Applications of 2D Detectors in X-ray Analysis

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ABSTRACT

X-ray transparent reaction vessels for the dynamic in-situ study of materials processes involving volatile agents have been developed. These chemically inert and airtight cells serve to uniformly heat the sample and its enclosed environment while minimizing the loss of vapor species from the cells. Currently these cells are being employed to study such applications as phase evolution in thallium-based superconductors and the incongruent reduction of oxides by magnesium-containing melts. The study of such processes has also been enabled by the use of a two-dimensional wire X-ray detector system. This detection system, along with integration software, enhances the identification of evolving phases while enabling simultaneous texture analysis. Results of the 2D texture analysis of Inclined Substrate Deposition HTSC epitaxial buffer layer thin films at various stages of preparation are presented.

INTRODUCTION

The use of two-dimensional multi-wire X-ray detectors in materials characterization has two key advantages over traditional powder diffraction profiles collected by point or extended wire (PSD) detectors: the two-dimensional image and integrated diffraction pattern contains far more information than traditional powder patterns and is collected in orders of magnitude less time [1,2]. One such two-dimensional detector, the Bruker-AXS General Area Detection Diffraction System (GADDS), permits the rapid viewing of a large volume of reciprocal space within a single collection frame. This added collection dimension capability becomes very significant for the accurate phase identification and quantitative analysis of textured, weakly scattering or large grained samples in which diffracted intensities differ greatly from expected values or are totally unregistered by 1D-type detectors. Texture analysis of quasi-single crystal textured thin films used as epitaxial buffer layers in making high-temperature superconductor tape is also dramatically improved by the analysis of partial Debye rings captured by the 2D detector.

The fast data acquisition speeds in conjunction with accurate phase identification capabilities not only increases sample throughput but also allows for the unprecedented study of phase formation, transformation, and evolution, as well as reaction kinetics. A high-temperature in-situ study of such phenomena facilitated by the construction of specialized environmental reaction cells will be discussed in this paper.
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METHODS

Inclined Substrate Deposition (ISD) derived thin films at progressive stages of preparation were provided by Argonne National Laboratory (the details of their fabrication have been given in previous reports [3,4]). Pole figure studies of these samples were made using a Scintag Pad V diffractometer equipped with a scintillation detector using Ni-filtered Cu radiation. Two-dimensional diffraction experiments were conducted with a fixed stage Bruker-AXS D8 diffractometer equipped with a GADDS detector and a Göbel mirror followed by a mono-capillary producing an intense, nearly-parallel, 0.8 mm diameter beam.

RESULTS & DISCUSSION

The volatile nature of some materials at elevated temperatures has traditionally hindered the conduction of dynamic in-situ XRD analyses, for the determination of fundamental processes occurring within many important materials systems. Newly-developed X-ray transparent heating cells will, however, facilitate such studies by isolating a small environment around the sample, allowing the entire specimen and contained atmosphere to be chemically and thermally equilibrated (i.e., steep thermal gradients due to usual strip heating and vaporization of compounds are avoided). This in-situ XRD characterization approach in conjunction with the advantages of a 2D diffraction system will have broad applications for research. Current studies utilizing this configuration focus upon the evolution of superconducting phases in melt-textured thallium based cuprates and the determination of the kinetic mechanisms governing the incongruent reduction of an oxide upon exposure to a molten reactive metal [5].

The demand for ceramic-bearing components of complicated geometries for advanced biomedical, sensor, aerospace and many other applications has spurred a significant effort to develop low-cost methods for the manufacturing of such materials in near net shapes [6-10]. In recent years, several new processes based upon the reaction and incongruent reduction of shaped oxides by reactive melts have been used to directly fabricate dense, near net-shaped ceramic/metal composites for such applications. Such approaches include: the Reactive Metal Penetration (RMP), the Displacive Compensation of Porosity (DCP), and the infiltration-Alumina-Aluminide-Alloy (i-3A) processes [5-8].

In order to characterize the initial stages of such processes, reaction-cell-facilitated in-situ 2D XRD analyses can be used to track, in real time, the formation of product spinel phases on Al₂O₃ surfaces immersed in Al-Mg liquid baths [9]. This characterization will be conducted with reactants contained within a graphite cell that is sealed by a thin graphite lid and gaskets (Fig.1). Passing current from a standard hot stage through the cell itself will accomplish heating of the apparatus resistively. Within such a sealed and confined chamber, equilibrium can be quickly established between magnesium vapor and magnesium dissolved in the liquid (note: Mg (gas) cannot react with graphite to form stable carbides at temperatures of interest, 800-1200°C [9]). During heating at a desired temperature, the nucleation and growth of spinel will be evaluated by passing X-rays through the top lid of the graphite cell and liquid bath to the sample surface. The GADDS system will be used to simultaneously monitor intensity changes.
for several spinel diffraction peaks within spans as short as a few milliseconds. This allows for the unprecedented study of a multitude of reaction variables such as temperature, melt composition, and specimen type (single vs. polycrystal Al₂O₃) on the rate and crystallite size of spinel layer formation.

Figure 1: Reaction vessel for in-situ detection of MgAl₂O₄ formation on an Al₂O₃ surface during passive incongruent alumina reduction by a Mg containing melt.

The melt processing of deposited constituent metals has been found to result in biaxial-texturing of Tl-Ba-Ca-Cu-O (TBCCO) films[10]. The volatile and toxic nature of thallium, as well as the superconductor’s stoichiometric sensitivity, however poses a challenge for in-situ XRD studies of these superconductors. A special X-ray transparent and chemically inert nickel-heating cell (Fig. 2) has been designed, to meet this challenge.

Figure 2: Reaction vessel developed for the in-situ XRD characterization of superconductor phase evolution from TBCCO precursor melts.

Unlike the cell designed for the study of incongruent reactions, TBCCO reactants are very sensitive to the presence of carbon; so alternative cell materials were utilized. A partially oxidized beryllium foil (to avoid Be/Ni reactions) is used to provide the X-ray
transparent environmental seal in place of a graphite lid. The necessary atmosphere within the enclosure can be provided by silver oxide for oxygen partial pressure and a crushed pellet of Tl-1223 for thallium partial pressure. The accurate control of the atmosphere surrounding the TBCCO sample is critical so that results may be correlated to the commercial processing of these materials [11]. The use of a two-dimensional diffraction system is extremely relevant for this study as the formation of the melted precursors will likely to be complicated by texturing and numerous overlapping diffraction peaks.

The in-situ analysis of the epitaxial nature of these thin films may also be conducted in conjunction with phase ID from the same Debye ring images. Single crystal, colony crystallite and random powder orientation effects that are critical to the electrical transport properties of these films may be easily distinguished by such analysis. The time required to conduct ex-situ texture analysis of thin films is also significantly reduced from hours for scintillation detector-gathered pole figures to seconds by the use of such a system.

Figure 3a. (220) Pole Figure of ISD MgO (epitaxial) layer collect with Para focusing optics and scintillation detector.

Figure 4a. (220) Pole Figure of Homo MgO layer collect with Para focusing optics and scintillation detector.

Figure 3b. (200) Pole Figure of ISD MgO (epitaxial) layer collect with Para focusing optics and scintillation detector.

Figure 4b. (200) Pole Figure of Homo MgO layer collect with Para focusing optics and scintillation detector.
of a 2D diffraction system. Pole figures of thin films created by the Inclined Substrate Deposition (ISD) technique show excellent texture (Figs. 3 and 4a-b) and appear to be identical to the analysis of ISD MgO films previously published [3,4]. Although similar analysis failed to reveal preferred texturing and suggests a loss of orientation between subsequently deposited layers, strong texturing of these layers is evident in the Debye rings captured with the use of a 2D detector (Figs 5a and b where YSZ means Yttrium Stabilized Zirconia and Hcmeans hastalloy).

The large build up of intensity into discontinuous sections at the theta angles corresponding to the (111) and (200) planes suggests a high degree of orientation in these
layers despite their failure to appear in their pole figures. The texturing of the first two MgO layers was also further substantiated in this way (Figs 5c and d). The powder diffraction pattern integrated from these Debye rings is presented in Figure 6.

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**SUMMARY**

Special reaction vessels, which are chemically inert to the process under study, contain X-ray transparent windows, and serve to resistively heat the sample and contained environment have been developed. These vessels will allow the \textit{in-situ} study of volatile reagents by limiting the loss of material from the system by rapidly establishing a partial pressure equilibrium within the airtight vessel. The rapid gathering of partial Debye ring patterns and precisely controlling the thermal and chemical environment surrounding a sample, valuable insight into the fundamental mechanisms of materials processes may be obtained. The use of a two-dimensional X-ray diffraction system with the cells enhances analysis by generating better statistics for phase identification while simultaneously allowing for monitoring the preferred texturing of the sample.

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