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Characterization of Oxide Nano-clusters in Mechanically Alloyed Nickel Alloys

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Following development of a new class of mechanically alloyed (MA) nano-structured ferritic alloys (NFA) with exceptional mechanical properties [1,2] that are largely due to the presence of high concentrations ($>10^{23}$ m^{-3}) of small (<5 nm diameter) Ti-Y-O nano-clusters (NC), an initial effort to produce NC in a face-centered cubic Ni matrix has been undertaken. As with NFA, there is major interest in potential applications to fission and proposed fusion reactors because NC-containing materials may be highly resistant to neutron radiation damage (swelling and embrittlement) [3]. In the present work, two MA Ni alloys were fabricated by ball milling Ni powder (<45 µm) for 40 h with (a) 30Ni-70Ti (<45 µm) and Y_2O_3 (17-31 nm) powders to produce Ni-1.00wt.%Ti-0.60%Y_2O_3 (NTYO) and (b) 30Ni-70Zr (<45 µm) and La_2O_3 (80 nm) powders to produce Ni-1.89wt.%Zr-0.86%La_2O_3 (NZLO). A water-cooled Zoz CM01 attritor ball mill was used with a 10:1 ball/powder ratio and Ar atmosphere. Specimens for transmission electron microscopy (TEM) were prepared by focused ion beam (FIB) milling with a Hitachi FB2000A using lift-out methods that yielded regions <50 nm thick with minimal ion-beam damage and Ga implantation. In order to image NC and small precipitates, energy-filtered TEM (EFTEM) was performed at 300 kV with a Philips CM30 (LaB_6) equipped with a Gatan imaging filter (GIF). In particular, Ni-M jump-ratio images produced from component images recorded with 10-eV slits at 54 and 80 eV and exposures of ≤2 s reveal NC (<2 nm diameter for regions <35 nm thick) in dark contrast. EFTEM was also used to perform thickness and elemental mapping (e.g. Y-M, Zr-M, O-K, Ti-L, and La-M) with 20- or 30-eV slits. Energy-dispersive X-ray spectroscopy (EDS) spectrum imaging was performed in scanning-TEM (STEM) mode at 200 kV with a Philips CM200FEG equipped with an EDAX detector/pulse processor and an Emispec Vision system, typically with a 1.5-nm probe (full width at half maximum) containing ~1 nA and 1 s dwell/pixel.

The grain size of the as-milled powders was only ~20 nm and, surprisingly, EFTEM revealed that high concentrations of small particles were present (Fig. 1). This is quite different behavior from that of NFA such as 14YWT [1] where NC are present only following high-temperature processing. Vacuum annealing ball-milled powders for 1 h at 750 and 800°C (potential extrusion temperatures) resulted in grain growth and considerable coarsening of the particles (Figs. 2 & 3). It is likely that most particles are conventional oxide phases but this is yet to be determined. Interestingly, the larger particles tend to be Zr- and Ti-rich while the smaller particles tend to be La- and Y-rich in NZLO (Fig. 3) and NTYO, respectively. Anneals at higher temperatures were performed to explore the stability of the particles since in NFA the NC show remarkable stability even after annealing at 1300°C. Ball-milled powders were consolidated by hot pressing at 950°C for 600 s to facilitate subsequent anneals at 1000, 1100 and 1200°C for 1 and 10 h. Grain growth and oxide-particle coarsening increased with increasing temperature. Particles as large as 100 nm were present after annealing at 1200°C. As with lower-temperature anneals, the larger oxide particles tended to be Zr- or Ti-rich (Figs. 4 & 5), but some were bi-crystals of a Ti-rich oxide grain with a Y-rich oxide grain (NTYO) or a Zr-rich oxide grain with a La-rich oxide grain (NZLO). In summary, the oxide particles in NTYO and NZLO alloys do not appear to share the unusual and attractive behavior of NC in NFA, an unfortunate result that is supported by first-principles calculations [4,5].

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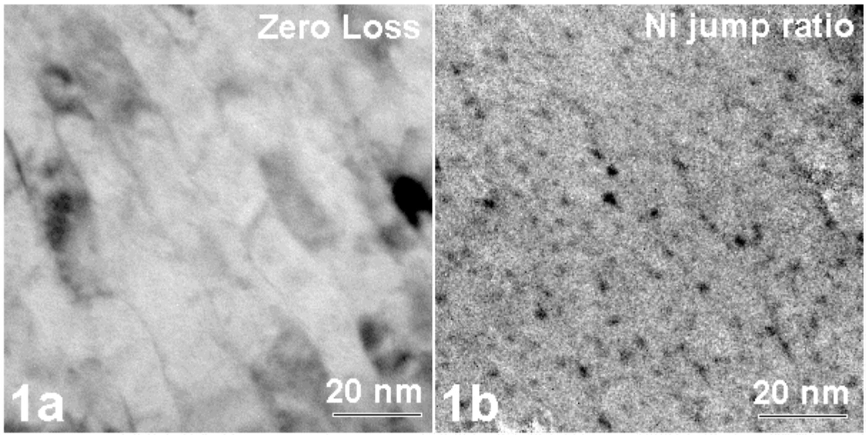
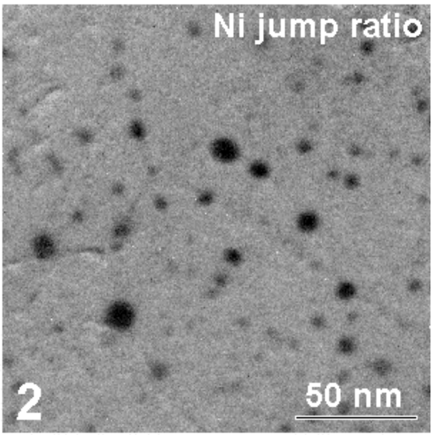




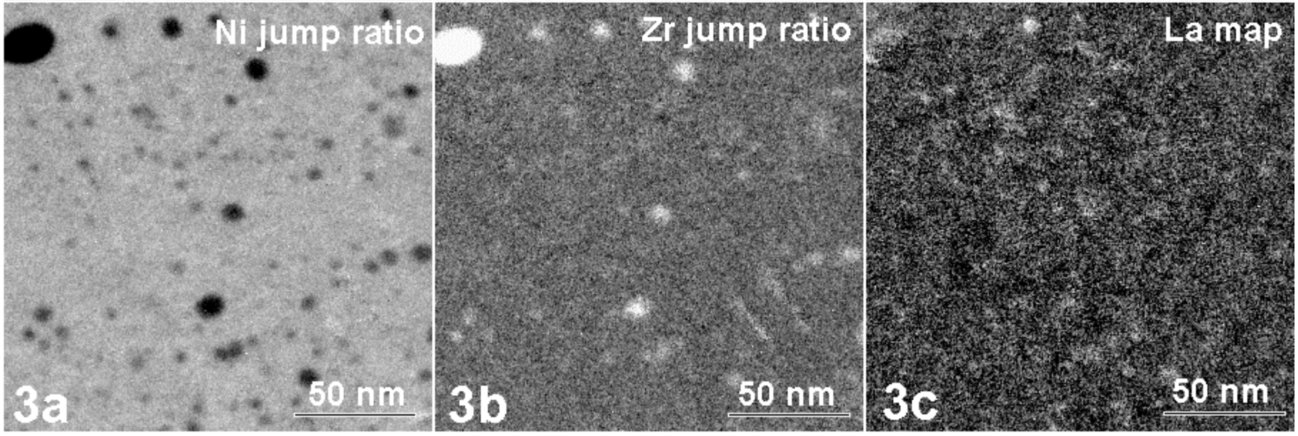
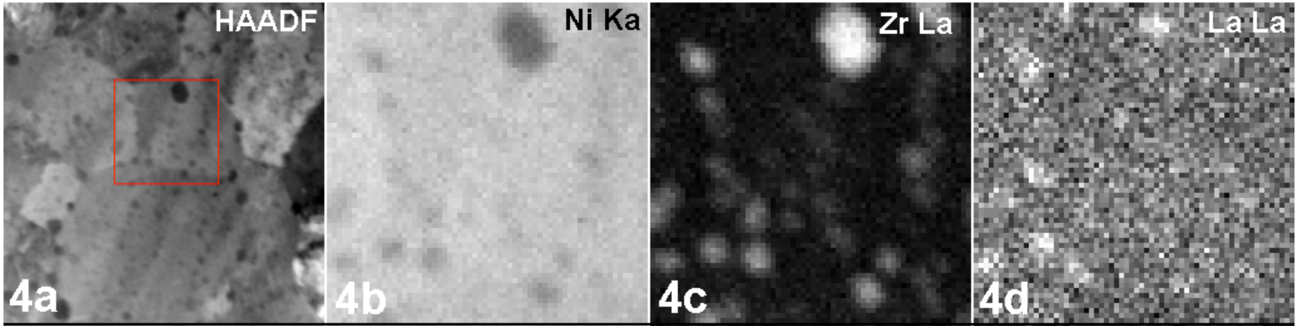


Fig. 1. EFTEM of as-milled NTYO (a) Zero-loss image (b) Ni-M jump-ratio image. Fig. 2. EFTEM Ni-M jump-ratio image of NTYO annealed 1 h at 750°C. Fig. 3. EFTEM of NZLO annealed 1 h at 750°C (a) Ni-M jump-ratio image, (b) Zr-M jump-ratio image, and (c) La-M elemental map.



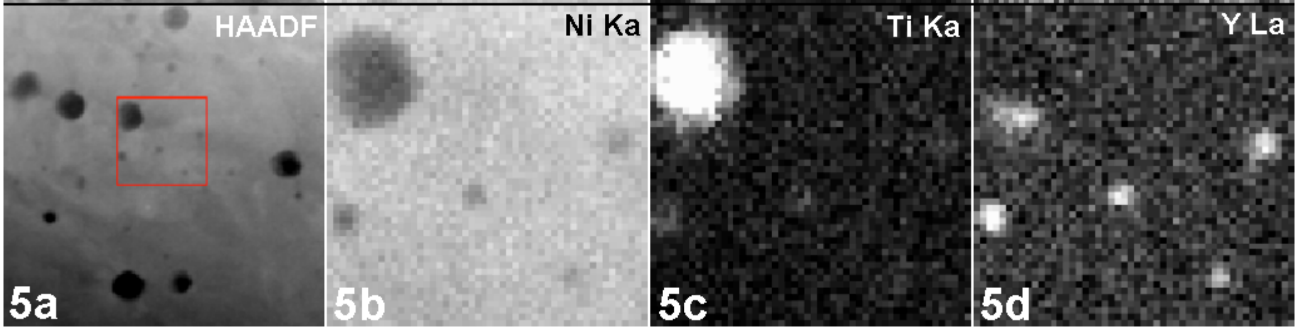


Fig. 4 NZLO and Fig. 5 NTYO, annealed 10 h at 1000°C. (4a, 5a) HAADF STEM images; (4b, 5b) Ni Kα, (4c) Zr Lα, (5c) Ti Kα, (4d) La Lα and (5d) Y Lα maps with 2-nm pixels extracted from spectrum images of (Fig.4) 128 x 128 nm and (Fig. 5) 100 x 100 nm areas marked in 4a and 5a.

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