J Appl Electrochem (2008) 38:1211–1216
DOI 10.1007/s10800-008-9535-1

ORIGINAL PAPER

Production of nickel powder by the titanium redox method and its application to conductive materials

Shinji Inazawa · Masatoshi Majima · Keiji Koyama · Yoshie Tani · Hideaki Toshioka · Misako Osoegawa · Hideki Kashihara

Received: 7 December 2007 / Revised: 26 February 2008 / Accepted: 26 February 2008 / Published online: 11 March 2008

Abstract An attempted was made to produce nickel powder in an electroless nickel plating bath using Ti (III) ions as the reducing agent. The crystallite diameter of the obtained nickel powder was about 1.7 nm. This nickel powder magnetically formed chain-like clusters, because the primary particles were small. The resistance of the chain-like powder paste-applied sheets was less than about 1/8 compared to that of the existing spherical powder-applied sheets. To exhibit the same resistance as the spherical nickel powder-applied sheets, the amount of nickel can be markedly reduced by applying the chain-like nickel powder.

Keywords Titanium redox · Metal powder · Nickel · Electroless plating · Conductive sheet

1 Introduction

Recently, a number of studies using micropowders have been conducted. Particles are classified into particles, microparticles, and nanoparticles according to their diameter. Although the classification is not strict, particles with a diameter of less than 100 nm are generally termed nanopowder [1]. This is because particles with a diameter of about 100 nm or smaller may exhibit new characteristics that are not observed in microparticles with a diameter of more than 100 nm. For example, magnetic materials, such as iron and nickel, transform from multi- into single-domain particles at a diameter of about 100 nm, and their magnetic characteristics change [2]. To produce particles with a diameter of more than 1 μm, break-down processing, in which metal blocks are mechanically crushed using grinders, is generally used. On the other hand, when particles with a diameter of less than 1 μm are produced, build-up processing, in which particles are enlarged through nucleation and growth, is useful [2]. For this, gas-phase methods, such as chemical vapor deposition (CVD), and liquid-phase methods to deposit metals in liquid using reducing agents, are employed. Since manufacturing facilities are simpler for liquid- than for gas-phase methods, the former is suitable for mass production, but contamination with impurities from solution during deposition has been a major problem [2–4].

In electroless plating by liquid-phase methods, codepositing of impure constituents derived from reducing agents is known [5], and phosphorus and boron are contaminants of deposited nickel. A new electroless nickel plating method using the (IV) / Ti(III) redox couple as the reducing agent has been investigated to eliminate such problems, which we named the titanium redox method [6–15]. In this method, the nickel film is deposited on substrates, such as Pd catalyzer-applied urethane, and the purity of the obtained nickel film was more than 99.9%. After plating, titanium ions can be regenerated using electrolysis. We examined the self-decomposition areas in electroless plating baths by evaluating the compositions of reaction solutions and reactive conditions for the titanium redox method, and clarified the conditions under which not nickel film but nickel micropowder is obtained. Furthermore, we produced various metal powders by dissolving metal ions, other than nickel ions, as the metal sources before reduction. In this study, we report nickel-powder

---

S. Inazawa (✉) · M. Majima · K. Koyama · Y. Tani ·
H. Toshioka · M. Osoegawa · H. Kashihara
Electronics and Materials R&D Laboratory, Sumitomo Electric Industries Ltd., 1-1-3 Shimaya, Konohana-ku, Osaka 554-0024, Japan
e-mail: inazawa@sei.co.jp

production conditions for the titanium redox method and characteristics of conductive sheets using nickel powder.

2 Experimental methods

2.1 Nickel-deposition rate and nickel-powder production conditions in the titanium redox method

Table 1 shows the basic compositions of plating solution for the titanium redox method. In this method, the oxidation of Ti (III) ions does not result in the irreversible decomposition in a plating solution; only a reversible change of the oxidation state of titanium ions from Ti (III) to Ti (IV) takes place during the Nickel deposition. The sum of Ti (III) ions as the reducing agent and Ti (IV) ions regenerated by electrolysis and reduction was set at twice the concentration of Ni (II) ions, taking into consideration the fact that the reduction of Ni (II) ions is a 2-electron reaction. Nitrilotriacetic acid and sodium citrate were used as complexing agents, 25% ammonia water as a pH adjuster, and a small amount of amino acids as a bath-stabilizing agent. All chemicals used were reagent grade, produced by Wako Pure Chemical Industries Ltd. The Ni (II) ion source was nickel sulfate pentahydrate, and the Ti (III) ion source was 20 wt% titanium trichloride. It was speculated that nickel powder was generated from the zone of high nickel deposition rate. We examined the nickel-deposition rate on 25 mm × 25 mm × 0.5 mm-sized rolled copper plates immersed in plating solution, and evaluated the conditions within the range of high nickel-deposition rates for the efficient production of nickel powder in the bath. If not indicated otherwise, the concentrations of Ti (III) and Ti (IV) ions were both 0.04 mol dm^{-3}, the pH was adjusted to 8.4 using ammonia in the initial stage of the new injection of plating solution into a plating bath on evaluation of the nickel-deposition rate, and the temperature of the bath was 323 K. After degreasing and rinsing of substrates in water, they were immersed in the plating bath and electroless nickel plating was performed for 10 min with nitrogen bubbling. After plating, the substrates were removed from the bath, rinsed in water, dried in air at 343 K, and subjected to analysis of the nickel film. When nickel powder was generated, the powder was filtered, rinsed in water, dried in air at 343 K, and subjected to various analyses.

Table 1 Basic composition of plating bath

Nickel sulfate	0.04 mol L^{-1}
Titanium chloride	0.08 mol L^{-1}
Trisodium citrate	0.24 mol L^{-1}
Nitrilotriacetic acid	0.04 mol L^{-1}
Amino acid	100–500 ppm
pH (adjusment with ammonia)	8–9
Bath temperature	50 °C

2.2 Analysis of nickel film and characterization of nickel powder

To determine the amount of nickel deposition on the copper plates, the nickel film was dissolved in 1 mol dm^{-3} nitric acid, and all metal components were measured by the ICP-MS method. The purity of nickel powder was determined by measuring all metal components by the ICP-MS method after dissolving in 1 mol dm^{-3} nitric acid. The nickel particle diameters were determined by the Scherrer method after powder X-ray diffraction measurement using RAD-RINT (Rigakusha). The powder conditions were observed by scanning electron microscopy (SEM) (JEOL Ltd.).

2.3 Production of conductive sheets using nickel powder

Predetermined amounts of nickel powder, produced by the titanium redox method, and polyvinylidene fluoride (PVdF) powder, as a binding agent, were mixed, and a paste of the mixture was produced using n-methyl-2-pyrrolidone. The dried paste was applied to polyimide film to a thickness of about 0.2 mm by the doctor blade method and dried at 150 °C for 2 h. The resistance of the sheets obtained was measured by the four-probe method. For the comparison of resistance, conductive sheets were produced using spherical nickel powder with a diameter of about 200 nm (JFE Mineral Inc.). The dried sheets were compressed to the predetermined thickness by the rolling press method, and their resistance was measured.

3 Experimental results and evaluation

3.1 Conditions for the generation of nickel powder by the titanium redox method

The effects of the composition of plating solution in the bath on the nickel film deposit rate were examined. Figure 1 shows the results obtained by changing the concentration of Ti (III) ions, which function as the reducing agent, at a constant concentration of Ti (III) and Ti (IV) ions of 0.08 mol dm^{-3}. The plating rate was constant (0.12 μm h^{-1}) at a concentration of Ti (III) ions of higher than about 0.04 mol dm^{-3}. Figure 2 shows the effects of the concentration of nickel sulfate on the nickel-deposition rate, which was slightly elevated at higher concentrations of Ni (II) ions.

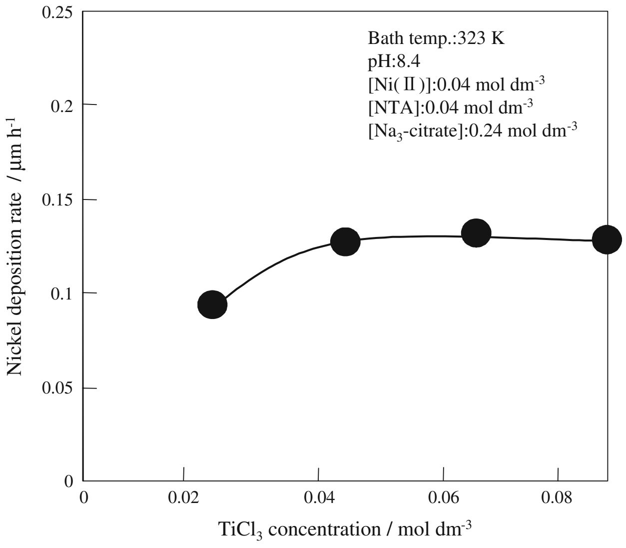

Fig. 1 Effects of Ti (III) concentration on Ni deposition rate

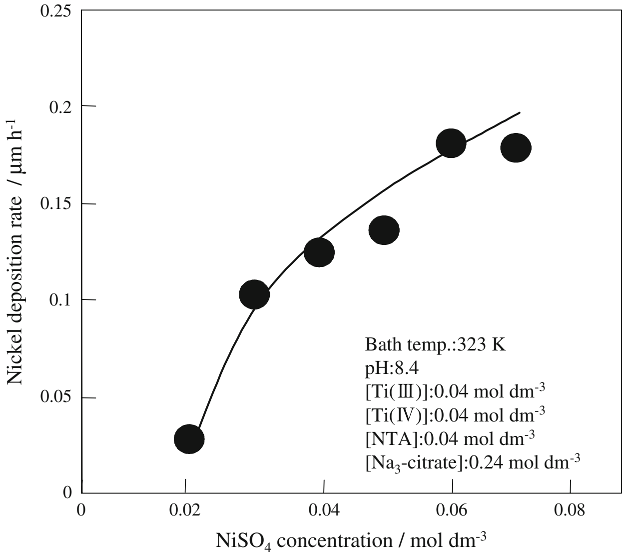

Fig. 2 Effects of Ni (II) concentration on Ni deposition rate

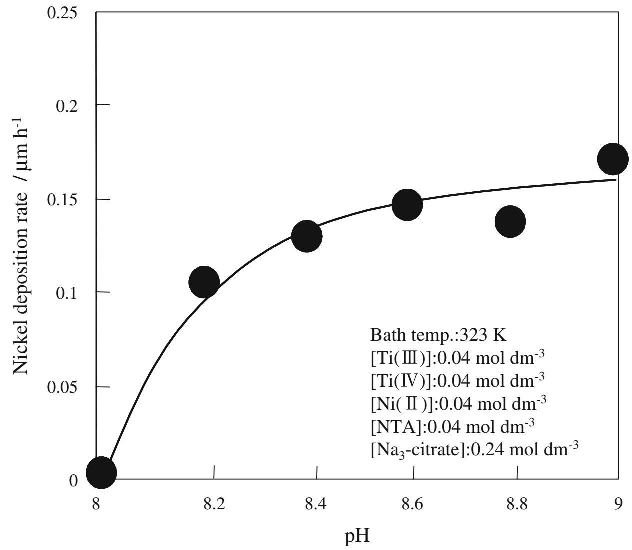

Fig. 3 Effects of pH on Ni deposition rate

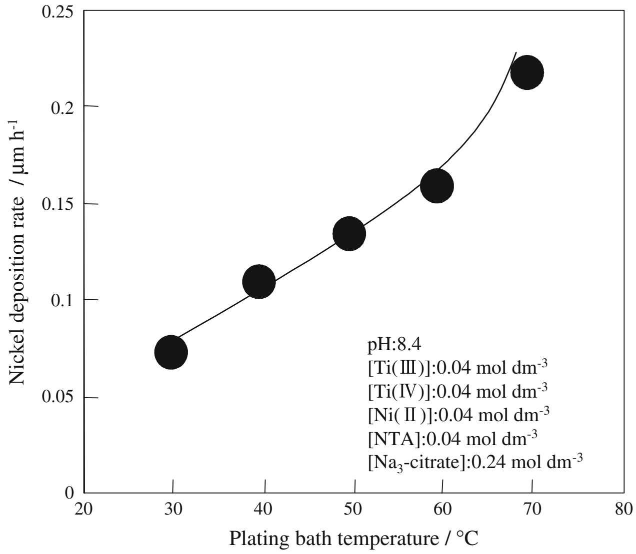

Fig. 4 Effects of bath temperature on Ni deposition rate

Nickel powder was generated at a concentration of Ni (II) ions of higher than about 0.1 mol dm^{-3}. Since it was confirmed that nickel powder was generated even at a low concentration of Ni (II) ions, for example, at 0.01 mol dm^{-3}, without amino acids, which had been added to stabilize the bath condition, we also performed nickel powder generation experiments without adding amino acids to the bath. Figure 3 shows the results obtained by changing the pH of the bath using ammonia. The plating reaction barely occurred at a pH lower than 8, while, at pH 8.2–9.2, the nickel film deposit rate was rapid, and the bath was relatively stable. At a pH of about 9.3, the generation of nickel powder was initiated, and it was significant at around pH 9.5. However, white titania was generated together with nickel powder at excessively high pHs. Figure 4 shows the results obtained by changing the temperature of the bath. The plating reaction occurred even at room temperature, and the rate of deposit was higher with increases in temperature. However, water evaporation and ammonia dispersal were not negligible at a temperature of more than 343 K. Based on these results, a bath temperature between room temperature and 323 K was considered appropriate for the generation of nickel powder. Figure 5 shows the results obtained by changing the concentration of nitrilotriacetic acid (NTA). The plating reaction was rapidly suppressed at an NTA concentration of more than 0.045 mol dm^{-3}, and nickel powder was readily generated at an NTA concentration of lower than 0.02 mol dm^{-3}. Since NTA suppressed the generation of nickel powder, but

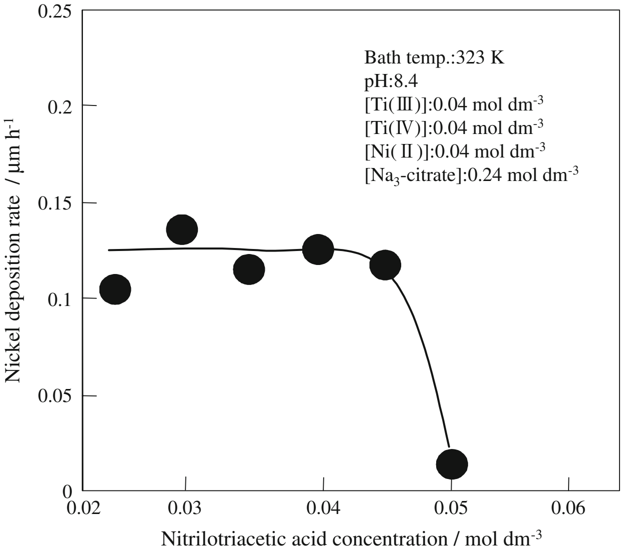

Fig. 5 Effects of nitrilotriacetic acid concentration on Ni deposition rate

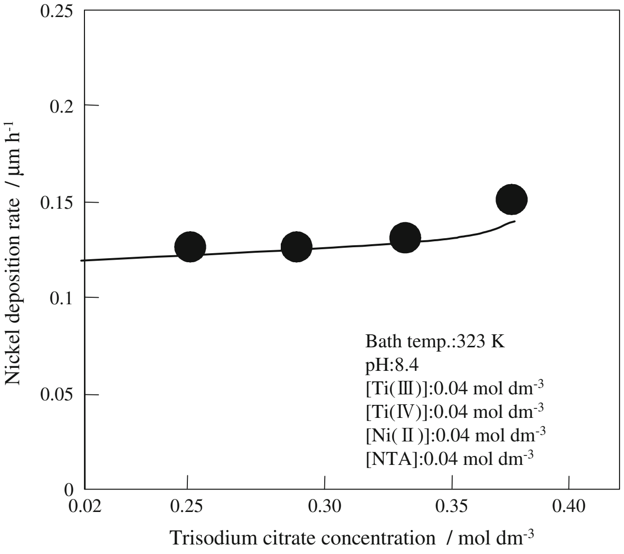

Fig. 6 Effects of trisodium citrate concentration on Ni deposition rate

did not enhance it, we examined the generation of nickel powder without adding NTA to the bath. Figure 6 shows the results obtained by changing the concentration of trisodium citrate. The concentration of trisodium citrate hardly affected the plating rate, but Ti (IV) ions were unstable on the highly alkaline side at a concentration of lower than 0.02 mol dm^{-3}, and white titania powder was generated. At a markedly high concentration of trisodium citrate, the plating rate did not change, but the electrolytic reduction from Ti (IV) ions to Ti (III) ions was difficult, as reported in the previous study [13].

These experimental results indicated that the concentration of nickel, pH, and temperature among various reaction factors greatly affected the generation of nickel

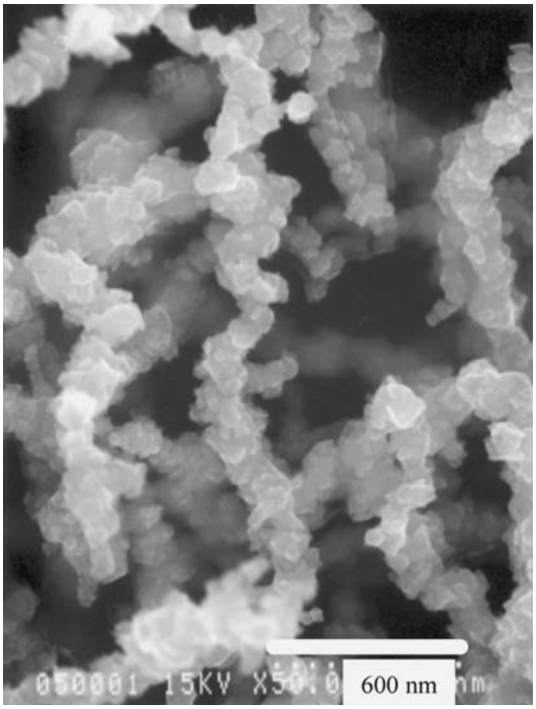

Fig. 7 SEM Image of nickel chain-like cluster

powder. As an example, the generation of nickel powder was performed under the following conditions: Without adding NTA to the bath, 0.3 mol dm^{-3} of trisodium citrate and 0.04 mol dm^{-3} of nickel sulfate (pH 9.5), in which the concentration of Ti (III) ions was 0.1 mol dm^{-3}, were agitated in the bath at about 400 rpm using a stirrer with a fluororesin propeller blade, and the reaction was performed at 308 K for about 60 min. Nickel powder was collected after filtration, rinsed with water, and dried. Figure 7 shows an SEM image of the nickel powder. The yield was 98.5%. The powder had a chain-like structure. SEM demonstrated that the mean thickness of the chains was about 150 nm, and the length ranged from 1 to 20 µm. The purity of the nickel powder determined by ICP was higher than 99.9%.

3.2 Application of nickel powder to conductive paste

The obtained nickel powder and commercially available nickel foil with a thickness of 1 mm (Nilaco Corporation) were examined by X-ray diffraction measurement. Figures 8 and 9 show the XRD patterns. These patterns indicated orientations of (111) in the nickel powder and (100) in the nickel foil. This difference in orientation may be caused by rolling for the production of nickel foil. The crystallite diameter determined by the Scherrer method was 1.7 nm for the nickel powder and 40.1 nm for the nickel foil, indicating that it was significantly smaller in the former. Nickel powder forms chain-like clusters through secondary agglutination, but the diameter of primary

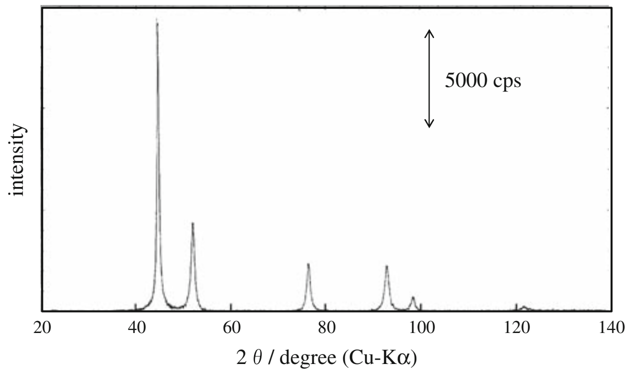

Fig. 8 XRD pattern of a nickel particle

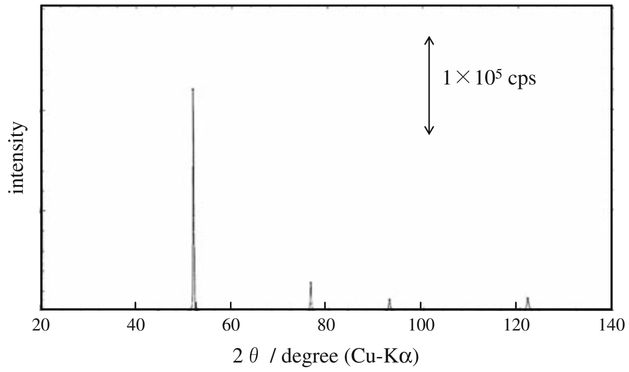

Fig. 9 XRD pattern of a nickel foil

particles is considered to be very small. Magnetic metals, such as nickel, transform from multi-domain into single-domain particles at a diameter of about 100 nm, and the magnetic characteristics change. Since each nickel particle with a primary diameter of less than about 10 nm acts like a magnet, which can have only two poles, magnetically connected chain-like clusters are considered to be formed. If a conductive paste is produced using such chain-like powder, it will be highly electroconductive.

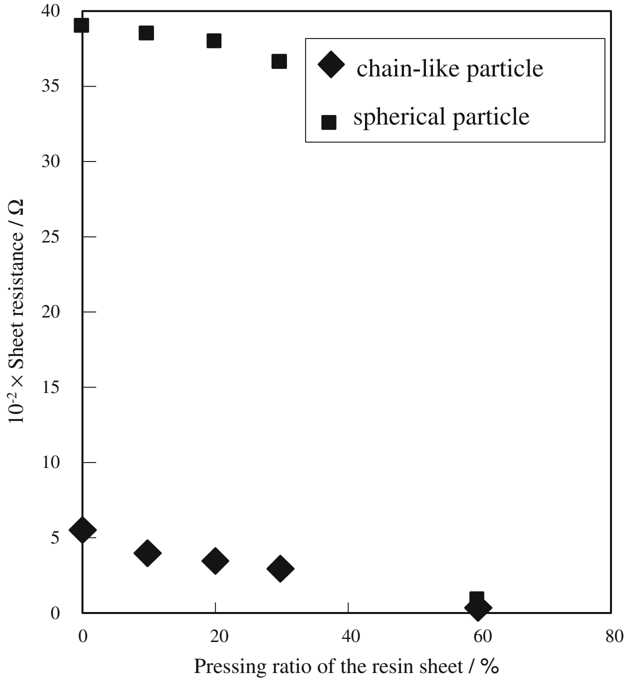

Fig. 10 Measurement of conductive sheet resistance

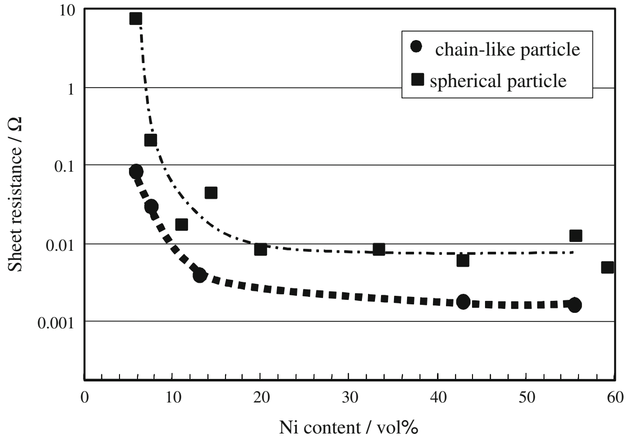

Fig. 11 Resistance dependence on powder content

Figure 10 shows the resistance of conductive sheets produced using nickel powder. Since the contact resistance between metal particles is reduced by compressing sheets using rollers, the resistance of sheets produced using the obtained nickel powder and commercially available spherical powder became slightly low, and finally reached almost the same level. However, the resistance of sheets after the application of the chain-like powder paste was less than about 1/8 compared to that after the application of the commercially available spherical powder. These results indicated that the chain-like powder paste-applied sheets exhibited high conductivity without compressing them. Figure 11 shows the relationship between the amount of various applied powders and resistance. To exhibit the same resistance as the spherical nickel powder, the amount of chain-like nickel powder can be reduced. Since resistance is low with a small amount of metal powder, the electrostatic capacity of metal powder-applied sheets can be low, suggesting that the nickel powder produced in this study can be used for various purposes other than as a conductive paste, such as to produce sheets that act against electrostatic discharge.

4 Conclusions

We examined conditions required for the production of nickel powder by the titanium redox method, and evaluated the applicability of the produced nickel powder to a conductive paste. The results were as follows:

(1) The purity of nickel powder produced by the titanium redox method was higher than 99.9%, and the crystallite diameter determined by the Scherrer method was 1.7 nm, which was smaller than that of commercially available nickel foil (40 nm).

(2) The nickel powder produced by the titanium redox method formed chain-like clusters. The resistance of the chain-like powder-applied sheets was less than about 1/8 compared to that of the spherical powder-applied sheets. To exhibit the same resistance as spherical powder-applied sheets, the amount of nickel can be reduced by applying the chain-like nickel powder.

References

1. Toray Research Center (1999) New development of nanoparticles. Toray Research Center, Tokyo
2. Koizumi M, Moku Y, Chujo S, Niihara K (2001) Newest technology for nanomaterials. CMC, Tokyo
3. Uchida M (1997) J Surf Finish Soc Jpn 48:400
4. Gutzeit G (1959) Plating 46:1275
5. Narcus H (1967) Plating 54:389
6. Warwick ME, Shirley BJ (1980) Trans Inst Met Finish 58:9
7. Obata K, Sonoda T, Dohi N (1982) J Met Finish Soc Jpn 33:375
8. Sviridov VV, Shevchenko GP, Susha AS, Diab NA (1996) J Phys Chem 100:19632
9. Nakao S, Kim D, Obata K, Inazawa S, Majima M, Koyama K and Tani Y (2001) Abstracts of Frontiers of Surface Engineering 2001 (FSE 2001), Nagoya, Japan, Oct 28–Nov 1:232
10. Inazawa S, Majima M, Koyama K, Tani Y, Nakao S, Kim D and Obata K (2001) Abstracts of Frontiers of Surface Engineering 2001 (FSE 2001), Nagoya Japan, Oct 28–Nov 1:231
11. Nakao S, Kim D, Obata K, Inazawa S, Majima M, Koyama K, Tani Y (2003) Surf Coat Technol 169–170:132
12. Inazawa S, Majima M, Koyama K, Tani Y, Nakayama S, Nakao S, Kim D, Obata K (2002) J Surf Finish Soc Jpn 53:694
13. Inazawa S, Majima M, Koyama K, Tani Y, Nakayama S, Nakao S, Kim D, Obata K (2003) J Surf Finish Soc Jpn 54:488
14. Inazawa S, Majima M, Kariya A, Koyama K, Nakayama S, Nakao S, Kim D, Obata K (2004) J Surf Finish Soc Jpn 55:741
15. Yagi S, Murase K, Tsukimoto S, Hirato T, Awakura Y (2005) J Electrochem Soc 152(9):C588–C592