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MICROSTRUCTURE AND CHEMISTRY OF MgO- AND CoO-DOPED NICKEL-TITANATE SPINELS

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When NiO-rich powder mixtures of NiO and TiO₂ are equilibrated in air above ~1425°C and subsequently quenched, X-ray diffraction patterns of the resulting specimens can be indexed with a single set of reflections in the Fd3m space group.^{1,2} Originally this result was cited as evidence of a highly nonstoichiometric single phase. However, subsequent TEM investigations showed that these specimens are composed of periclase- and spinel-structured phases with small domains and coherent phase boundaries.³⁻⁵ Periclase-structured domains are distributed throughout the spinel with two distinct morphologies: cuboidal particles, faceted on {100}, of uniform size that increases from 30 to 150 nm with increasing NiO-mole-fraction; and an isotropic interconnected two-phase microstructure, also of uniform size, varying from 2 to 5 nm seemingly independent of composition. The finer-scale features strongly resemble those arising from spinodal decomposition in an isotropic medium and can be ascribed to decomposition of a nonstoichiometric spinel phase during quenching. It has recently been suggested that the faceted particles coexist with the nonstoichiometric spinel at the equilibration temperature.⁵

An early X-ray diffraction study of MgO- and CoO-doped spinel-containing nickel-titanate showed that the doping results in diffuse reflections.⁶ However, the microstructures and the chemistries of such doped specimens were not examined. An examination of the variation of the microstructural features with dopant concentration may further clarify the origins of the two morphologies.

Four specimens of composition Me_xNi_{1-x}O - 14.2 mol% TiO₂, with Me ∈ {Mg, Co} and x ∈ {0.1, 0.2}, were prepared by cold-pressing powder mixtures into tablets and firing in air at 1600°C for 1 h and 1500°C for 8 h. Slices cut from each of the four tablets were heated together in a crucible at 1450°C for 2.5 h and quenched in water. Three-millimeter discs were cut from each slice with an ultrasonic drill, ground to ~100 μm thickness, dimpled to ~20 μm, and ion-milled to perforation. The specimens were examined in a Philips CM12 transmission electron microscope operated at 120 kV. Preliminary energy-dispersive X-ray spectrometry (EDXS) was performed with an EDAX 9900 analyzer.

Figures 1 and 2 show dark-field (DF) images of the MgO- and CoO-doped specimens, respectively, recorded near the [001]-pole of the two cubic phases with the spinel (220) reflection. In these images, the spinel-structured phase appears bright and the periclase-structured phase appears dark. The microstructure of the specimen doped with 10% CoO, shown in Fig. 2a, is similar to that of undoped material, except the faceted particles are roughly twice as large.^{4,5} The microstructures of the MgO-doped specimens, shown in Fig. 1, exhibit the same general features as Fig. 2a, but with coarser faceted particles and finer isotropic interconnected two-phase microstructures. However, the microstructure of the specimen doped with 20% CoO, shown in Fig. 2b, is clearly different. The spinel- and periclase-structured phases form a continuously interpenetrating network with a characteristic scale of ~40 nm. This change in the microstructure might correlate with a change in the site-distribution of atoms in the spinel. A preliminary examination of the site-distributions in the 20% CoO-doped specimen with the ALCHEMI (atom location by channeling-enhanced microanalysis) technique indicates that the Ti cations primarily occupy the octahedral site. In contrast, these cations occupy the tetrahedral site in undoped nickel-titanate spinel.⁷ The 20% MgO-doped specimen does not exhibit the same change in microstructure. However, an early study of the phase relations in the system MgO-NiO-TiO₂ performed at 1400°C showed that even at this high temperature, a spinel of composition MgNiTiO₄, which would allow the Ni and Ti cations to occupy their preferred octahedral site, is unstable.⁸ The MgO-doped specimens might therefore be expected to exhibit the microstructure in Figs. 1 and 2a, which is characteristic of the defect spinel structure of nickel-titanate, over a wider range of composition.

The arrangement of some of the faceted particles in groups, particularly evident in Fig. 1b, suggest that a large periclase-structured particle may have subdivided. This distribution of particles is similar to those of L1₂-ordered Ni₃Al (γ') particles in a Ni (γ) matrix.⁹ Such a subdivision results from the competition between elastic and interfacial contributions to the free energy of the two-phase system. This "decoarsening" of the microstructure

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occurs over a long time scale and is inconsistent with the hypothesis that the faceted particles form during quenching. The faceted $\sim 100\text{nm}$ -scale particles are therefore likely present as a second phase during the equilibration process. In Figs. 1 and 2a, the coarser microstructures accompanying doping may arise for thermodynamic or kinetic reasons. The presence of the dopant may change the equilibrium size of the faceted particles or may inhibit the evolution of the microstructure. The noncuboidal shapes of some of the particles in Fig. 1b suggests that the microstructure was still evolving when the heating cycle was terminated.¹⁰

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FIG. 1 - DF images of equilibrated and quenched $\text{Mg}_x\text{Ni}_{1-x}\text{O}$ - 14 mol% TiO_2 with (a) $x = 0.1$ and (b) $x = 0.2$. The spinel-structured phase appears bright and the periclase-structured phase appears dark.

FIG. 2 - DF images of equilibrated and quenched $\text{Co}_x\text{Ni}_{1-x}\text{O}$ - 14 mol% TiO_2 with (a) $x = 0.1$ and (b) $x = 0.2$. The spinel-structured phase appears bright and the periclase-structured phase appears dark.

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