Atomistic understanding of structural evolution in alnico alloys using advanced AC-STEM

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Understanding architecture in materials down to atomic level is a key for design and fabrication of advanced materials as devices become smaller and interfacial effects dominate performance. Aberration-corrected STEM (AC-STEM) combined with energy-loss and energy-dispersive x-ray spectroscopic techniques (EELS and EDS) provide the necessary quantitative elemental information with sub-nanometer spatial resolution. Utilizing advanced TEM holders, which can provide materials with external effects during imaging process, including thermal, stress/strain, electric field and magnetic field *et. al.*, in addition, enables characterizing materials with both spatially and temporally resolved perspective. This paper describes an overview of our recent progress in a characterizing a magnetic alloy, alnico, using state-of the-art electron beam characterization tools located at the Sensitive Instrument Facility (SIF) in Ames Laboratory.

Alnico alloys (containing Al, Ni, Co, Ti, Fe, and Cu) show great potential for replacing the best commercial Nd-based rare-earth alloys for applications above 200°C. The coercivity of alnico depends on its nanostructure, in particular, the composition and morphology of the Al-Ni-rich, Fe-Co-rich and Cu-enriched phases that developed during spinodal decomposition. The spinodal decomposed structures are developed after a lengthy heat-treatment process, including high temperature solutionization (~1250°C), magnetic-field annealing (~840°C) to induce anisotropic growth of the SD phases, and drawing (~600-700°C) to optimize the magnetic properties. Both *ex situ* and *in situ* TEM are performed to better elucidate the relationship between processing conditions, microstructure and property. Figure 1 shows results on commercial alnico 9 alloy. The Cu-enriched phase was discovered to have a defective structure (Figs. 1a) with a gradual increase of Cu-concentration into the center of the precipitate. Geometric phase analysis (GPA) from Fig.1a indicates the Al-Ni-rich phase is under tensile strain (Fig. 1b). Moreover, chemical composition in this alloy at individual lattice sites was determined by TEM. In the B2 Fe-Co-rich phase the sites exhibit ~ 76 at.% Fe and ~ 40% Fe ordering in the two sites (Fig. 1c), and, in the L2$_1$-ordered Al-Ni-rich phase, the A-sites, BI-sites and BII-sites have compositions of ~ 48 at. % Ni and Co, Al, and ~80 at. % Ti and Fe, respectively [1, 2]. A Ni-enriched/Ti-deficient region at the FeCo/AlNi-rich interface was also detected.

Figure 2 (a) and (b) show high-resolution STEM image and corresponding EDS elemental mapping of Cu in an alnico alloy after solutionization. The Cu-enriched phase has segregated out and formed a coherent lattice structure (*bcc*) with the L2$_1$ matrix. Analysis on a sample with further magnetic field annealing (840°C) and drawing (650°C) showed that the Cu-enriched phase is coarsened, as shown in Fig. 2 (c, d). The Cu/AlNi interface is semicoherent. Shear along the [110] direction was observed in the Cu-enriched phase, which indicating deviation of their lattice from *bcc* crystal structure. This change in microstructure is accompanied by substantial increase of coercivity of the alloy from 35Oe to 1707Oe between solutionized and full heat treated samples.

[1] Lin Zhou , M. K. Miller, Ping Lu, Liqin Ke, R. Skomski, M. McCartney, D. Smith, H. Dillon, Q. Xing, A. Palasyuk, S. Constantinides, R.W. McCallum, I. E. Anderson, V. Antropov, and M. J. Krame, Acta Materilia, 74, (2014), 224.
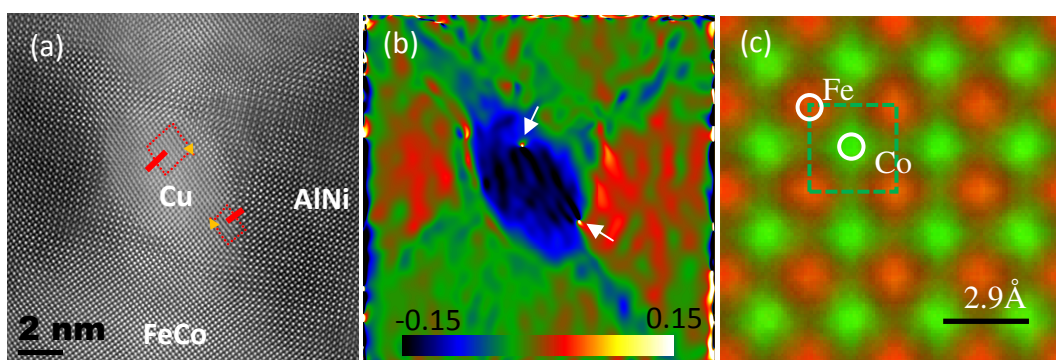[2] P. Lu, L. Zhou L, M. Kramer, D. J. Smith, Scientific Reports 4 (2014) 3945.

Fig. 1 – (a) High-resolution HAADF-STEM image of alnico taken along [001] around a Cu-enriched precipitate. Alternating contrast of (100) planes in the AlNi-rich phase confirmed chemical ordering of this intermetallic. Two dislocations are clearly observed, as indicated by red line with corresponding burgers loop; (b) GPA strain (εxx) map of image (a) showing the AlNi-rich phase is under tensile strain. High compressive strain is observed in the Cu-enriched phase. The position of misfit dislocations is indicated by white arrows. (c) Composite color map of Fe-Kα (red) and Co-Kα (green) showing ordering in FeCo-rich bcc phase. [2]
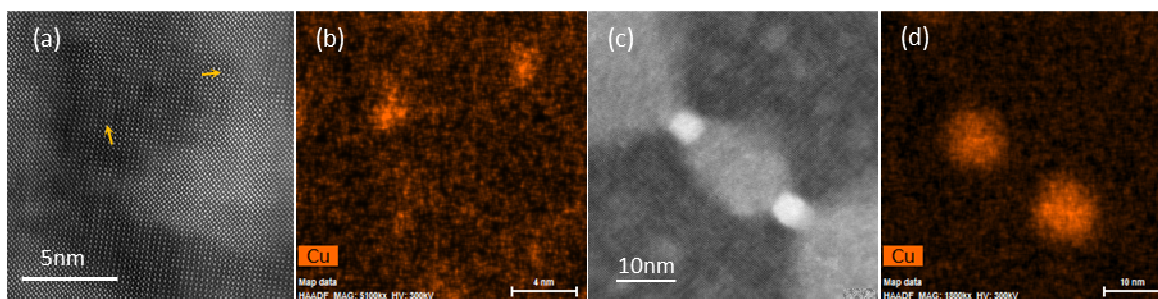

Fig. 2 – High-resolution STEM image and corresponding EDS Cu elemental mapping of an alnico alloy after solutionization at 1250°C(a, b) and further magnetic field annealing (840°C) and draw(650°C) (c,d).