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Description

The invention relates to methods of plating substrates and in particular to methods of coating substrates by electroless plating.

5 In plating methods, a substrate, which may be a metallic alloy, composite or non-metallic substrate, is immersed in a plating solution to provide the substrate with a desired coating. The coating may be obtained by the application of an electric current (electrolysis) or without such a current (electroless). In electroless plating, the substrate is inserted in a container of a suitable plating solution which is in turn inserted in a thermostatically controlled water bath. The solution is heated to a temperature and for a time sufficient to
10 provide a required coating thickness.

In such plating, for a particular plating solution the rate of deposition and the grain structure of the plating are controlled by adjusting the current (electrolytic plating) or by the electrolyte temperature (electroless plating). However, such increases in current/ temperature can have disadvantages in reducing the life of the plating solution.

15 According to the invention, there is provided a method of depositing a coating on a substrate comprising inserting a substrate into a plating solution for coating of the substrate and then heating the plating solution in a chamber by a microwave source during the plating process to produce a required coating.

Preferably, the method also comprises heating the plating solution by the microwave source prior to
20 insertion of the substrate.

It has been found that by using a microwave source for heating improvements in deposition rate and grain structure can be achieved.

Preferably the method also includes adjusting the power output of the microwave source to control the temperature of the plating solution.

25 The method may also comprise controlling the temperature to a constant temperature throughout the coating process. Alternatively, the method may comprise pulsing the power to the microwave source. The method may also include heat treating the coated substrate.

Preferably, the plating process is an electroless plating process.

The following is a more detailed description of some embodiments of the invention, by way of example,
30 reference being made to the accompanying drawing and electron micrographs in which:-

Figure 1 is a schematic view of an apparatus for coating a metallic substrate by an electroless process and including a source of microwave power,

Figure 2a is two micrographs of the crystal structure of a copper substrate with a nickel-phosphorus coating from a first plating solution applied by a known method (left) and by a first exemplary method
35 according to the invention (right),

Figure 2b is two scanning electron micrographs of the crystal structure of a mild steel substrate with a nickel-phosphorus coating from a first plating solution applied by a known method (left) and by a first exemplary method according to the invention (right),

Figure 2c is two micrographs of the crystal structure of a stainless steel substrate with a nickel-phosphorus coating from a first plating solution applied by a known method (left) and by a first
40 exemplary method according to the invention (right),

Figure 3a is two scanning electron micrographs of the crystal structure of a copper substrate after treatment in a second plating solution by a known method (left) and by a second exemplary method according to the invention (right),

45 Figure 3b is two scanning electron micrographs of the crystal structure of a mild steel substrate after treatment in a second plating solution by a known method (left) and by a second exemplary method according to the invention (right),

Figure 3c is two scanning electron micrographs of the crystal structure of a stainless steel substrate after treatment in a second plating solution by a known method (left) and by a second exemplary method
50 according to the invention (right),

Figure 4 is six scanning electron micrographs at a magnification of x2000 showing the surface topography, and in three vertically arranged pairs, each pair showing respectively the topography of a copper substrate, a mild steel substrate and a stainless steel substrate each with a nickel-phosphorus coating from a first plating solution applied by a known method (upper micrographs) and a third
55 exemplary method according to the invention (lower micrographs),

Figure 5 is two scanning electron micrographs at a magnification of x2000 of the surface topography of a mild steel substrate with a nickel-phosphorus coating formed from a second plating solution applied by a known method (above) and by a fourth exemplary method according to the invention (below).

Referring first to Figure 1, the apparatus for electroless plating comprises a domestic microwave oven 10 having a maximum power output of 500W from a microwave source 12. The oven is equipped with an internal turntable 11 and a microwave stirrer to ensure an even distribution of energy within the chamber. The oven 10 is modified to achieve continuous irradiation with variable power by use of a Variac 13.

An accurate indication of the temperature of the plating solution can be readily achieved by use of a miniature gas thermometer. This is connected, by a capillary 14, to a pressure transducer 15 mounted outside the microwave cavity. The output from the transducer 15 is connected to a digital voltmeter 16. In this way by using a gas thermometer of known dimensions as described in the article by G. Bond, R.B. Moyes, S.D. Pollington and D.A. Whan, **Meas. Sci. Technol.** 2 (1991), 571-572, and with air as the operating gas, calibration of the thermometer can be achieved by reference to fixed points or by the simultaneous immersion of the gas thermometer and a thermocouple in a heated liquid in the absence of microwave energy. During the course of the experiment, the thermometer is inserted into the bath and by monitoring of the output from the pressure transducer 15 a constant temperature can be maintained.

A 500 millilitre beaker 17 is used to contain plating solutions and substrates described below.

Tests were conducted using three different substrates and two different plating solutions.

The substrates had the following compositions and dimensions:-

Substrate No.	Material	(cm) width	(cm) length	(mm) thickness
1	Copper(Goodfellow,99.9% purity, half hard)	2	8	0.25
2	Mild Steel	2	8	0.8
3	Stainless Steel	2	8	0.8

The two plating solutions compositions used were as follows:-

PLATING SOLUTION 1	
Nickel sulphate	30g/l
Sodium hypophosphite	20g/l
Lactic acid	25g/l
Propionic acid	5g/l
Lead as lead nitrate	4mg/l
pH	4.5

PLATING SOLUTION 2	
OMI proprietary solution pH (at 90 °C)	Enplate NI 425A,425B (sold by OMI-IMASA Marketing(Europe)Ltd) 5

Prior to coating, each substrate was pre-treated as follows. First, the substrate was soaked in Enbond 808 (trade mark) at 80 °C for 3 minutes and then rinsed. The substrate was then soaked in Enbond 808 (trade mark) and subjected to anodic electrolytic cleaning for 3 minutes at 80 °C at a current density of 6 A/dm² and then rinsed. It was then dipped in tin chloride (SnCl₂), rinsed, dipped in palladium chloride (PdCl₂) and rinsed.

The substrates were then treated by two different methods. In the first method (method 1), the plating solution (either plating solution 1 or plating solution 2) was placed in a beaker and the beaker placed in a thermostatically controlled water bath. The bath was kept at a temperature of 80 °C (plating solution 1) or 85 °C (plating solution 2), and the rate of deposition of the coating measured with a total treatment time of two hours.

In the second method (method 2), the appropriate plating solution was placed in the beaker 17 with the substrate and the beaker placed on the tray 11 of the microwave chamber 10 described above with reference to Figure 1. The plating solution may be heated using the microwave source prior to insertion of the substrate. The microwave power source was turned on and the required temperature (80 °C for plating solution 1, 85 °C for plating solution 2) maintained by use of the Variac 13. Again, the plating rate was measured with a total treatment time of two hours. The use of the microwave power source was found to

obviate the need for agitation of the plating solution. In addition, the fact that the chamber is closed was found to allow containment of any mess that may arise during the process.

The results of these coating methods are set out in the accompanying Table 1.

5 Results with Plating Solution 1

It will be seen that, for all substrates, the plating rate was greater with method 2 (the method according to the invention) than with method 1 (the prior art method). For copper, the proportion of nickel to phosphorus in the coating was substantially unchanged by use of method 2. As seen in Figures 2a, 2b and 10 2c, the morphology of the nickel-phosphorus coating on the copper and mild steel and stainless steel substrates coated by method 1 are comparable to those coated by method 2. These Figures also indicate that different substrates can produce different coating structures for both methods. Nevertheless, the surface coat texture of the coatings of method 2 are superior to those of method 1. The surface topography of the coating on the stainless steel substrate for the two methods (examples 9 and 10) tend to differ 15 slightly, which can be taken as further proof that surface texture is dependent on substrate type.

Results with Plating Solution 2

It will be seen that, with plating solution 2, the coating rate on mild steel was greater with method 2 than 20 with method 1 (examples 7 and 8). Coating was unsatisfactory on both copper and stainless steel with both methods.

Figures 3a,3b and 3c show the surface topography of substrates after treatment in plating solution 2. These confirm that the copper substrate was not coated by either method 1 or method 2. This could be due to the fact that plating solution 2 is a proprietary solution designed to be used on substrates other than 25 copper, according to the manufacturer's indications.

Figure 3c confirms that the coating obtained on a stainless steel substrate by method 1 was patchy and that no deposition takes place with method 2. Again, this may be because plating solution 2 is said to be designed for substrates other than stainless steel.

Substrates according to examples 1 and 2 were then taken and heat treated in a muffle furnace at 30 400 °C for 80 minutes. Knoop microhardness measurements were carried out on the examples before and after heat treatment using a Leitz (trade mark) miniload Knoop microhardness tester.

The results were as follows:-

35	Example No.	Heat treated	Average ₆ (HK ₆)	ΔHK
	1	No	266.1	266.1±23.3
	2	No	301.2	301.2±11.8
	1	Yes	322.6	322.6±13.1
40	2	Yes	395.1	395.1±47.05

It will be seen that even without heat treatment, substrates coated according to method 2 are generally harder than substrates treated by method 1. After heat treatment, the hardness of substrates treated by 45 method 2 remain superior to the hardness of substrates treated by method 1. The mean microhardnesses, Δ HK , indicate that the variations in values do not overlap so implying that consistent improvements in hardness can be expected from method 2.

Figure 4 shows the surface topography of the substrates of examples 1, 2, 5, 6, 9 and 10 after being heat treated at 400 °C for 80 minutes. Figure 4 shows substrates of examples 7 and 8 heat treated at 50 400 °C for 80 minutes. These clearly show that the structures after heat treatment become smoother. The hardness of the deposits is enhanced because smoothness is directly related to the grain size, i.e. the smaller the grain size the higher the hardness values. In addition, it can be seen that the coated substrates of method 2 have smoother coatings than those of method 1 which account for the improved hardness of coated substrates according to method 2.

It will thus be seen that the use of a microwave power source for heating the plating solution produces 55 increased plating rates as compared with a water bath method. Thus, the use of a microwave source can allow satisfactory plating rates to be achieved at lower temperatures than with a water bath. In addition, the use of a microwave power source can allow improvements in grain structure (and hardness) to be achieved at lower temperatures than with a water bath. This can prolong the life of the plating solution and avoid

instability in the plating solution.

Although the substrates described above are metals or metal alloys, the substrates could be of any other suitable material.

5 The use of microwave heating can also bring improvements in grain structure and plating rates when used with electrolytic plating and other anodic electrolytic processes.

It will be appreciated that the plating solution used could be any suitable plating solution, such as a plating solution for copper plating a substrate.

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TABLE 1

Example No	Substrate No	Electrolyte No	Method No	Coating(m/hr)Rate	Nickel%	Phosphorus%
1	1	1	1	4.95	88.94	11.06
2	1	1	2	5.63	89.45	10.55
3	1	2	1	No deposition		
4	1	2	2	No deposition		
5	2	1	1	3.49		
6	2	1	2	4.88		
7	2	2	1	14.27		
8	2	2	2	11.73		
9	3	1	1	4.05		
10	3	1	2	5.35		
11	3	2	1	4.65(patchy)		
12	3	2	2	No deposition		

Claims

1. A method of depositing a coating on a substrate comprising inserting a substrate into a plating solution (17) for coating of the substrate and then heating the plating solution in a chamber by a microwave

source (12) during the plating process to produce a required coating.

2. A method according to claim 1 and further comprising heating the plating solution by the microwave source (12) prior to insertion of the substrate.

3. A method according to claim 2 and comprising adjusting the power output of the microwave source (12) to control the temperature of the plating solution.

4. A method according to claim 3 comprising controlling the temperature to a constant temperature throughout the coating process.

5. A method according to claim 3 comprising pulsing the power to the microwave source.

6. A method according to any one of claims 1 to 5 and further comprising heat-treating the coated substrate.

7. A method according to any one of claims 1 to 6 wherein the plating process is an electroless plating process.

8. A method according to any one of claims 1 to 7 wherein the substrate is a metallic substrate.

9. A coated substrate when made by the method of any one of claims 1 to 8.

Patentansprüche

1. Verfahren zum Niederschlagen einer Überzugs auf einem Substrat, das ein Einsetzen eines Substrats in eine Beschichtungslösung (17) zum Überziehen des Substrats und dann ein Beheizen der Beschichtungslösung in einer Kammer durch eine Mikrowellenquelle (12) während des Beschichtungsprozesses, um einen erforderlichen Überzug zu produzieren, umfaßt.

2. Verfahren nach Anspruch 1 und das weiterhin ein Beheizen der Beschichtungslösung durch die Mikrowellenquelle (12) vor dem Einsetzen des Substrats umfaßt.

3. Verfahren nach Anspruch 2 und das weiterhin eine Einstellung der Leistungsabgabe der Mikrowellenquelle (12), um die Temperatur der Beschichtungslösung zu regeln, umfaßt.

4. Verfahren nach Anspruch 3, das weiterhin die Regelung der Temperatur auf eine konstante Temperatur während des Überzugsprozesses umfaßt.

5. Verfahren nach Anspruch 3, das weiterhin ein Pulsen der Leistung der Mikrowellenquelle umfaßt.

6. Verfahren nach einem der Ansprüche 1 bis 5 und das weiterhin eine Wärmebehandlung des überzogenen Substrats umfaßt.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei der Beschichtungsprozeß ein stromloser Beschichtungsprozeß ist.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei das Substrat ein metallisches Substrat ist.

9. Beschichtetes Substrat, das durch das Verfahren nach einem der Ansprüche 1 bis 8 hergestellt ist.

Revendications

1. Procédé de dépôt d'un revêtement sur un substrat consistant à insérer un substrat dans une solution de plaquage (17) pour recouvrir le substrat et à chauffer ensuite la solution de plaquage dans une chambre par une source à hyperfréquence (12) pendant le procédé de plaquage pour produire un revêtement nécessaire.

2. Procédé selon la revendication 1 et consistant en outre à chauffer la solution de plaquage par la source à hyperfréquence (12) avant l'insertion du substrat.
3. Procédé selon la revendication 2 et consistant à ajuster la puissance débitée de la source à hyperfréquence (12) pour régler la température de la solution de plaquage.
4. Procédé selon la revendication 3, consistant à régler la température jusqu'à une température constante tout au long du procédé de déposition.
5. Procédé selon la revendication 3, consistant à fournir des impulsions au courant de la source à hyperfréquence.
6. Procédé selon l'une quelconque des revendications 1 à 5 et consistant en outre à traiter thermiquement le substrat recouvert.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le procédé de plaquage est un procédé de plaquage sans courant.
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le substrat est un substrat métallique.
9. Substrat revêtu, fabriqué par le procédé de l'une quelconque des revendications 1 à 8.

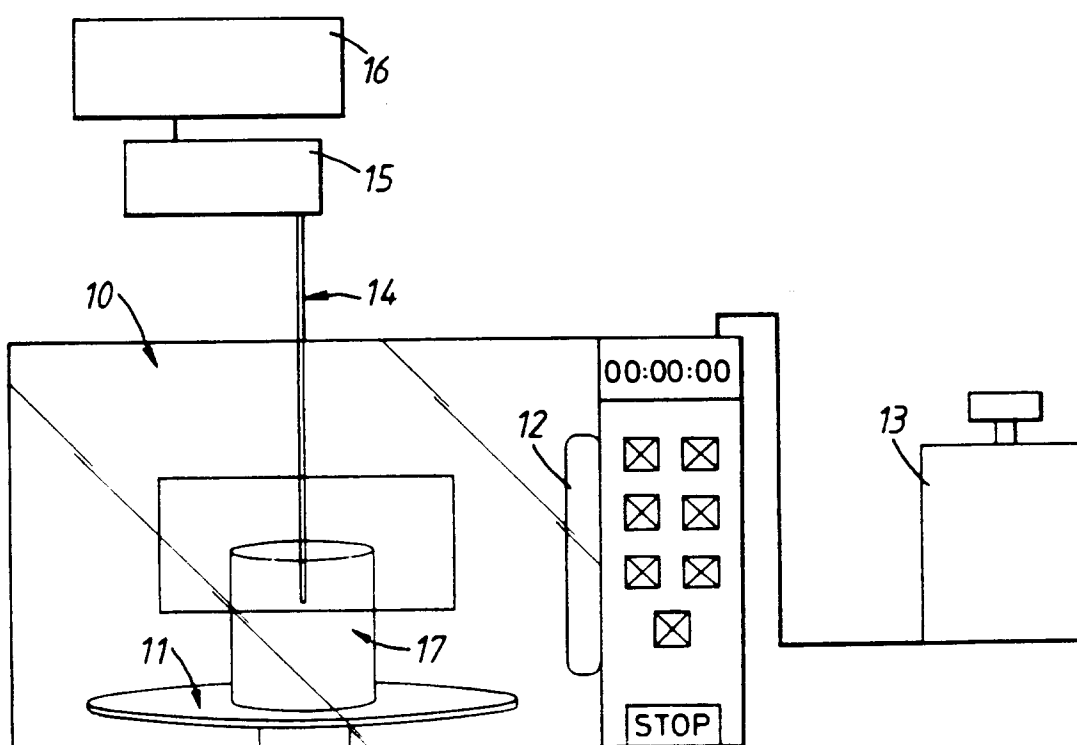


FIG.1.

L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Elec; Cu, #1



L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Micro; Cu, #1



FIG. 2a

L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Elec; M.Steel, #1



L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Micro; M.Steel, #1

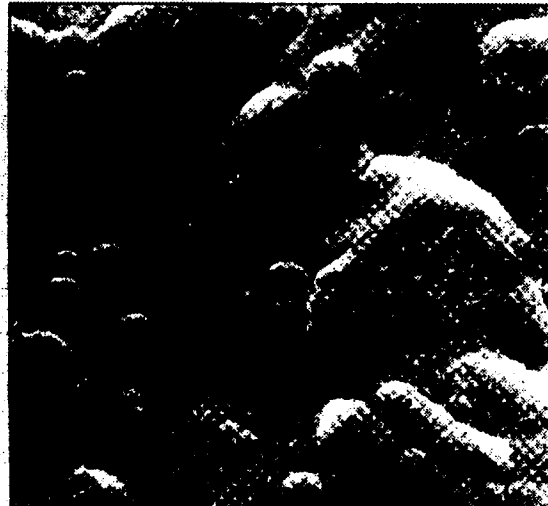
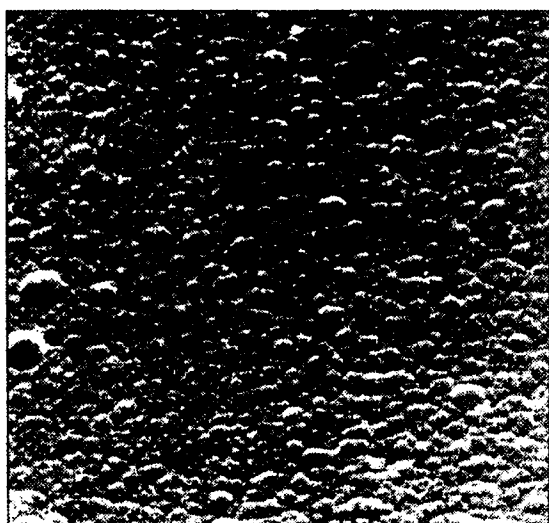


FIG. 2b

L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Elec; S.Steel, # 1



L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Micro; S.Steel, # 1

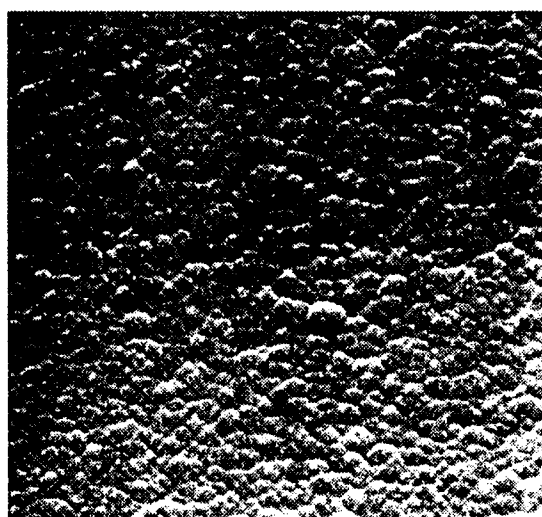
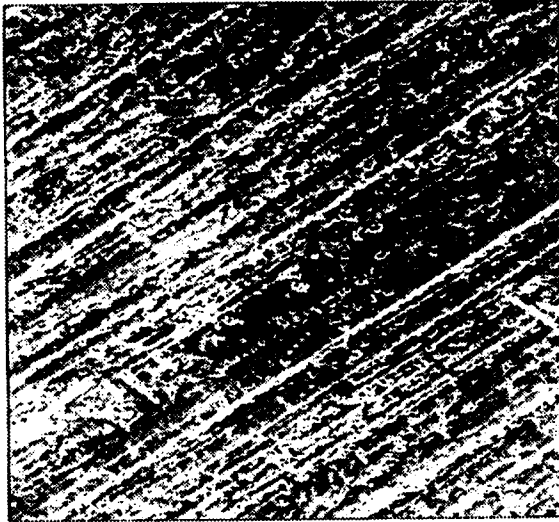


FIG. 2c

L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Elec; Cu, # 3



L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Micro; Cu, # 3

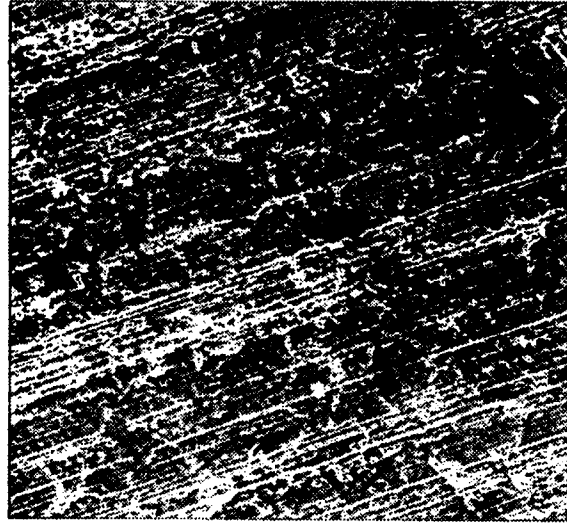
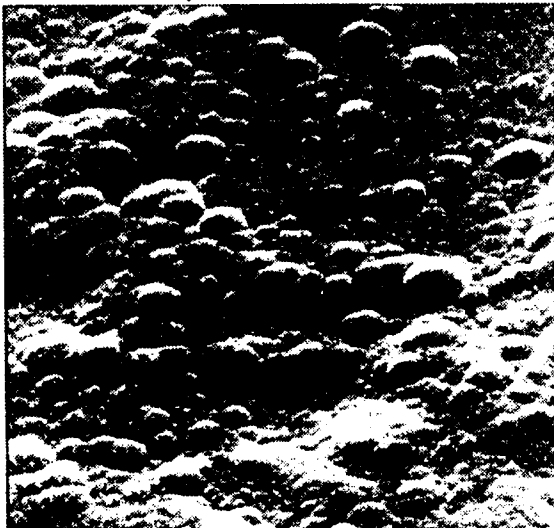


FIG. 3a

L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Elec; M.Steel, #3



L=SE1 EHT=15.0KV WD=7 mm
50.0 μ m
Micro; M.Steel, # 3

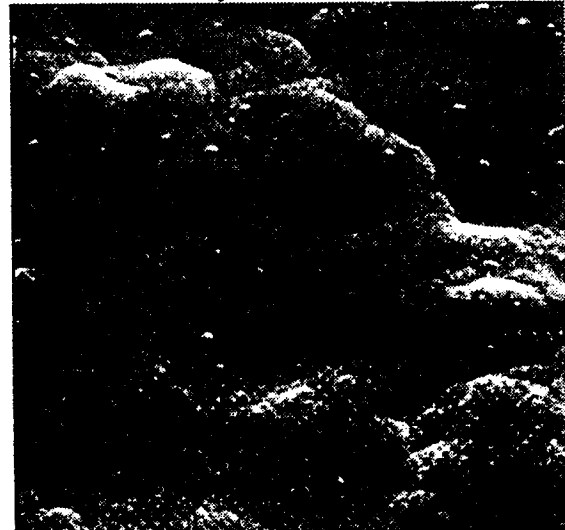
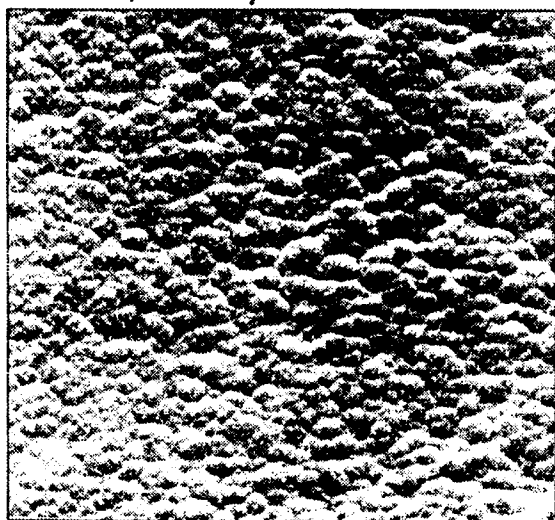


FIG. 3b

L = SE1 EHT = 15.0KV WD=7 mm

500μm

Elec; S.Steel, # 3



L=SE1 EHT= 15.0KV WD=6 mm

500μm

Micro; S.Steel, # 3

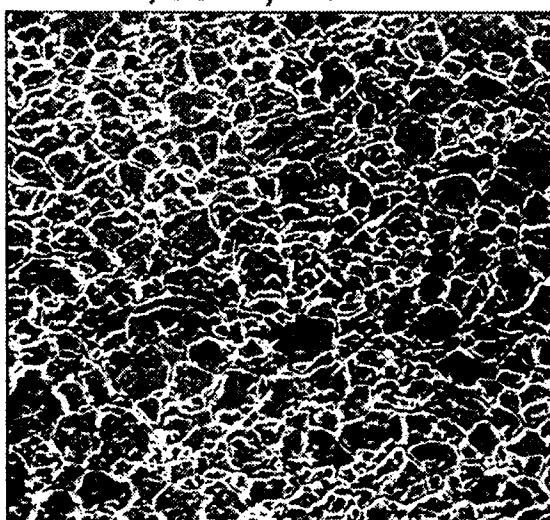


FIG. 3c

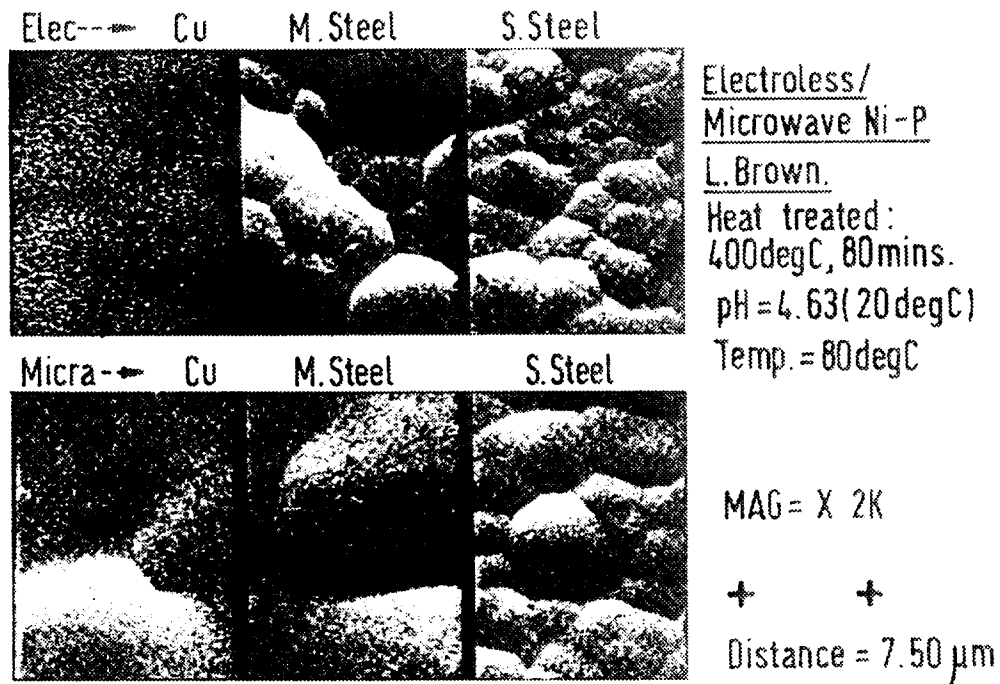


FIG. 4

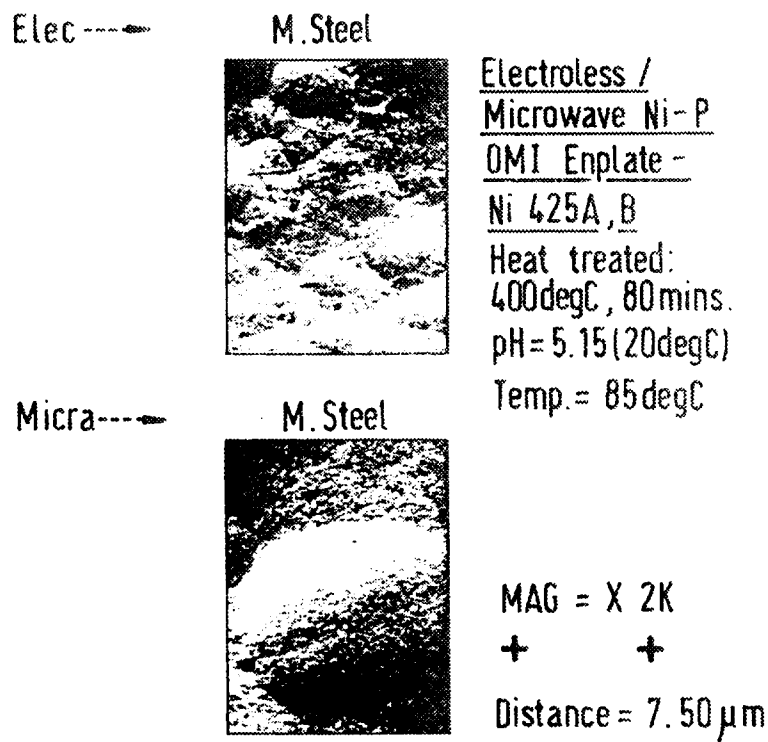


FIG. 5