Rapid Structural and Chemical Characterization of Ternary-phase Diagrams by Using Synchrotron Radiation

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Introduction

The development of new materials by combinatorial synthesis and design has recently received much attention because of the potential this technique offers for discovering new materials and improving existing ones. Combinatorial materials science is based on two key elements: (1) simple synthesis techniques that can be used to create large libraries of specimens of varying composition and structure and (2) simple characterization techniques that can be used to rapidly assess the structure and properties of the material libraries. One popular method for synthesizing combinatorial material libraries uses vapor deposition or sputtering to make thin films in which the composition varies continuously in the plane of the film. By these methods, high-quality films with compositions that vary continuously across the binary- or ternary-phase system have been produced [1-4].

Point-to-point characterization of the crystal structures and compositions of the phases in the thin film material libraries can be used to determine the binary or ternary equilibrium phase diagrams. However, in order to be applied efficiently to a large number of material compositions, the techniques must provide for rapid data collection and analysis. Here we describe a technique based on x-ray diffraction and fluorescence that uses synchrotron radiation to achieve these goals. The technique is applied to the Fe-Ni-Cr ternary metallic alloy system, which contains a large number of technologically important metallic materials, such as stainless steel, invar, and nichrome. The technique was used to fully characterize the structure and composition of ternary alloy films annealed at approximately 850°C from which isothermal sections of the phase diagram and contour maps of lattice parameters were constructed. Approximately 2500 compositions were examined in a single experiment that took about 4 hours. Results obtained by the method are compared to the well-established phase diagram and lattice parameter measurements.

Methods and Materials

The samples were prepared by physical vapor deposition followed by annealing. Sequential layers of Fe, Ni, and Cr were deposited on Al_2O_3(0001) sapphire substrates, 50 mm in diameter, by electron beam evaporation in a vacuum of 10^{-6} to 10^{-7} Torr. Each layer was grown with a linear thickness gradient by sliding a stepping-motor-driven shutter located between the specimen and the evaporation target. After a layer was deposited, the sample was rotated 120° for deposition of the next layer. This resulted in a triangular region with an elemental distribution close to that of the composition triangle of a standard ternary-phase diagram. Film thickness was ~2 μm. The layers were alloyed by annealing at approximately 850°C in a vacuum of 5×10^{-7} Torr.

X-ray diffraction and fluorescence data were collected at beamline 33-ID-D of the APS. Undulator radiation, monochromatized to 15 keV by Si(111) crystals and focused to 0.25×0.5 mm^2, was incident on the sample. Diffraction patterns were recorded by a 1024×1024 x-ray charged-coupled device camera. Fluorescence was measured by a thermoelectrically cooled Si PIN photodiode. The sample was rastered on a 1×1 mm^2 grid, with a set of data collected at each point, at 7-s intervals. The composition at each point was calculated from the ratios of fluorescent intensity.

Diffraction patterns were analyzed by using the FIT2D package [5, 6]. The 2-D images were integrated to yield 1-D scans of intensity versus plane spacing. Qualitative phase identification and quantitative lattice parameters were calculated from the integrated patterns.

Results and Discussion

The diffraction patterns reveal another advantage of the CCD detector in addition to its speed. The bcc phase often grows with good epitaxy, while the fcc phase is weakly textured. Data collected with a point or linear detector would incorrectly suggest that the an equal combination of fcc and bcc phases is almost entirely bcc, while the integrated patterns give a more nearly correct ratio of intensities.

A typical experimental ternary-phase diagram section is shown in Fig. 1, along with the known equilibrium phase diagram section for 850°C [7]. The agreement is generally good. The fcc single-phase

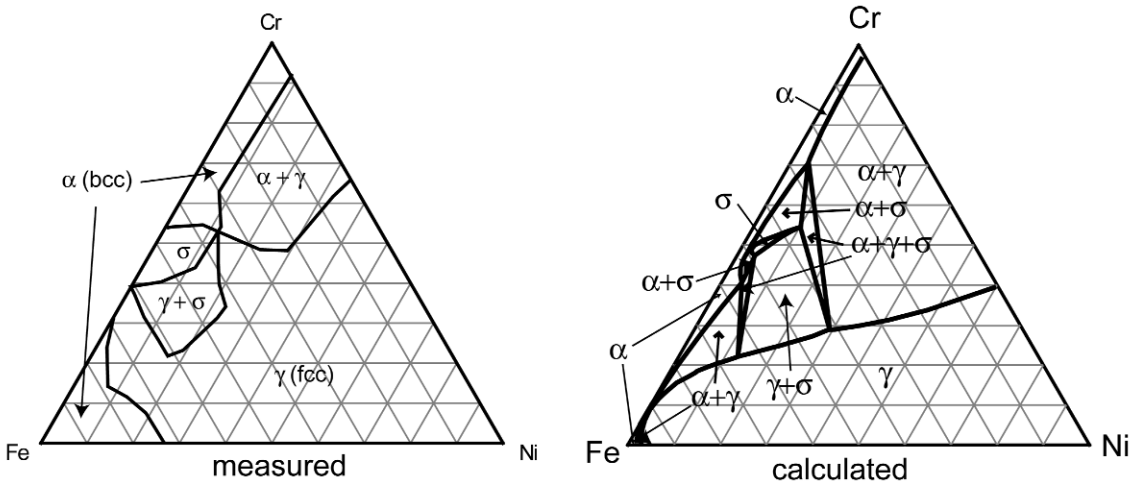

FIG. 1. Phase diagram for a Ni/Fe/Cr/Al_2O_3 film annealed for 20 hours at 850°C, compared to the calculated equilibrium diagram [7].

region extends much further into the Cr-rich area than expected. As a result of the unintended oxidation of these samples. Cr_2O_3 is observed to form on the Cr-rich material, leaving the metal deficient in Cr. The phase boundary will therefore be at a composition with less Cr than indicated by the fluorescence measurement. Abrupt transitions from single-phase α to σ confirm that the measurement achieves resolution of 2 at. %.

There is no significant variation in the lattice parameter of the bcc or s phases. The lattice parameter for the fcc phase, calculated from the (200) reflection, is shown in Fig. 2, along with the results obtained by conventional methods [8]. The agreement is generally good, although some artifacts can be seen along the line of zero Cr concentration, presumably due to starting of the shutter motion. As expected, lines of constant lattice parameters follow tie lines across the two-phase fcc-bcc region.

Acknowledgments

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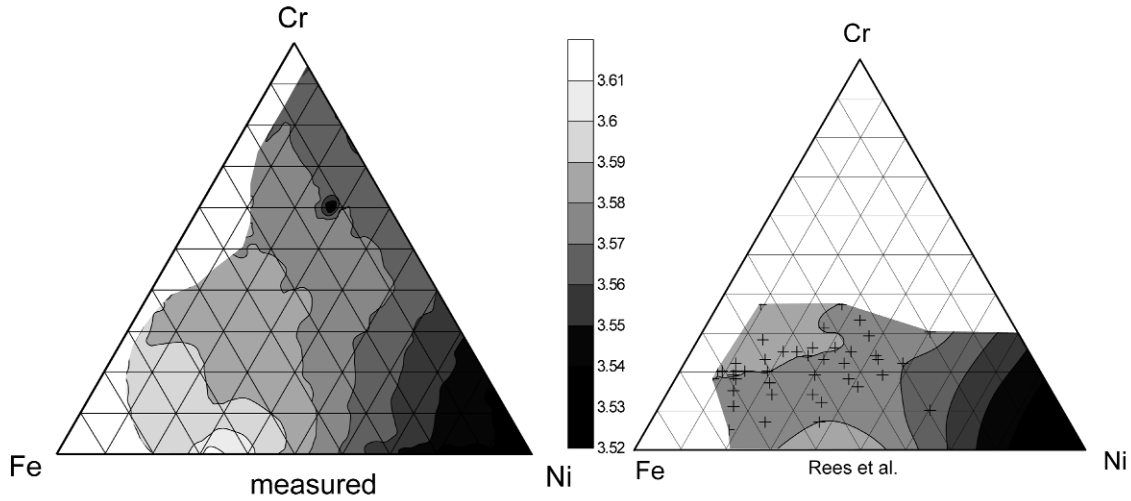

FIG. 2. The fcc lattice parameters (same sample as Fig. 1), compared to equilibrium values [8].

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