Structure of Iron/Nickel Composite Cluster Assemblies Prepared by Double Glow-Discharge-Sources

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Using a double-grow discharge cluster source system Fe and Ni clusters have been produced and deposited simultaneously on a substrate. A mixture of Fe and Ni clusters have been obtained with inserting separation plates between two grow discharge rooms and in the center of a growth tube, where partially alloyed cluster assemblies are formed. Fe-Ni alloy cluster assemblies have been obtained without inserting the separation plate. This alloying behavior is different from core-shell cluster formation in simultaneous deposition of Co and Si clusters, and Fe and Si clusters without inserting the separate plate. The present results suggest that structure and morphology of composite clusters strongly depend on the surface energy and degree of oxidation of elemental clusters. [doi:10.2320/matertrans.47.1949]

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1. Introduction

Assembling of nanometer size clusters is a unique method for fabricating nano-scale structure-controlled materials in contrast to conventional precipitated materials. In the latter, since small particles are made from supersaturated solution via low temperature heat treatment, the particle size and inter-particle distance cannot be adjusted independently owing to the materials balance. In order to utilize the size-dependent characteristics of nano-clusters, we have to make regular size clusters, and to prevent their surface oxidation and inter-cluster aggregation. Using a plasma-gas-condensation-type (PGC) cluster deposition system, we have succeeded in preparing mono-dispersive size transition metal clusters whose mean diameters, \( d \), range between 6 and 15 nm with the standard deviation less than 10% of \( d \).² In the PGC which is a combination of sputter vaporization³ and gas-condensation techniques,⁴ metal atoms vaporized from the targets rapidly lose their kinetic energy by collisions with the Ar atoms, leading to formation of cluster nuclei. Then these cluster nuclei collide and coalesce each other, forming larger clusters in fright space.⁵ When we deposit such clusters on a substrate and increase the deposition time, the number of clusters increases and small micro-clusters can very quickly migrate on a substrate even at ambient temperature being similar to surface diffusion of adatoms on a substrate.⁶,⁷ This feature is attributed to surface melting and/or defect-induced diffusion of nanometer-size clusters. In cluster-metallurgy is the spontaneous alloying of island-like metal clusters prepared on transmission electron microscope grids by thermal evaporation:⁷,⁸ the initially formed metal clusters are alloyed with metal atoms supplied by the post-evaporation. If the collision and coalescence stages of different kinds of vaporized metal atoms and/or single element clusters are controlled, various kinds of clusters such as compound clusters and composite clusters are expectable. In this report, we describe structures and morphologies of Fe/ Ni composite cluster assemblies prepared by the double glow discharge sources. We also discuss the alloying behaviors in Fe/Ni comparison with the previous results for Co/Si and Fe/Si clusters because the equilibrium phase diagram of Fe/ Ni alloys is of a solid solution type, and those of Co/Si and Fe/Si are of a compound formation type.⁹–¹¹

2. Experimental

We made a double-source PGC cluster deposition system by modifying our previous co-sputter-deposition apparatus, which has a couple of facing target-type sputtering rooms used for preparing alloy and multilayer films.¹² Figure 1 shows a schematic drawing of the PGC system. In this study, each cluster source was operated with a dc glow discharge mode, whereas one cluster source was previously operated with an rf glow discharge mode. For preparing clusters, we reduced the distance between the target–shield space to prohibit corona-discharge in the high Ar gas atmosphere (from 0.1 to 1 kPa).¹³ We provided an air-tight wall between sputtering chamber and deposition chamber to differentiate the pressure and vacuum conditions of these two regions. Removable separation plate could be placed in the center of the growth tube and between chambers 1a and 1b, where the vacuum conditions of both chambers were almost the same.
A large amount of Ar gas with the flow rate, \( R_{\text{Ar}} \), \( (= 3.33 \times 10^{-6} \text{ m}^3/\text{s}) \) was introduced into the sputtering chamber from a gas inlet, and evacuated by a powerful mechanical booster pump (500 m\(^3\)/h) through a small nozzle. Clusters formed in the growth tube were ejected together with Ar gas through this small nozzle with the diameter of 3 mm. Chemical compositions, morphologies and structures of Fe, Ni and Fe/Ni composite clusters deposited on carbon-coated microgrids were measured by a transmission electron microscope (TEM) (Hitachi Co., HF-2000) operating at 200 kV in which an energy dispersive X-ray analyzer (EDX) was installed. The size distribution of deposited cluster was estimated by direct measurement of bright-filed TEM images by a ruler.

### 3. Results

Figures 2(a) and (b) show typical bright-field TEM images of elemental Fe and Ni clusters obtained by a single discharge mode. The dc input power, \( P_w = 250 \text{ W} \) for both Fe and Ni targets. In these images, cluster sizes are not so monodisperse as those prepared using our previous single source- PGC cluster deposition system. In this experiment, since cluster nucleation and growth regions were not confined in a small space, the cluster sizes were widely distributed. As shown in Fig. 2, the average sizes of Fe and Ni clusters are almost the same being about 5.5 nm.

Figure 3(a) shows a bright-field TEM image of an Fe/Ni composite cluster assembly prepared without placing the separation plate; \( P_w = 300 \text{ W} \) for both the Fe and Ni targets. As seen in Fig. 3(a) the mean cluster diameter is about 7.6 nm and their sizes are not monodispersive, where the standard deviation is about 39% of \( d \). The average (overall) cluster composition determined by EDX observation of cluster assemblies deposited on the microgrid area of 1\( \mu \text{m} \) was about 58 at% Ni. We also measured chemical compositions of individual clusters using a nano-beam analysis and confirmed that they were not so different from the average within the experimental error. Figure 3(b) is the corresponding electron diffraction (ED) pattern. The diffraction rings indicated by arrows can be indexed as an fcc-(\( \gamma \)-Fe-Ni) structure and the estimated lattice constant is about 0.357 nm. Since the PGC cluster deposition is a rapid cooling process the high temperature fcc phase is stabilized.\(^9\)

Figures 4(a) and (b) are bright-field TEM images taken at different positions of the one carbon microgrid on which Fe/ Ni composite clusters were prepared with inserting the separation plates between chamber 1a and 1b, and in the
center of the growth tube; $P_w = 300$ W for the Fe target and $P_w = 100$ W for the Ni target. The average composition is about 31 at% Ni in Fig. 4(a), while it is about 71 at% Ni in Fig. 4(b). These figures show that Fe (Fe-rich) and Ni (Ni-rich) clusters are separately deposited on different positions of a substrate. Figures 4(c) and (d) show the ED patterns of Fe/Ni composite cluster assemblies corresponding to Figs. 4(a) and (b). They consist of diffractions rings of fcc-(γ-Fe-Ni) and bcc-(α-Fe-Ni) structures, where the bcc rings in Fig. 4(d) are much weaker than the fcc ones in Fig. 4(c), reflecting their compositional difference.

Figure 5 shows lattice constants as a function of the average chemical composition of Fe/Ni composite cluster assemblies prepared by several experimental conditions. As shown in Fig. 5, the lattice constants of the fcc phases in Fe/Ni composite clusters prepared without inserting the separation plate roughly agrees with those of the bulk fcc Fe-Ni alloys, indicating that partial alloying between Fe and Ni clusters is induced during the collision and coalescence processes on the substrate.

4. Discussion

As described in the previous section, Fe and Ni clusters are not well alloyed even when they collide and coalesce each other on the substrate, at most leading to partially alloyed cluster assemblies. However, Fe-Ni alloy cluster assemblies are formed when Fe and Ni clusters collide and coalesce each other in the flight space and deposited together on the substrate. The latter results are consistent with the reported behaviors: Au island with Cu and Zn adatoms on substrate: nanoscale island-like clusters on a substrate are immediately alloyed with postdeposited atoms at ambient temperature as long as the sizes of island-like clusters are smaller than 10 nm.\(^7,8\)

Formation of Fe\(_2\)Ni, FeNi and FeNi\(_3\) ordered phases have been reported for Fe and Ni composite particles obtained by a gas evaporation technique.\(^{16}\) In such a preparation process, cluster nuclei are moderated when they pass through the heating zone before the deposition. Then, the formation of ordered phases is attributed to the appropriate annealing above 470 K. In the present experiment, on the other hand, Fe and Ni clusters are not well alloyed when they collide and coalesce each other on the substrate, at most leading to partially alloyed cluster assemblies. With inserting the separation plate, cluster nuclei are further cooled down. In this case they are not well mixed each other even when they collide and coalesce each other on substrate.

Finally it is worth to compare the present results with those for Co/Si and Fe/Si composite clusters using the same double cluster source PGC system. The formation enthalpies of Co-Si and Fe-Si are as $-48$ and $-39$ kJ/mol, respectively.\(^{17}\) However, a core shell morphology, no alloy and no compound phases were obtained in Co/Si and Fe/Si composite clusters without separation plate.\(^{10,11}\) Since the surface energy of Si is much lower than those of Co and Fe cluster,\(^{18}\) Si clusters preferentially cover Co cluster surfaces, leading to the core-shell cluster formation. Moreover, since the formation enthalpy of Si oxides is much higher than those of Co and Fe oxide, Si cluster nuclei are so easily oxidized to form primary Si oxide clusters, leading no formation of alloy and/or compound clusters with Co and Fe. On the contrary, the formation enthalpy of Fe-Ni is $-1.3$ to $-5.4$ kJ/mol,\(^{17}\) being much smaller than those of Co-Si and Fe-Si. These are no marked difference in the surface energies and oxide formation enthalpies between Fe and Ni.\(^{19}\) However, Fe-Ni alloy clusters are formed when Fe and Ni cluster nuclei collide and coalesce each other in the flight space, while only partial alloying at the Fe and Ni clusters interfaces when they collide on the substrate. These results suggest that the surface energy and degree of oxidation of elemental clusters play key roles to determine the structure and morphology of composite clusters.
5. Summary

We generated and deposited Fe and Ni clusters whose mean size were about 5 to 10 nm using the double-source plasma-gas-condensation apparatus. In Fe/Ni composite cluster assemblies, an fcc phase was obtained when they were prepared without inserting the separation plate, while Fe and Ni clusters were separately formed with inserting the separation plate though their interfaces were partially alloyed. Therefore, novel nano-scale heterogeneous Fe and Ni composite materials, which cannot be prepared by conventional annealing and sintering processes, are available by the double discharge cluster sources.

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