Transactions of the Materials Research Society of Japan 25 [1] 43-46 (2000)

Morphology and Hydrogen Desorption Characteristics of Ni-TiN Nanocomposite Particles Prepared by DC Plasma and RF Plasma

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Mixed and composite Ni-TiN nanoparticles were prepared by an active plasma-metal reaction (a DC plasma) method. Homogeneous distribution of spherical Ni and cubical TiN nanoparticles is observed for the mixed Ni-TiN nanoparticles. Dumbbell-like or dice-like morphology is seen for the composite Ni-TiN nanoparticles. Good thermal stability of both nanoparticles was confirmed. Hydrogen sorption-desorption characteristics of the nanoparticles were examined by temperature-programmed desorption measurements. Hydrogen desorption at 620-680 K is observed for the composite Ni-TiN nanoparticles, that is considered to be due to the spillover hydrogen. Effect of CO coadsorption on the hydrogen desorption is also examined and new adsorption sates are suggested. To increase the catalitic properties finer Ni-TiN nanocomposite particle was prepared by RF plasma, where the raw Ni-Ti alloy powder feeded into the plasma was prepared by combustion synthesis of Ni and Ti powders. The morphology of the composite Ni-TiN particles was similar to that produced by DC plasma. The amount of hydrogen desorption is much larger than that prepared by the DC plasma method.

Key words: nanoparticle, nanocomposite, Ni, TiN, hydrogen desorption

1. INTRODUCTION

Since Ni is one of the most active catalysts for the reactions of hydrogenation of carbon monoxide to hydrocarbons [1], its nanoparticle is expected to be an excellent catalyst. However the smaller the particle size, the lower the thermal stability. Therefore, metal nanoparticles must be stabilized by stable materials. In the previous paper, we prepared metal, nitride and their bonded nanoarticles by vaporization-condensation of metals or alloys in N_2 and /or H_2 atmosphere using a DC arc plasma [2]. In the present paper, preparation of Ni-TiN nanocomposite particle is conducted using the DC and RF plasma methods. Then morphology and hydrogen sorption-desorption characteristic of the prepared Ni-TiN nanocomposites are examined. The results are compared with Ni-TiN mixed nanoparticle prepared by the DC plasma method and a role of the interface of Ni and TiN is estimated.

2. EXPERIMENTAL

2.1 Sample preparation by DC plasma

The apparatus for preparing nanoparticles by reactive plasma-metal reaction method (DC plasma) was described elsewhere [2]. Ni-TiN mixed nanoparticles were produced by mixing Ni and TiN nanoparticles in a mixer with the aid of circulating gas [3], where the two kinds of particles were generated separately by arc melting Ni (99.95 % purity) and Ti (99.9 % purity). Ni-TiN nanocomposite particles were synthesized by arc melting Ni-Ti parent alloy under the following condition [4]; sample volume 3 cm^3, atmosphere $7\%N_2$-$46H_2$-Ar, total pressure 0.1 MPa, gas flow rate 0.2 m/s, arc current 250 A, arc voltage 25-28 V, reaction time 60-1200 s.

2.2 Sample preparation by RF plasma

NiTi alloy raw powder, which fed into the RF plasma by the carrier gas, was prepared by combustion synthesis in a vacuum [5]. Production of nearly 100 % NiTi intermetallic compound was confirmed by X-ray diffraction (XRD) measurement. The combustion-synthesized porous NiTi ingot was ground and NiTi alloy powder was prepared. This method is useful to obtain the alloy powder.

The apparatus for preparing nanoparticles by RF plasma was shown elsewhere [6]. The apparatus consists of an RF generator, a plasma reactor, a powder feeder, gas supply system, and exhaust system. The torch has four independent gas flow: two types of outer flows, inner flow and carrier gas flow. Argon gas was added to the outer flow, and the alloy powder was fed into the plasma by the carrier gas through the center tube. Operating conditions were as follows; gas flow rate (Inner Ar: 20 l/min, Outer Ar: 15 l/min, Another Outer Ar: 15 l/min, Powder carrier N_2 gas: 2 l/min), Power output : 14 kW (4.2 kV, 3.3 A). Nanoparticles produced are carried and gathered on a filter with an aid of suction pump.

2.3 Characterization

The morphology and the structure were examined by transmission electron microscopy (TEM) observations and XRD measurements.

Temperature-programmed desorption (TPD) experiments were performed to determine the sorption-desorption characteristics of hydrogen on the nanocomposite particles[7]. After reduction treatment at the temperature range of 573-673 K, that were confirmed by TG-DTA, the samples were heated to 773 K in vacuum. Then the samples were cooled down to fixed temperatures followed by exposure to hydrogen at a pressure of 350 Torr for 1 h, and cooled to room temperature rapidly. After sufficient evacuation (approximately 10^{-8} Torr) at room temperature, the samples were heated at a constant rate of 5 K/min. The gases that evolved were monitored with a quadruple mass spectrometer. Coadsorption of CO was also examined, where the sample was exposed to 350 Torr H_2 followed by 150 Torr CO at fixed temperatures for 1h.

3. RESULTS AND DISCUSSION

3.1 Sample characterization prepared by DC plasma

Figure 1 shows TEM micrographs of Ni, TiN and mixed Ni-TiN nanoparticles. The morphology of the Ni nanoparticles is spherical and that of TiN is cubical. In the mixed nanoparticles, the spherical Ni and cubical TiN nanoparticles are distributed homogeneously.

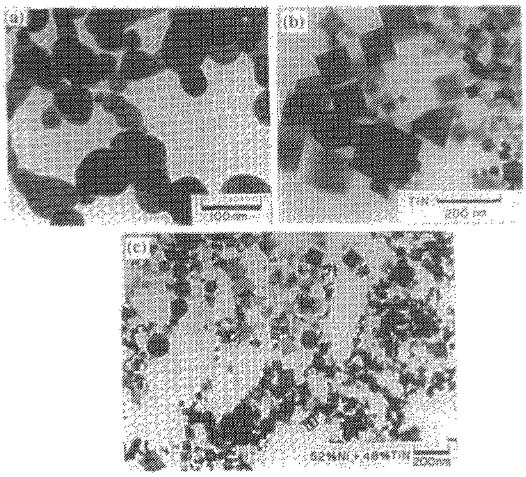

Figure 1. TEM micrographs of Ni (a), TiN (b) and mixed Ni-TiN (c) nanoparticles.

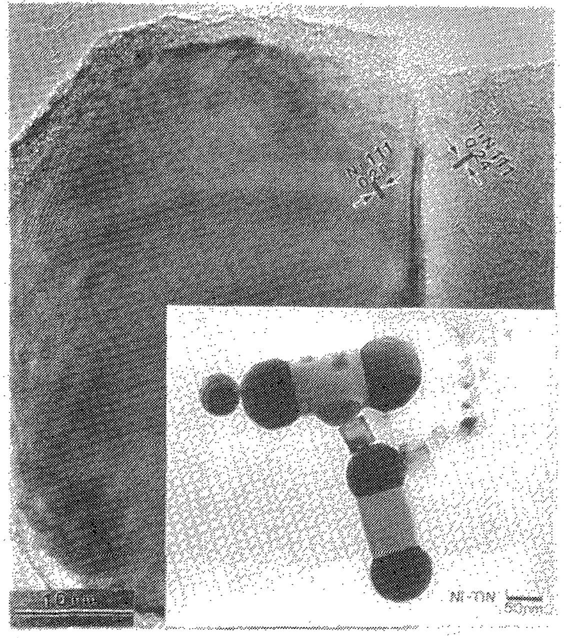

Figure 2. TEM and HR-TEM micrographs of Ni-TiN nanocomposite particles prepared by DC plasma.

Figure 2 shows typical TEM and HR-TEM micrographs of Ni-TiN nanocomposite particles. Dumbbell-like structure is seen. From an energy dispersive X-ray analysis, it is seen that Ni particle is spherical and TiN particle is cubical. The lattice spacing of the rod part is 0.24 nm, whose value corresponds to that of TiN(111) plane. The spacing of the spherical part is 0.20 nm, whose value corresponds to that of Ni(111) plane. This TEM micrograph supports the formation mechanism of the nanocomposite particle presumed by Ohno *et al.* [4[: (i) vaporization of Ni and Ti into the nitrogen atmosphere, (ii) nucleation of TiN owing to the reaction of Ti vapor with nitrogen, (iii) deposit of a Ni-Ti-N melt on the TiN nucleus, (iv) crystallization of TiN on the TiN nucleus from the Ni-TiN melt and (v) solidification of residual Ni rich melt.

XRD measurements of the Ni-TiN nanocomposite showed small amount of Ni_3Ti phase in addition to the Ni and TiN phases. The lattice constant of the TiN phases in the nanocomposite particles takes a constant value (a=0.4240), which is coincident with the JCPDS's value (6-0642: 0.4240 nm), which indicates that the composition of Ti to N is nearly stoichiometry. On the other hand, increase of the lattice constant of Ni in the Ni-TiN was observed up to about 12 mol% TiN content in the nanocomposite in comparison with the undoped one. This result suggests that nitrogen, Ti and/or TiN is dissolved into Ni in the nanocomposite particles, which also supports the above formation mechanism of the nanocomposite particle.

Since the particles have been exposed to air; therefore the surfaces of them are oxidized and contaminated with various gases. From the TPD, XRD, FTIR, XPS and HR-TEM measurements, the surface chemistry of the nanoparticles is concluded as follows [8-10]. The surfaces of the Ni and TiN nanoparticles contain NiO and amorphous TiO_2, respectively. Moreover the surfaces of the oxides contain hydroxide-like and/or carbonate-like compounds. When heating the TiN nanoparticle, which have been exposed air, at 973K in vacuum, TiN and TiO_2 (anatase) were observed. This suggests that the surface of the TiN nanoparticle is similar to TiO_2.

SEM micrographs showed that significant grain growth is observed for the Ni nanoparticles but not for the nanocomposite particles after heating 773 K for 1 h in hydrogen.

3.2 Sample characterization prepared by RF plasma

Figure 3 shows TEM micrograph of distorted dumbbell-like Ni-TiN nanoparticles. From the EDAX, it is confirmed that the middle part is TiN and both sides are Ni. The surface chemistry and thermal stability were similar to those prepared by DC plasma.

3.3 Hydrogen desorption

Figure 4 compares TPD spectra of hydrogen from the Ni-TiN mixed and two types of nanocomposite

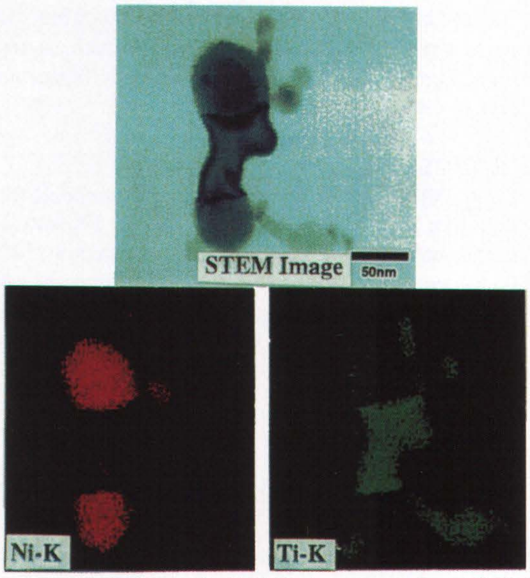

Figure 3. TEM and EDAX images of Ni-TiN nanoparticles prepared by RF plasma.

particles after the cleaning procedure followed by exposure to hydrogen at fixed temperatures. The desorption peaks are observed in the temperature ranges of 380-430 K for the mixed nanoparticles. On the other hand, another desorption peaks are observed for the nanocomposite particle in the temperature range of 620-680 K prepared by DC plasma and 500-700 K prepared by RF plasma, and it is seen that the higher the exposing temperature shifts the higher the peak temperature.

In case of TiN nanoparticle alone, no hydrogen desorption peaks were observed [8]. As for the adsorption of hydrogen on surface of Ni, two hydrogen desorption peaks from Ni nanoparticles have been detected at around 380 K and 430 K [7] at above room temperature.

The appearance of the hydrogen desorption at higher temperatures in Figs. 4(b) and (c) imply that new adsorption state of hydrogen exists over the nanocomposite particles. Spillover hydrogen [11] desorbed from TiN surface may be a feasible explanation. Similar spillover hydrogen desorption was observed at 720 K from alumina supported Ni [12] and at 623-723 K from titania supported platinum [11].

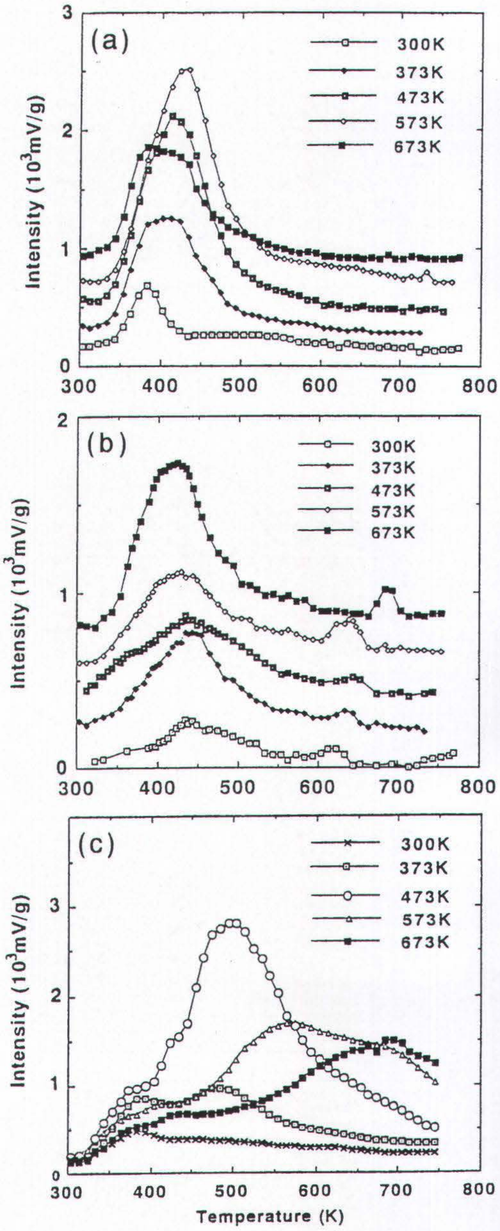

Figure 4. TPD spectra of H_2 from the mixed Ni-TiN (a), nanocomposite particles prepared by DC plasma (b), and by RF plasma (c) after exposure to 350 Torr H_2 for 1 h at fixed temperatures.

3.4 Effect of CO coadsorption on hydrogen desorption

From the gas phase analysis after exposure to H_2 and CO for 1h, no other species but H_2, CO or H_2O were observed for the nanocomposite particles exposed at 300K. For the sample exposed at 573 K, however, CH_4 and C2-C6 gases were detected. Figure 5 shows the TPD spectra of H_2 and CO for the Ni-TiN nanocomposite particles prepared by DC plasma after exposure to H_2+CO at fixed temperatures for 1h. Concerning the sample exposing at 300 K, the hydrogen desorption spectrum is not so influenced by the coadsorption of CO. As for the sample exposing to H_2+CO at 573 K, however, a new hydrogen desorption peak at 550 K is observed and at the same temperature CO desorption peak is also observed. This result implies that new desorption states associating with CO arise. The complexes may be formed by an activated process in which CH_3O or H and CO spillover on to the TiN surface [13].

3.5 Comparison

Figure 6 shows the amount of hydrogen desorption as a function of exposing temperatures for both H_2 and H_2+CO atmospheres. The amount of hydrogen desorption increase with the exposing temperatures up

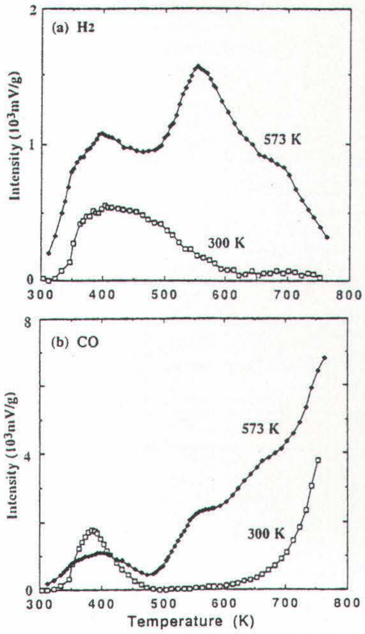

Figure 5. TPD spectra of H_2 (a) and CO (b) from the Ni-TiN nanocomposite particles prepared by DC plasma after exposure to H_2+CO.

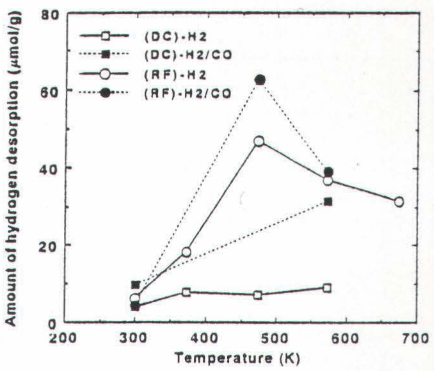

Figure 6. Comparison of exposing temperature dependencies on the amounts of H_2 desorption from two types of Ni-TiN nanocomposite particles.

to 473 K. In the absence of CO the amount of hydrogen desorption of the Ni-TiN by the RF plasma is much larger than that by the DC plasma, but in the presence of CO those are not so different. In case of the Ni-TiN by the DC plasma, the amount of hydrogen desorption increases in the presence of CO. However, in case of the present Ni-TiN by the RF plasma, the amount of hydrogen desorption is not so influenced by the coadsorption of CO. Similar result is observed for Co-TiN nanocomposite particles prepared by the DC plasma [14]. These phenomena are supposed to be influenced not only by the interface of nanocomposite particle but also surface contamination such as free carbon. Further studies on the surface chemistries are needed to explain those phenomena.

4. CONCLUSION

Composite Ni-TiN nanoparticles with dumbbell-like or dice-like morphology were produced by DC and RF plasma methods. Hydrogen desorption peaks at 500-700 K are observed, which indicates that a new adsorption state of hydrogen exists. The amount of hydrogen desorption from th nanocomposite particles prepared by RF plasma was much larger than that prepared by DC plasma.

Acknowledgment

This work was supported by Special Coordination Funds of the Japanese Science and Technology Agency.

REFERENCES

1. M. A. Vannice and R. L. Garten, J. Catal. 56, 236 (1979).
2. S. Ohno and M. Uda, J. Jpn. Inst. Met. 48, 640 (1984).
3. S. Ohno, Y. Sakka, H. Okuyama, K. Honma and M. Ozawa, MRS International Meetings on Adv. Mater. 3, 3 (1989).
4. S. Ohno, K. Honma, H. Okuyama and M. Ozawa, J. Jpn. Inst. Met. 53, 936 (1989).
5. M. Ohtaguchi, Y. Kaieda , N. Oguro, S. Shite and T. Oie, J. Jpn. Inst. Met., 54, 214 (1990).
6. Y. Sakka, H. Okuyama, T. Uchikoshi and S. Ohno, Nanostruct. Mater., 8, 465 (1997).
7. T. Uchikoshi, Y. Sakka, S. Ohno, H. Okuyama and K. Yoshihara, Surf. Sci. 287/288 1082 (1993).
8. Y. Sakka, S. Ohno and M. Uda, J. Am. Ceram. Soc. 75, 244 (1992).
9. Y. Sakka and T. Uchikoshi, Powder Met. 36, 179 (1993).
10. T. Uchikoshi, Y. Sakka, M. Yoshitake and K. Yoshihara, Nanostruct. Mater. 4, 199 (1994).
11. D. D. Beck and J. M. White, J. Phys. Chem. 88 , 2764 (1984).
12. R. Kramer and M. Andre, J. Catal. 58, 287 (1979).
13. B. Sen and J. L. Falconer, J. Catal. 122, 68 (1990).
14. Y. Sakka and S. Ohno, Appl. Surf. Sci. 100/101, 232 (1996).

(Received December 17,1999 ; Accepted February 15,2000)