THE CORROSION RESISTANCE OF Ni-TiO$_2$ AND Ni-SiC NANOCOMPOSITE COATINGS PREPARED BY BRUSH PLATING TECHNOLOGY

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ABSTRACT

Brush plating is an electroplating process which is similar to painting operation. By using compact equipment, brush plating is easily carried out at the jobsite. Nowadays, this technology has been proved to have widespread applications in engineering, especially in which requiring high corrosion resistance.

Nanocomposite containing titania and/or silicon carbide nanoparticles in a nickel matrix has been prepared by brush plating method. Deposits have been characterized by EDS and SEM for structural analysis. Corrosion properties and microhardness have also been investigated. Besides, pure Ni deposits were also produced under the same experimental conditions for comparison. Experimental results showed that the change in current density and the content of nano SiC and nano TiO$_2$ could change the structure and corrosion resistance of nanocomposite coatings.

1. INTRODUCTION

Today, brush plating has gained widespread (or diverse) applications in engineering.

This flexible and multi-functional technology can be used almost everywhere, in the laboratory or on site. In addition, many of its advantages are considered, such as easy to operate, quick deposition rate, various coatings, accurate control of the coating thickness, saving time and money, reducing investment cost and environmental pollution. As a consequence, brush plating has found its role in producing, repairing, strengthening and remanufacturing a new deposition.

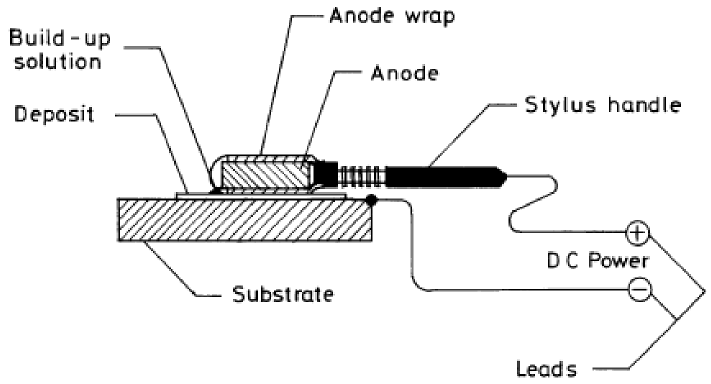


Figure 1. Schematic diagram of brush plating

Brush plating equipment includes power packs, solutions, plating tools, anode covers, and auxiliary equipment (Fig. 1).

The power pack has two leads. One is connected to the plating tool and the other is connected to the work piece to be plated. The anode is covered with an absorbent material which holds the solution. The operator dips the plating tool in the solution and then brushes it against the surface of the workpiece that is to be finished. When the anode touches the work surface a circuit is formed and an electrodeposit is produced. Plating occurs only where the anode contacts the work piece. During the brush plating process, the plating tool is always kept in motion whenever it is in contact with the work surface. The movement will apply even plating on the entire area being plated and ensure a quality finish.

Nano-brush plating is a kind of advanced surface engineering technology which was developed on the foundation of the traditional brush plating. The composite solution (electrolysis solution) was prepared by joining the nanoparticles into the matrix metal solution (MMS). In the process of brush plating, the nanoparticals suspended in the solution were co-deposited with the matrix metal on the matrix surface under the action of electric-field power and complex ion and the composite coatings were obtained with the distribution of the scattering nanoparticals.

2. EXPERIMENT

Nano-brush plating samples are made of C45 steel and cut into pieces of 30 × 10 × 1.2 (mm) in size. Samples are ground, polished, oil cleaned and dried.

There are many factors affecting the quality of coatings from brush plating technology, such as composition and property of plating solution, brush speed of anode onto metal surface (cathode), ... among which, authors are mainly interested in two important factors, the concentration of nanoparticles in electrolysis solution and plating’s current density.

The composition of electrolysis solution is described in Table 1.

Table 1. Formula of electrolysis solution

No.	Chemical composition	Content (g/l)	Remark
1	Nickel chloride	500	Matrix metal solution (MMS)
2	Ammonium chloride	120	
3	Ammonium citrate	80	
4	Saccharine	2	
5	Sodium lauryl sulfate	0,05	
6	Chlohydric acid	Adjust pH	
7	Nitric acid	Activate metal surface	
8	Nano silicon carbide	1 ÷ 10	Nanoparticals
9	Nano titania	1 ÷ 10	Nanoparticals

Schematic diagram of plating is shown in Fig .1. The specification is described in Table 2.

Table 2. Technological conditions

No.	Conditions	Range
1	Current density	600 ÷ 1200 mA/cm^2
2	Temperature	25^{o}C
3	Time	10 min
4	Stir	On
5	Brush speed of anode on metal surface (cathode)	15 m/min
6	Contact area of anode with cathode	15%

The structures of the the nanocomposite Ni-SiC-TiO_2 coatings were characterized by some methods such as polarization curves determination (Tafel graphs), salt resistance measurement in corrosion test chamber, energy dispersive X-ray analysis (EDX), scanning electron microscope (SEM) and micro hardness.

3. RESULTS AND DISCUSSION

3.1. Polarization curves (Tafel graphs)

Table 3. Corrosion data by polarization curves

No.	Composition of electrolysis solution	Current density (mA/cm^2)	E0	I corr (A)	Corrosion rate (mm/year)
1	MMS	800	-250	1,00E-05	0,1025
2	MMS + 1 g/l SiC, 1g/l TiO_2	800	-240	3,00E-06	0,0308
3	MMS + 2 g/l SiC, 2g/l TiO_2	600	-237	3,20E-06	0,0328
4	MMS + 2 g/l SiC, 2g/l TiO_2	800	-230	2,80E-06	0,0287
5	MMS + 2 g/l SiC, 2g/l TiO_2	1000	-235	2,80E-06	0,0287
6	MMS + 2 g/l SiC, 2g/l TiO_2	1200	-230	4,00E-06	0,0410
7	MMS + 5 g/l SiC, 5g/l TiO_2	800	-228	2,80E-06	0,0287
8	MMS + 10 g/l SiC, 10g/l TiO_2	800	-230	3,20E-06	0,0328

The determination of corrosion resistance of C45 steel results in E_0 = -682, I_{corr} = 3,414E-05 and corrosion rate of 0,35 mm/year.

Corrosion resistance of the nanocomposite $Ni\text{-}SiC\text{-}TiO_2$ coatings were determined. Results shown in Table 3 prove that when the C45 steel surface was protected by a nano-brush coating, corrosion resistance increased and corrosion rate decreased in accordance with the concentration of nanoparticles in electrolysis solution and plating's current density.

It can be explained from the results that the nano size feature of the particals joining electrolysis solution makes change in their brush-coatings properties, especially corrosion ones.

As the corrosion resistance and the stability of titanium (IV) oxide is remarkable, coating containing titanium (IV) oxide performs a diminishing corrosion rate in comparison to that containing only silicon carbide.

3.2. Salt resistance in corrosion test chamber

In order to assert polarization's results, salt resistance in corrosion test chamber is determined, in which corrosion rate of material is accelerated.

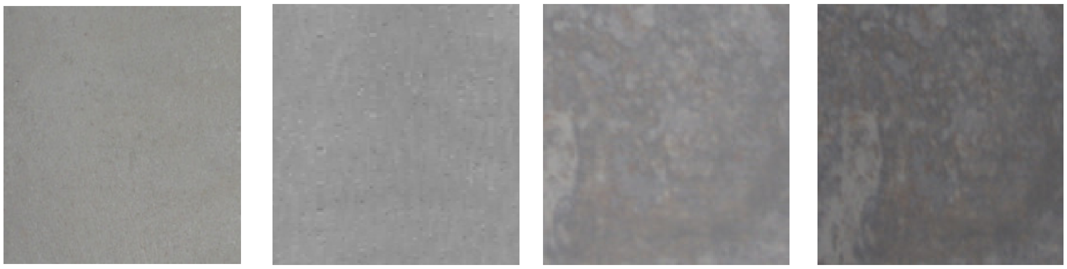
Results are shown in figure 2.

after 3 days after 12 days after 24 days after 30 days

(a) C45 steel

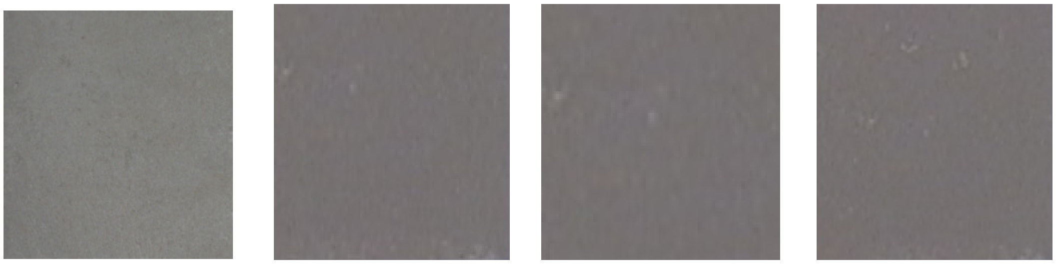
after 3 days after 12 days after 24 days after 30 days

Nanocomposite was plated from MMS with current density was 1000 mA/cm^2 and time was 10 minutes



after 3 days after 12 days after 24 days after 30 days

(b) Nanocomposite was plated from MMS + 1g/l SiC, 1g/lTiO$_2$ with current density was 1000 mA/cm^2 and time was 10 minutes



after 3 days after 12 days after 24 days after 30 days

(d) Nanocomposite was plated from MMS + 2 g/l SiC, 2 g/lTiO$_2$ with current density was 1000 mA/cm^2 and time was 10 minutes

Figure 2. Image of coating surfaces in salt resistance test

Results in figure 2 show that: if not being protected by coating, sample a (C45 steel) will corrode immediately after 30 days exposed in corrosion test chamber, showing an ulcerated surface and some large rust stains. Sample b (brush-plating steel), after 12 days exposed in corrosion test chamber, reveals white streaks on gray-yellowish color of the coating. Up to 30 days, the number of white streaks increased, creating blisters on the coating. Meanwhile, samples c and d, after 30 days exposed in corrosion test chamber, have had almost no white streaks on the surfaces, indicating no signs of salt corrosion. This confirms that corrosion resistance of nanocomposite is higher than that of pure nickel plated and when the concentration of nanoparticles increased (of sample d is higher than of the sample c), the corrosion resistance also increased.

3.3. Microhardness of nano-coatings

The results of microhardness test are shown in table 4 and figure 3.

The results show that samples plated by nanocomposite had a higher microhardness than that of pure nickel coating. It can be explained that the hardness of coatings depends on its crystal structure: small fine crystals make it hard for the sliding surface of the crystal to be deformed which increase the hardness. The penetration of hydrogen into metal makes the crystal lattice deflect which increases the internal stress and hardness. Electrolysis solution had high polarization resulting in the small fine crystal structure of the coatings. When there are more particles in the electrolysis solution, coating structure was clearly improved.

Table 4. Microhardness of coatings

No.	**Composition of electrolysis solution**	**Current density (mA/cm^2)**	**Microhardness (kG/mm^2)**
1	MMS	1000	450
2	MMS + 1 g/l SiC, 1 g/lTiO2	1000	640
3	MMS + 2 g/l SiC, 2 g/l TiO_2	1000	700
4	MMS + 1 g/l SiC	1000	740
5	MMS + 1 g/l TiO_2	1000	640

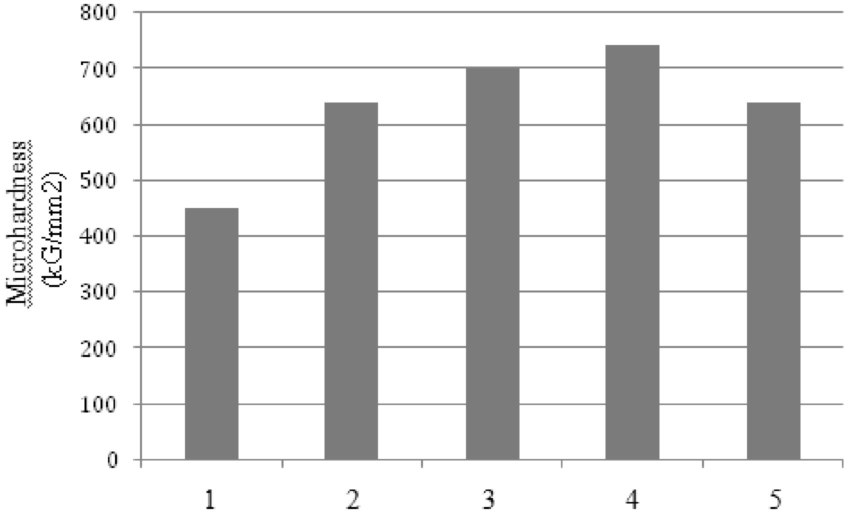


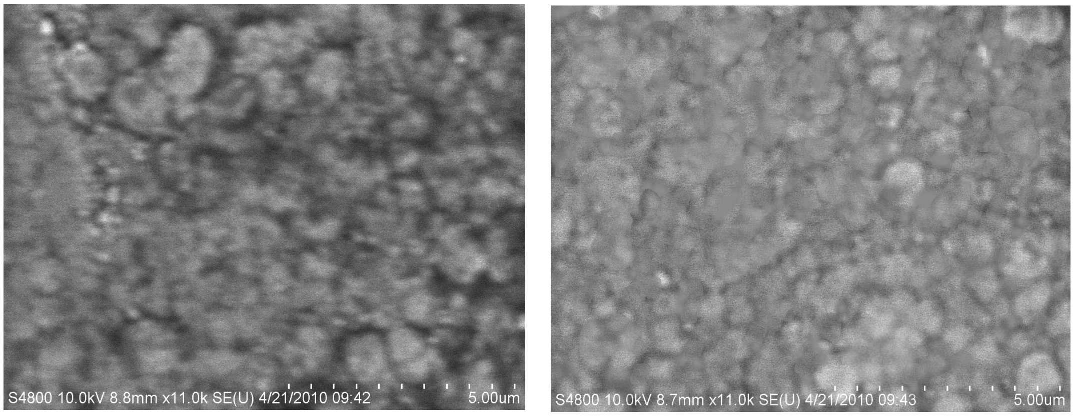
Figure 3. Microhardness chart of coatings

It is also found that nanocomposite coatings containing silicon carbide particles had the highest hardness, for the solid silicon carbide has very high hardness which can be compared with diamond.

3.4. Coatings structure by scanning electron microscope (SEM)

The results of coatings structure by SEM were shown on figure 4.

SEM images from figure 4 show that sample when being added silicon carbide particles has a more finely coating surface, more uniform crystal size and evenly distributed solid particles.



(a) Nanocomposite was plated from MMS with current density was 1000 mA/cm^2 and time was 10 minute

(b) Nanocomposite was plated from MMS + 2g/l SiC, 2 g/lTiO_2 with current density was 1000 mA/cm^2 and time was 10 minute

Figure 4. SEM of nanocomposite Ni-SiC-TiO_2

3.5. Component of coatings structure by energy dispersive X-ray analysis (EDX)

The results of components of coatings by EDX after calculating nanoparticles content were shown in table 5 and figure 5.

Table 5. Nanoparticals content of coatings by EDX

No.	Composition of electrolysis solution	Plated potential	Current density (mA/cm^2)	% SiC	% TiO_2
1	MMS + 2 g/l SiC, 2 g/l TiO_2	6 V	600	0.35	0.17
2	MMS + 2 g/l SiC, 2 g/l TiO_2	8 V	800	0.42	0.20
3	MMS + 2 g/l SiC, 2 g/l TiO_2	10 V	1000	0.44	0.24
4	MMS + 2 g/l SiC, 2 g/l TiO_2	12 V	1200	0.38	0.22

The results in table 5 and figure 5 show that: brush-plating is similar to conventional electroplating process in that the plated potential (or current density) can greatly affect the composition and coating properties. The increase in plated potential (or current density) can increase the content of solid particles on the coating, leading to the improvement of coating properties. Samples a, b, c, using a plated potential correspond respectively to 6, 8, 10V from which, the content of solid particles on coating increased as follows: SiC particles from 0.35 to 0.42; 0.44% mass; TiO_2 particles from 0.17 to 0.20; 0.24%.

However, when the plated potential increases to 12 V, the content of solid particles on the coating tends to decrease. This result can be explained that: at low plated potential (or current density), the exhaust of hydrogen is negligible, so inert particles cannot be pushed away from the electrode surface. The particles adhere easily to the electrode surface, increasing the numbers of particles on coatings surface. When increasing the plated potential to a too high point, the particles content in the coatings decreased because hydrogen gas strongly exhausted and pushed out the solid particles, leaving only a portion of solid particles buried on the coatings surface. In addition, when current density increased, the amount of nickel on coating was large so the percentage of solid particles decreases.

Therefore, if the speed of anode brushed on cathode is 15m/minute, area of anode contact with cathode is 15% and plated during 10 minutes at room temperature (25^{o}C). The electrolysis solution consists of MMS, 2 g/l SiC and 2 g/l TiO_2, the plated potential should be10 V.

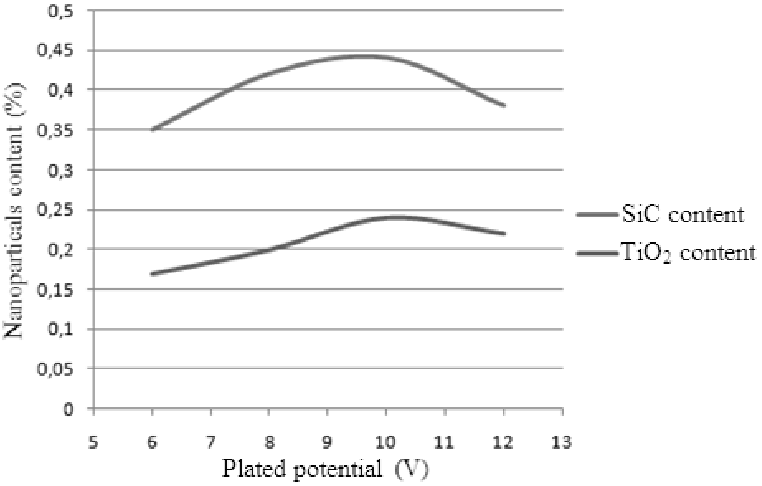


Figure 5. The dependent of nanoparticals content on plate coatings on plated potential

4. CONCLUSION

Nanocomposite Ni-SiC-TiO_2 coatings have high corrosion resistance, uniform distribution of nanoparticals and smooth surface structure. If composition of coating contains more amounts of nanoparticals, the properties of coatings would be better. However, the amount of nanoparticles should be considered for the reason of economy.

Quality of nanocomposite Ni-SiC-TiO_2 coatings prepared by manual brush plating technology is limited by operator. This technology will be more useful and accurate if the equipment was upgraded to automatic equipment.

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