MULTI-PHASE HIGH TEMPERATURE ALLOYS AND PROGRESS IN CONTROLLED OXIDATION FOR FUNCTIONAL AND PROTECTIVE SURFACES

Michael P. Brady
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115
bradymp@ornl.gov; Tel: (865) 574-5153; FAX (865) 241-0215

C.T. Liu
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115
liuct@ornl.gov ; Tel: (865) 574-4459; FAX (865) 574-7659

E. Andrew Payzant
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6064
payzanta@ornl.gov; Tel: (865)574-6538; FAX (865) 574-3940

Peter F. Tortorelli
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156
tortorellipf@ornl.gov ; Tel: (865) 574-5119; FAX (865) 241-0215

Yukinori Yamamoto
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115
yamamotoy@ornl.gov ; Tel: (865) 576-7095; FAX (865) 574-7659

Larry Walker
Oak Ridge National Laboratory, Oak Ridge, TN 37831- 6064
walkerlr@ornl.gov; Tel: (865) 574-5339; FAX (865) 576-5413

ABSTRACT

FY2004 was a transition year with the completion of work devoted to the multi-phase Cr-base alloy development effort for aggressive high-temperature environments and the initiation of new projects, based on unique findings and understanding gained from this program. An effort was initiated for the development of intermetallic Laves-phase strengthened Fe-base alloys for improved elevated temperature strength in fossil energy system components such as superheater tubes and industrial gas turbines. Exploratory efforts were also initiated for proof of principle assessment of a novel synthesis approach to near-surface, complex ceramic phase structures of interest for functional applications by the control of oxidation reactions of multi-component/multi-phase metallic precursor alloys. Initial results from these efforts are presented.

INTRODUCTION

Efforts devoted to the development of multi-phase Cr-base alloys for aggressive high temperature environments will be completed in fiscal year (FY) 2004. Final results pertaining to the Cr_2Ta-reinforced Cr family of alloys [1,2] will be published in the open literature. For the

oxide dispersion ductilized Cr-base alloys also studied under this effort [3,4], industrial scale up and technology transfer activities will be pursued, in addition to the dissemination of results in open literature publications. The understanding of the manipulation of multi-phase microstructures gained under this program was transitioned to two new efforts during FY 2004. An effort was initiated for the development of intermetallic Laves-phase strengthened ferritic and austenitic alloys for improved elevated temperature strength in applications such as superheater tubes and industrial gas turbine components. Exploratory efforts were also initiated for the synthesis of functional surfaces by the control of oxidation (nitridation, carburization, etc.) reactions, based on phenomena observed during the oxidation of the multi-phase Cr_2Ta-reinforced Cr alloys. Preliminary results from these new projects will be presented in this report.

DISCUSSION OF CURRENT ACTIVITIES

Intermetallic Strengthened Austenitic and Ferritic Steels

High-temperature strength is a major issue for hot components in advanced fossil energy conversion and combustion systems. For example, the efficiency of boiler/steam turbine power plants is a strong function of steam temperature and pressure [5]. Coarsening of carbide dispersions currently limits Fe-base alloys to ~600-650°C in many critical applications. Nickel-base superalloys with elevated temperature strength above this range are available, but they are costly and may suffer from inadequate high-temperature corrosion resistance, particularly under sulfidation conditions due to the formation of low melting point Ni-S compounds. Multi-phase microstructures utilizing intermetallic phases for high-temperature strengthening and, depending upon the specific alloy system, a reservoir for protective-scale forming elements, offer a possible path to achieve a balance properties in Fe-base alloys sufficient to enable increased operating temperatures. A synergistic approach to improving elevated temperature strength utilizing solid solution, carbide, and intermetallic phase strengthening was therefore adopted (Fig. 1).

A initial series of alloys based on Fe-(10-20)Ni-20Cr atomic percent (at.%), with carbide, solid solution, and intermetallic forming alloying additions, was cast, forged, and heat treated to explore control of intermetallic precipitate phase equilibria and morphology to increase elevated temperature strength. (Full compositional and processing details are currently proprietary). Additions of Al in quantities potentially sufficient to promote Al_2O_3-base scale formation were also pursued. Preliminary results have indicated that the Al-modified alloys, in particular, show potentially attractive microstructures containing fine, uniform dispersions of carbide and intermetallic strengthening phases.

A typical microstructure is shown in Fig. 2a. Backscatter scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) indicated that the microstructure consisted of submicron dispersions of an MC carbide phase (M = transition/refractory metal elements) and at least two intermetallic phase precipitates. Preliminary transmission electron microscopy (TEM) analysis (Fig. 2b) suggests that the intermetallic precipitates were C14 Laves phase, based on Fe_2Nb, and B2 NiAl-based. The C14 phase was present primarily as finely distributed 500 nm size range plates, although it was also observed as occasional, coarse (2 μm range) precipitates (fine white phase and coarse white phase regions, respectively, in Fig. 2a). The morphology of the B2 phase was roughly spherical 300 nm size range precipitates (fine dark phase in Fig. 2a).

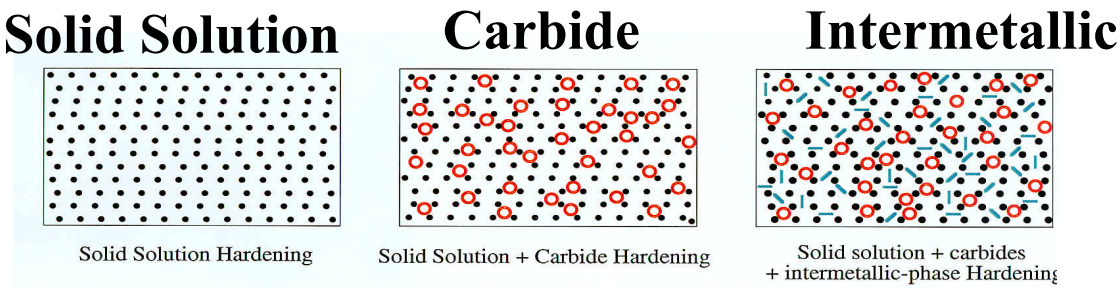

Fig. 1- Schematic cartoon of strengthening mechanisms.

a)

b)

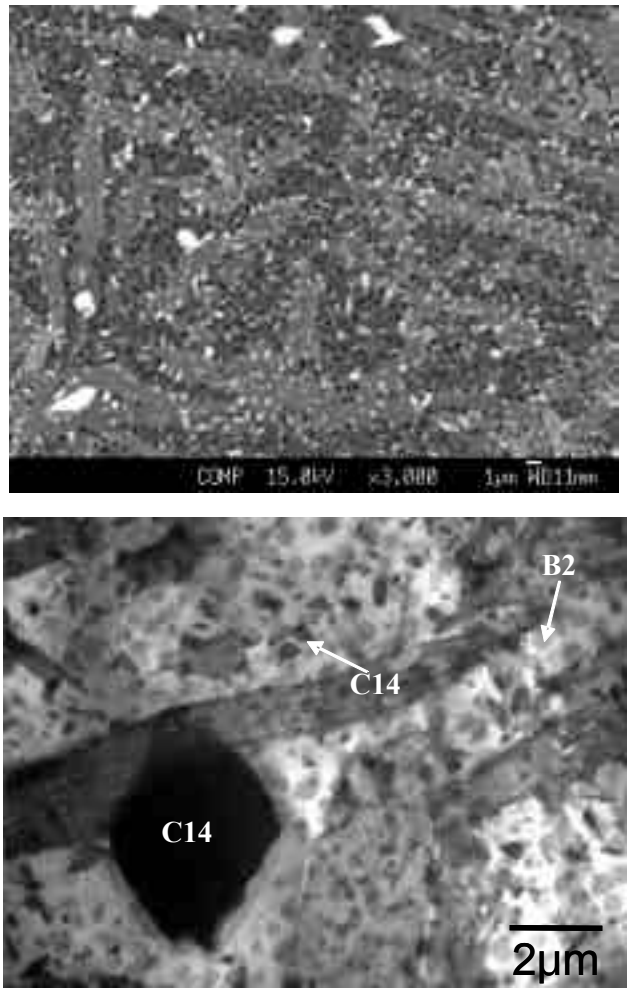

Fig. 2- Typical microstructures achieved for Al-modified Fe-20Cr-(10-20Ni) at.% base alloy.
a) Backscatter mode SEM b) Bright field TEM

Hardness measurements indicated an increase from the 250 Vicker's hardness range in the Al-free alloys to over 450 in the highest Al containing alloy, presumably due in part to the fine B2 precipitates.

Measurement of room and elevated temperature tensile properties are currently being pursued. Although this development effort is at a very early stage, the microstructures obtained thus far show definite promise for achieving improved elevated temperature strength. The C14 and B2

precipitates, in particular, are expected to be very stable to temperatures exceeding 700°C. Further, the observation of potentially attractive microstructures in the Al-modified alloys is particularly encouraging, as Al_2O_3-base scales offer superior environmental resistance compared to Cr_2O_3-base scales due to their lower growth rates and greater stability in H_2O-containing environments such as those encountered in advanced fossil energy steam plants.

Controlled Oxidation for Near Surface Functional Structures

Oxidation (nitridation, carburization) reactions are one of the most rapid, inexpensive, and technologically relevant methods of self constructing near-surface ceramic structures. Gaseous reactions of alloys can result in the formation of a myriad of ceramic phase arrangements, ranging from nanoscale clusters and dispersions to external layers, ranging from nanometers to tens and hundreds of microns thick. From a fundamental standpoint, many aspects regarding how the initial alloy composition and microstructure determine which, and how, the subsequent oxidation products are formed are not well understood. This is particularly true in ternary and higher order alloys under conditions where more than one alloy component can react, and, especially, when the alloy components are partitioned in a multi-phase microstructure. There are two ideal, yet technologically relevant and fundamentally interrelated, limiting cases: 1) the complete conversion of several or all of the reactive components in an alloy to form complex (ternary and higher order) ceramic phases, either as a dispersed internal phase or as an external layer, which is of interest as a method for the synthesis of functional materials for applications ranging from catalysts, sensors, and smart materials to wear and oxidation resistant surfaces, and, 2) the preferential oxidation of only one of the reactive components in an alloy to establish an external layer of a simple ceramic phase, i.e. selective oxidation phenomenon for the protection of materials in aggressive high-temperature environments. Initial efforts in FY 2004 were directed toward the first limiting case and the assessment of the potential of controlled oxidation to synthesize functional near-surface structures needed for a variety of applications in advanced fossil energy conversion and combustions systems. The origins of this work were the observations of unique internally nitrided structures that formed during the oxidation of Cr-Cr_2Ta alloys in air, in particular the preferential formation of ternary nitrides at Cr_2Ta precipitate sites [2].

Recent work at ORNL demonstrated that intermetallic phases show potential to be used as precursors to complex nitride and carbide phases by nitridation and carburization reactions [6-8]. A model intermetallic Cr_3Pt alloy yielded an external, single-phase scale of the complex perovskite phase Cr_3PtN on thermal nitridation. Further, internal nitridation of a two-phase Cr_3Pt dispersed Cr precursor alloy yielded dispersions of Cr_3PtN at Cr_3Pt sites, effectively utilizing the Cr_3Pt precipitates in the initial alloy microstructure as a template. The key issue to address in FY2004 was if such phenomena can be induced in systems of technological interest for the Fossil Energy Program.

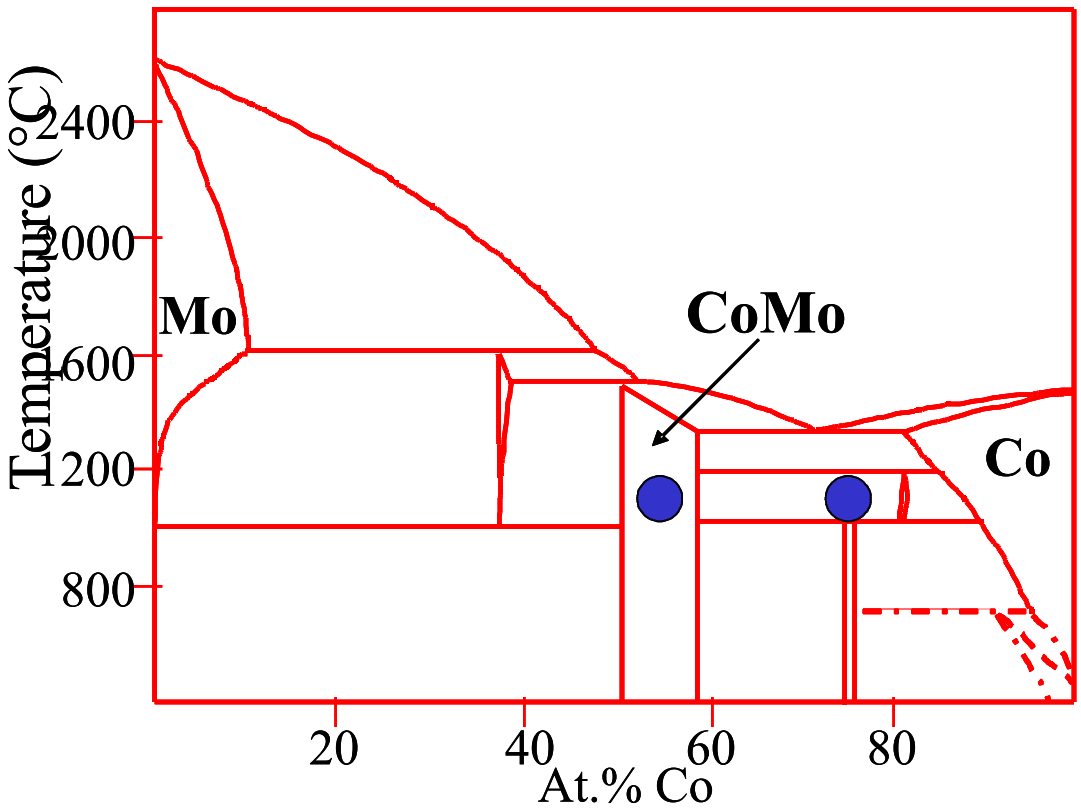

Fig. 3- Schematic Co-Mo phase diagram [after reference 16].

In particular, complex transition and refractory metal nitride and carbide phases are of increasing interest as catalysts for a variety of industrial processes, including hydrotreating to remove S, N, and O impurities from fossil fuels, ammonia synthesis, water gas shift reaction to produce hydrogen, and fuel cell catalysts [9-12]. These type phases are typically synthesized by gas reactions of complex oxide precursors or by molecular precursor or chemical synthesis [13-15] routes. The use of intermetallic precursors offers the potential to leverage a different set of precursor stoichiometries and structures, with the corresponding potential to form new complex carbide and nitride phases not attainable by currently used synthesis routes. It also offers the opportunity to leverage the initial metallic phase equilbria of the precursor alloy to control the morphology and structure of the phases that are formed; for example to synthesize a near-surface composite structure based on an initial two-phase alloy precursor microstructure. As a first step, a series of alloys based on the intermetallic CoMo phase were selected for study, in an attempt to form $Co_6Mo_6C_2$ and related complex carbide phases of interest for catalysis.

Figure 3 shows a schematic of the Co-Mo phase diagram [16]. A single-phase CoMo alloy, Co-45Mo, and a two phase Co(Mo) + CoMo alloy, Co-25Mo at.%, were selected for study. Coupons were cut from as arc-cast buttons and prepped to a 240 grit surface finish. Carburization was conducted at 1050°C in H_2-CH_4 mixtures (details of the processing are proprietary). A typical x-ray diffraction (XRD) pattern after carburization is shown in Fig. 4.

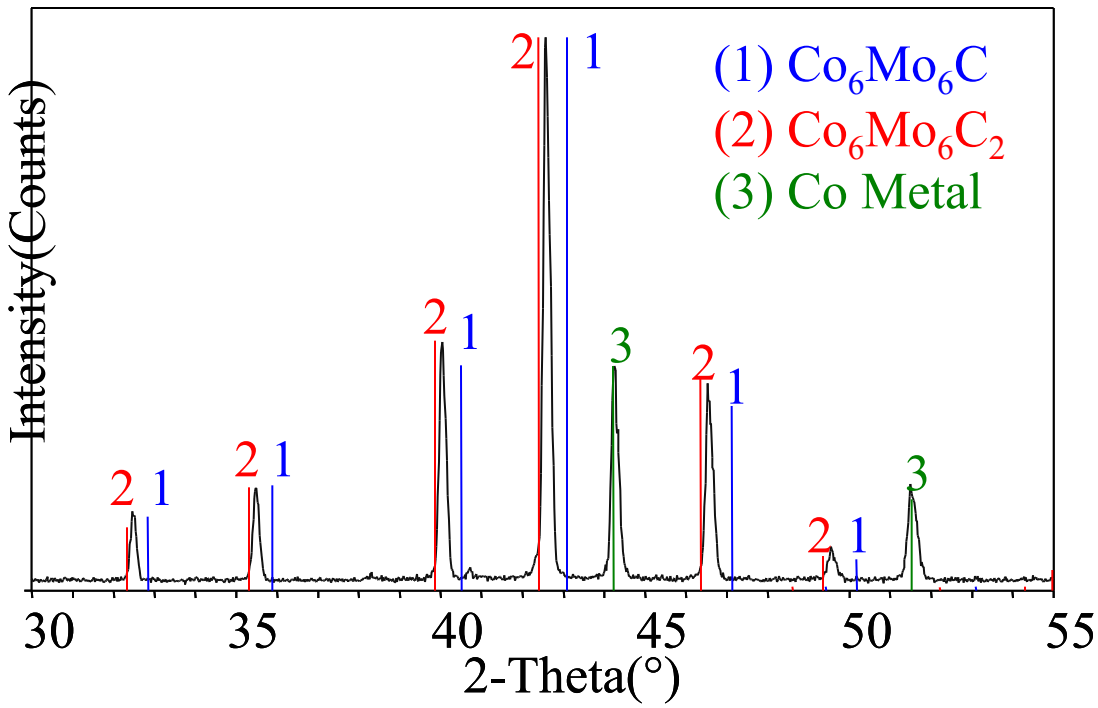

Fig. 4-Typical XRD data for carburized CoMo alloys

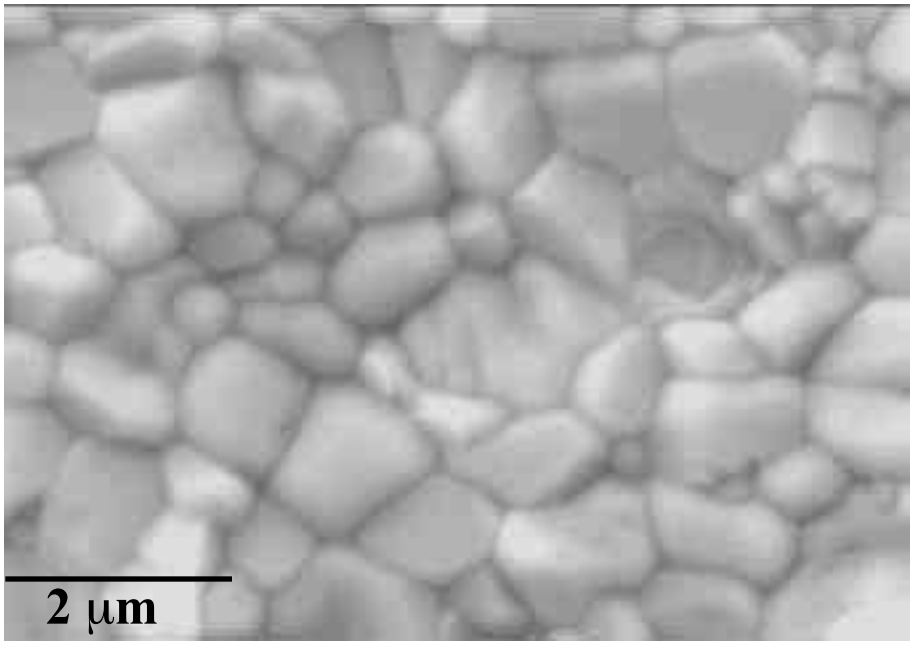

Fig. 5-Secondary mode surface SEM of Co-45Mo after carburization

Two phases were evident, slightly carbon-lean $Co_6Mo_6C_2$ and Co(Mo) metal. The relative amounts of the phases depended on the initial alloy composition, with Co-25Mo showing significant quantities of Co(Mo) metal, and Co-45Mo only trace levels. Surface SEM and EPMA analysis of the carburized coupons (Fig. 5 and 6) were consistent with the XRD data.

The surface of carburized Co-45Mo consisted of essentially single-phase Co-Mo carbide of average composition 45Mo-42Co-13C at.%, consistent with a slightly carbon-lean $Co_6Mo_6C_2$

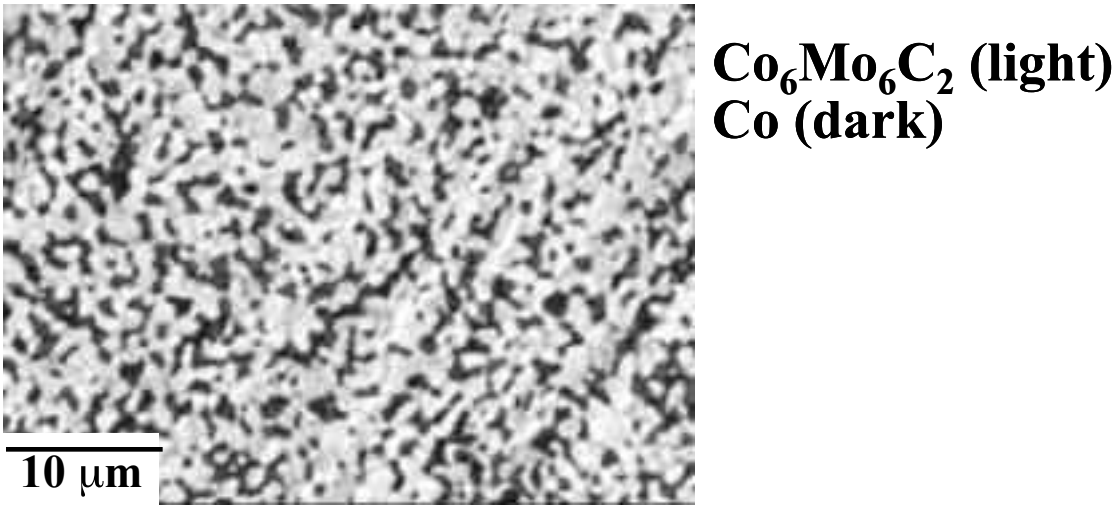

Fig. 6-Backscatter mode surface SEM of Co-25Mo after carburization.

(Fig. 5). A local composite surface structure of $Co_6Mo_6C_2$ and Co(Mo) solid solution metal was formed on Co-25Mo (Fig. 6). These results establish proof of principle for the synthesis of complex carbide phases of interest for catalysis by the carburization of intermetallic precursor alloys.

FUTURE WORK

For the intermetallic-strengthened steel effort, studies of precipitate phase equilibria and morphology as a function of composition and processing will be pursued. These will be correlated with mechanical property measurements, particularly elevated temperature tensile properties and creep behavior. An exploratory effort will also be pursued for multi-phase strengthened TiAl +Nb, W base alloys for applications above 800°C (industrial steam turbine blades and related components), including evaluation of alloying additions to promote protective Al_2O_3 scale formation.

For the controlled oxidation synthesis effort, further studies of carburization reactions in the Co-Mo and related systems will be pursued to gain insight into the relationships between the initial precursor alloy composition and structure, and the resultant carburized surface that is formed. Efforts to synthesize new phases in these systems will also be explored. Emphasis will also be placed on establishing collaborations to explore the catalytic properties of complex carbide structures synthesized from intermetallic precursors and their potential for technological impact.

REFERENCES

1. M.P. Brady, J.H. Zhu, C.T. Liu, P.F. Tortorelli, L.R. Walker, C.G. McKamey, J.L. Wright, C.A. Carmichael, D.J. Larson, M.K. Miller, and W.D. Porter, *Mate. High Temp.*, vol. 16, no. 4, pp. 189-193 (1999).
2. M.P. Brady, J.H. Zhu, C.T. Liu, P.F. Tortorelli, and L.R. Walker, *Intermetallics*, 8, 9-11, pp. 1111-1118 (2000).

3. D.M. Scruggs, 'Ductile Chromium Composition", U.S. Patent 3, 175, 279 (Mar. 30, 1965).
4. M. P. Brady, I.M. Anderson, M.L. Weaver, H.M. Meyer, L.R. Walker, M.K. Miller, D.J. Larson, I.G. Wright ,V.K. Sikka, A. Rar, G.M. Pharr, J.R. Keiser, and C.A. Walls, *Mater. Sci. Eng. A* 358 (1-2): 243-254 (2003)
5. R. Viswanathan and W. Bakker Journal Of Materials Engineering And Performance, 10 (1): 81-95 (2001)
6. M.P. Brady, S.K. Wrobel, T.A. Lograsso, E.A. Payzant, D.T. Hoelzer, J.A. Horton, and L.R. Walker, Chemistry of Materials 16 (10): 1984-1990 (2004).
7. M.P. Brady and P.F. Tortorelli, Intermetallics (in press).
8. M.P. Brady, D.T. Hoelzer, E.A. Payzant, P.F. Tortorelli, J.A. Horton, I.M. Anderson, L.R. Walker, S.K. Wrobel, Journal of Materials Research, Vol. 16, No. 10, 2784-2787 (2001).
9. S. Korlann, B. Diaz, M.E. Bussell, Chem Mater, 14, 4049-4058 (2002)
10. V. Schwartz V, S.T. Oyama, J.G.G., Chen Journal of Physical Chemistry B, 104 (37), 8800-8806 (2000).
11. J. Patt, D.J. Moon, C. Phillips, L. Thompson, Catalysis Letters, 65 (4): 193-195 (2000).
12. R. Kojima and K. Aika, Applied Catalysis A-General, 219 (1-2): 141-147 (2001).
13. S.H. Elder, L.H. Doerrer, F.J. DiSalvo, J.B. Parise, D. Giyomard, J.M. Tarascon, Chem. Mater., 4, 928 (1992).
14. R. Marchand, Y. Laurent, J. Guyader, P. L'Haridon, P. Verdier, J. Europ. Ceram. Soc., 8, 197 (1991)
15. K.S. and P.N. Kumta, Materials Science And Engineering B-Solid State Materials For Advanced Technology, 38 (1-2): 109-117 (1996).
16. ASM Binary Alloy Phase Diagrams Handbook Vol. 2, T.B. Massalaski et al, editors (1990).

ACKNOWLEDGEMENTS

This research was sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research Materials (ARM) Program. Oak Ridge National Laboratory is managed by U.T.-Battelle, LLC for the U.S. Department of Energy. The authors thank B.L. Armstrong and J.H. Schneibel for reviewing this manuscript.