerse panels in 10 percent by weight solution of sulfonic acid for 10 seconds.

6. Return panels to bath in 2 above and plate with 0.005 inch of Nickel at 50 ASF for 2 to 2½ hours using shielding to prevent edge buildup.

7. Rinse and dry the panels.

8. Cut (band saw) one (1) inch wide strips across the panels perpendicular to the painted strip — cutting through the electrodeposit to the basis metal.

9. File/grind panels along painted edge and lift nickel tab away from panels at the painted surface.

10. Peel the nickel tab back in the manner indicated above for the conventional Jacquet test.

11. Record highest value obtained.

The test panels, depending on their composition, are pretreated in the manner known to those skilled in the art to obtain maximum adhesion of all deposits. Hence aluminum is first zincated in the customary manner followed by a copper or nickel strike before depositing the nickel test strip. For cast iron and copper, the nickel may be deposited directly on the panel or in the alternative may be struck with cyanide copper, or iron. The only criterion then is that the known techniques for obtaining maximum adhesion of all deposits be used.

In examples of this process, 3003, 380 die cast, F—132, and 6061—wrought aluminum alloys were zincated (i.e., Macdermid Alumetex immersion salts) and coated with about 0.0001 inch of low pH cyanide copper prior to iron plating. The thusly prepared substrate was immersed in a 180° F solution, such as described in my earlier patent U.S. Pat. No. 3,404,074 which contains 205 g/l of ferrous ion, and 1 g/l of the anti-pitting agent, Blancol N. They were first plated with low stress iron at a rate of about 1 mil/hr at 20 ASF. After the desired thickness of low stress iron was plated, the plating conditions were changed to produce high stress iron. To convert from the low stress plating conditions to the high stress plating conditions the temperature of the bath was lowered to about 160° F without changing the current density. Once the solution reaches 160° F, the current density was increased to at least about 100 ASF and plating continues to produce the desired thickness of 30,000+ psi iron.

In other examples of this process 13M cast iron and deoxidized copper samples were directly plated with the low stress iron without an intermediate copper or nickel strike. The samples were immersed in the U.S. Pat. No. 8,404,074 bath above and iron plated under the same conditions.

Another simpler version involves holding the solution temperature constant at about 160° F for both the low and high stress iron deposition sequences. The low stress iron is deposited at less than about 25 ASF followed by the high stress iron plated at current densities in the 100 to 200 ASF range.

It has been observed that, regardless of the composition of the substrate, the low stress iron layer should be at least about 0.001 inch thick. The minimum thickness required for any given application to prevent rupture of the substrate's surface-subsurface bond will of course depend upon the strength of that bond and the thickness of the high stress iron. In general, it has been observed that the weaker surface-subsurface bonds require greater thicknesses of low stress iron than do the stronger surface-subsurface bonds. Similarly, as the thickness of the high stress iron increases, so must the thickness of the low stress layer to accommodate the greater forces acting on the substrate's surface-subsurface bond. As a practical matter, it has been found that low stress iron layers rarely need exceed about 0.006 inch. In this respect it has been observed that when the low stress iron layer exceeds about 0.006 inch the surface-subsurface bond remains intact. For example, in one instance of a copper struck 380 die cast aluminum (Peel strength *ca* 60 lbs/in), a 0.006 inch low stress iron layer accommodated a 0.034 inch high stress layer without rupture of substrate.

The current density and/or temperature requirements for forming either the low or high stress deposits are affected by the ferrous ion concentration as is well known to those skilled in the art. Accordingly, there is no intent to be limited here to precise recitations of temperature, current density and/or concentration but rather only to the establishment of plating conditions

necessary to deposit iron layers having the recited low and high stresses. The values set forth herein are guidelines for achieving these results, but the invention is intended to be limited only to the extent hereinafter set forth in the claims which follow.

We claim:

1. A process for making a plated composite body including a substrate with low surface strength, a low stress first iron layer on the surface and a high stress second iron layer on the first layer comprising the steps of:

contacting a substrate which has a surface-subsurface strength of less than about 200 lbs/in with a first iron plating solution consisting essentially of at least 100 grams per liter of ferrous ion;

cathodizing said substrate and electrolyzing said solution at a sufficiently low current density to deposit a first layer of iron on the substrate said layer having a first predetermined thickness of at least about 0.001 inch and a tensile stress of less than about 15,000 psi;

contacting said iron coated substrate with a second iron plating solution; and

cathodizing said coated substrate and electrolyzing said second solution at a sufficiently high current density to deposit on said first iron layer at least 0.001 inch of iron having a tensile stress of at least about 30,000 psi; said first layer of low stress iron being sufficiently thick to mitigate the surface disruptive affects of the high stress iron layer on the substrate.

2. The process of claim 1 wherein the first low stress iron plating solution and the second high stress iron plating solution are one and the same.

3. A process for making a plated composite body including a substrate with a low strength surface, a low stress first iron layer on the surface and a high stress second iron layer on the first layer comprising the steps of:

contacting a substrate which has a surface-subsurface strength of less than about 200 lbs/in with an iron plating solution at a first predetermined temperature and consisting essentially of at least one ferrous salt selected from the group consisting of ferrous chloride and ferrous fluoborate;

cathodizing said substrate and electrolyzing said solution at a sufficiently low current density at that first predetermined temperature to deposit a first layer of iron on the substrate, said first layer having a predetermined thickness of at least about 0.001 inch and a tensile stress of less than about 15,000 psi;

while maintaining said substrate in said solution reducing said temperature to a second predetermined temperature lower than the first predetermined temperature; and

increasing the current density to a second predetermined current density higher than said low current density and sufficient at said second temperature to deposit a second layer of iron having a tensile stress of at least about 30,000 psi on said first layer; and

continuing to cathodize said substrate and electrolyze said solution at said higher current density to deposit at least about 0.001 inch of iron on said first layer.

4. An article of manufacture comprising:

a metallic substrate having a surface-subsurface strength of less than about 200 lbs/in;

a first layer of electrodeposited iron on said surface, said layer being at least 0.001 inch thick and having an internal tensile stress of less than about 15,000 psi;

and a second layer of iron on said first layer, said second layer having a thickness of at least about 0.001 inch and an internal tensile stress, in the as-plated condition, of at least about 30,000 psi;

said first layer being sufficiently thick to mitigate the surface disruptive affects of the second iron layer on the substrate which thickness varies inversely with the strength of the surface-subsurface bond and directly to the thickness of the second layer.

* * * * *