Study on the Chemical State of Polyimide Resin Films Containing Ni-Co Alloy Nanoparticles Synthesized by Liquid Phase Reduction Method

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Composite polymers containing nanoparticles have been widely studied for their scientific and industrial interest. However, most of these polymers were synthesized with single metal nanoparticles. There are few reports on the composite polymers containing alloy nanoparticles [1]. In this study, we focused on polyimide composites that can be simply and easily incorporated with metal nanoparticles [2].

The polyimide composite films containing Ni-Co alloy nanoparticles were prepared by liquid-phase reduction of Ni^{2+} and Co^{2+} ions with potassium borohydride (KBH_4) [3]. A polyimide film was modified by being immersed in a 5.0 mol dm^{-3} KOH solution at 30 ºC for 5 min. The treated film was then immersed in an $NiSO_4$ + $CoSO_4$ mixed aqueous solution at 30 ºC for 5 min to adsorb Ni^{2+} and Co^{2+} ions. The molar ratios of Ni:Co in each mixture solution were 25:75, 50:50, and 75:25. The films with the adsorbed ions were reduced with a 0.60 mol dm^{-3} KBH_4 aqueous solution at 50 ºC for 20 min. The polyimide nanocomposite films containing Ni-Co alloy nanoparticles (Ni-Co NPs/PI) were treated with a 0.25 mol dm^{-3} CH_3COOH solution at 30 ºC for 1 min to remove residual ions. The obtained Ni-Co NPs/PI was heat-treated at 200 ºC for 1 h under vacuum.

Figure 1 shows the results of STEM-HAADF and EDX mapping images of a G3 film that was subjected to three repetitive adsorption/reduction processes using a mixed solution with an Ni:Co molar ratio of 75:25. The size of the obtained nanoparticles was found to be about 6-20 nm in diameter by TEM observation, and the results of EDX mapping showed that Ni and Co atoms coexisted in the same particle. The atomic ratio of Ni and Co in the alloy nanoparticles reflected the concentration of doped Ni^{2+} and Co^{2+} ions. The number of the nanoparticles increased as the adsorption/reduction cycles of both ions were repeated.

Figure 2 shows XAFS spectra of Co-K and Ni-K absorption edges of reduced films that were measured at BL-3 of the SR Center, Ritsumeikan University. The spectra of the non-reduced films are similar to those of $CoSO_4$, CoO, $NiSO_4$ and NiO. Both metal ions adsorbed on the non-reduced film were revealed to exist in the form of Ni^{2+} and Co^{2+} ions. On the other hand, for the reduced films, the shapes of the absorption edge shoulders are close to those of Ni and Co metals, suggesting that both metal ions are reduced to the metals. The chemical state analysis by electron diffraction and XAFS methods revealed that the nanoparticles are amorphous metal alloys.

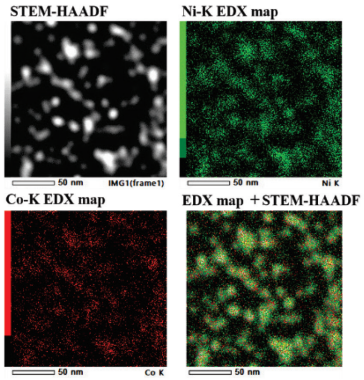

Fig. 1 STEM-HAADF images and EDX elemental analysis maps of Ni-Co-NPs/PI films (G3: $Ni_{75}Co_{25}$).

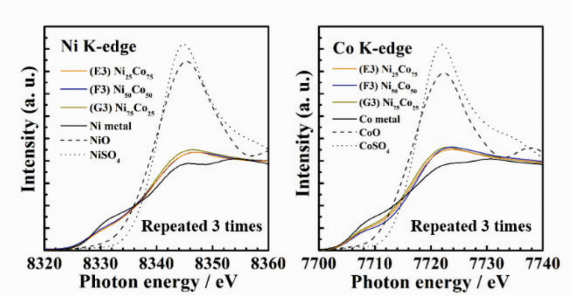

Fig. 2 Co and Ni K-edge XAFS spectra of Ni-Co NPs / PI films of (E3) $Ni_{25}Co_{75}$, (F3) $Ni_{50}Co_{50}$ and (G3) $Ni_{75}Co_{25}$. The spectra are for the samples that were repeatedly reduced three times. Ni metal, NiO, $NiSO_4$, Co metal, CoO, and $CoSO_4$ were used as standard samples.

References

[1] R. Shimizu, et al., *RSC Adv.*, **2016**, *6*, 19846.
[2] D. Fujioka, et al., *RSC Adv.*, **2019**, *9*, 6438.
[3] D. Fujioka, et al., *Mater. Sci. Tech. Jpn.*, **2020**, *57*, 136.