1. **Project Name:** **Development of Combinatorial Methods for Alloy Design and Optimization**

2. **Lead Organization:**
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3. **Principal Investigator:**
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4. **Project Partners:** Oak Ridge National Laboratory - national laboratory partner that participates directly through separate funding provided directly from DOE; contacts: Dr. Easo P. George and Dr. Michael L. Santella.

   Duraloy Technologies - in-kind support of materials and technical advice; contact: Dr. Roman Pankiw.

   Nooter Fabricators - in-kind support through technical advice; contact: Dr. Maan H. Jawad

5. **Date Project Initiated and FY of Effort:** April 1, 2002; project entered second FY on April 1, 2003

6. **Expected Completion Date:** March 31, 2005

7. **Project Technical Milestones and Schedule:**

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1.1	Modify e-beam deposition system	6/30/02	6/30/02	
1.2	Deposit films	3/31/03	12/31/02	
1.3	Alloy films	9/30/03		proceeding on schedule
2.1	Assess chemical compositions	9/30/03		proceeding on schedule
2.2	Assess phases and structures	9/30/03		proceeding on schedule
3.1	Measure alloy library mechanical properties by nanoindentation	3/31/04		
4.1	Prepare conventional alloys	12/31/03		Proceeding on schedule
4.2	Measure conventional alloys by nanoindentation	3/31/04		

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
5.1	Assess carburization resistance	12/31/04		
5.2	Assess corrosion resistance	12/31/04		
6.1	Characterize structure by micro-focus x-ray techniques	12/31/04		proceeding ahead of schedule
7.1	Prepare final report	3/31/05		

8. **Past Project Milestones and Accomplishments:**

• *Designed and constructed controllable shutter system for the electron beam vapor deposition system in which alloy libraries are made.* The shutter allows for deposition of thin films with wedge shaped profiles that can be subsequently alloyed by solid state diffusion or melting with electron beams, lasers, and IR radiation. The shutter system is based on two fully automated precision stepper motors that are vacuum compatible: one drives the shutter while the other rotates the specimen. Binary and ternary alloys can be made in this system with compositions spanning the entire phase diagram.

• *Determined optimum conditions for depositing wedge shaped films of iron, chromium, and nickel onto sapphire substrates to make a tri-layer specimen.* Deposition was successful only after modifying the system to allow for substrate heating.

• *Deposited iron, nickel and chromium films of uniform thickness (about 1 micrometer) on sapphire substrates to systematically identify conditions under which alloying can be achieved by solid-state diffusion.* An x-ray technique was developed to determine when alloying is complete based on fluorescence of the three component species as a function of the x-ray beam angle. Studies revealed that complete through thickness alloying are achieved by annealing at 850°C for 20 hours. A specimen with wedge shaped layers of Fe, Ni, and Cr was annealed under these conditions to produce the first ternary alloy library.

• *Examined quality of the first ternary alloy library using microfocus x-ray techniques at the Advanced Photon Source at Argonne National Laboratory.* Techniques were developed that can be used to determine the structure, composition, and lattice parameters all in one scan of the ternary alloy library. Data were obtained in a single experiment lasting about 4 hours which sampled 2500 different positions on the specimen surface. From the data, the 850°C isotherm of the ternary phase diagram was constructed for comparison to the known ternary diagram (see highlight). The two diagrams are remarkably similar, with all the expected phases appearing, including the intermediate sigma phase (tetragonal). In addition to the phase diagram, a contour map of the lattice parameters was constructed from the synchrotron data that also compares well with known behavior. The new contour map extends over the entire 850°C isotherm of the ternary phase diagram, unlike the published data which are available only for some ternary compositions.

• *Began to explore alternative methods for alloying based on melting with an electron beam welding unit and a high-powered pulsed laser system.* Operating conditions for the e-beam welder were established that can be used to melt thin films of Cr on Ni substrates such that the substrate is melted to different depths in order to vary the binary composition. Initial results look promising. The laser system is being used to locally melt thin films of nickel and chromium on sapphire substrates.

9. Planned Future Milestones:

• *Prepare fully interdiffused ternary alloy library specimens of Fe-Ni-Cr for chemical and structural characterization and nanoindentation testing.*

• *Develop techniques for rapid assessment of chemical compositions, phases and structures based on electron microprobe analysis, x-ray diffraction, and synchrotron radiation methods.*

• *Prepare conventional alloys for comparison of properties to alloy libraries.*

• *Develop methods for measuring mechanical properties of alloy libraries by nanoindentation and compare to conventionally prepared alloys.*

• *Explore further the use of e-beam and laser melting as a means for preparing alloy libraries.*

10. Issues/Barriers:

Two technical problems were encountered last year. First, the metal films of interest were found to adhere well to sapphire substrates only if the substrate was heated to about 200°C during deposition. The substrate heater normally used in the deposition system proved difficult to use for this purpose because it also heated the stepper motors used to drive the shutter and rotate the sample, producing unacceptably high temperatures in the motors. A system modification was made to incorporate a quartz lamp to heat the specimen from behind. This successfully resolved the problem.

The second problem was that chromium oxide formed on the chromium rich corner of the fully alloyed Fe-Ni-Cr specimen after annealing. The presence of the chromium oxide causes a distortion in the location of the chromium phase boundaries. We are currently working to minimize this problem by improving our vacuum conditions and encapsulating the specimens in quartz tubes and tantalum foil during annealing.

11. Intended Market and Commercialization Plans/Progress:

The product of this research will be a more efficient and less time consuming methodology for alloy design and optimization. Because conventional techniques for alloy preparation are unavoidably restrictive in the range of alloy composition that can be examined, combinatorial methods promise to significantly reduce the time, energy, and expense needed for alloy design. In addition to optimizing existing alloys, the combinatorial technique may result in the discovery of entirely new ones because large numbers of alloy compositions can be screened relatively quickly. Industry has been hindered in developing combinatorial alloy design methods largely because simple and effective techniques for fabricating and characterizing alloy libraries have not yet been developed. The sophisticated research equipment needed to accomplish these tasks is capital intensive and thus more likely to be found in universities and national laboratories than in industrial settings. In addition, most private companies do not have the in-house technical expertise needed to develop combinatorial methods.

While the research in progress is limited to one simple ternary alloy system, once the basic methodology is developed and validated in this project, it will be applicable to a wide variety of other alloys, thus leading to improved materials that crosscut the needs of a large number of industries. Among the IOF's that would be directly impacted are those relying heavily on metals and alloys, including, but not limited to: aluminum, chemicals, forest products, glass, metal casting, petroleum, steel, and forging, heat treating, and welding.

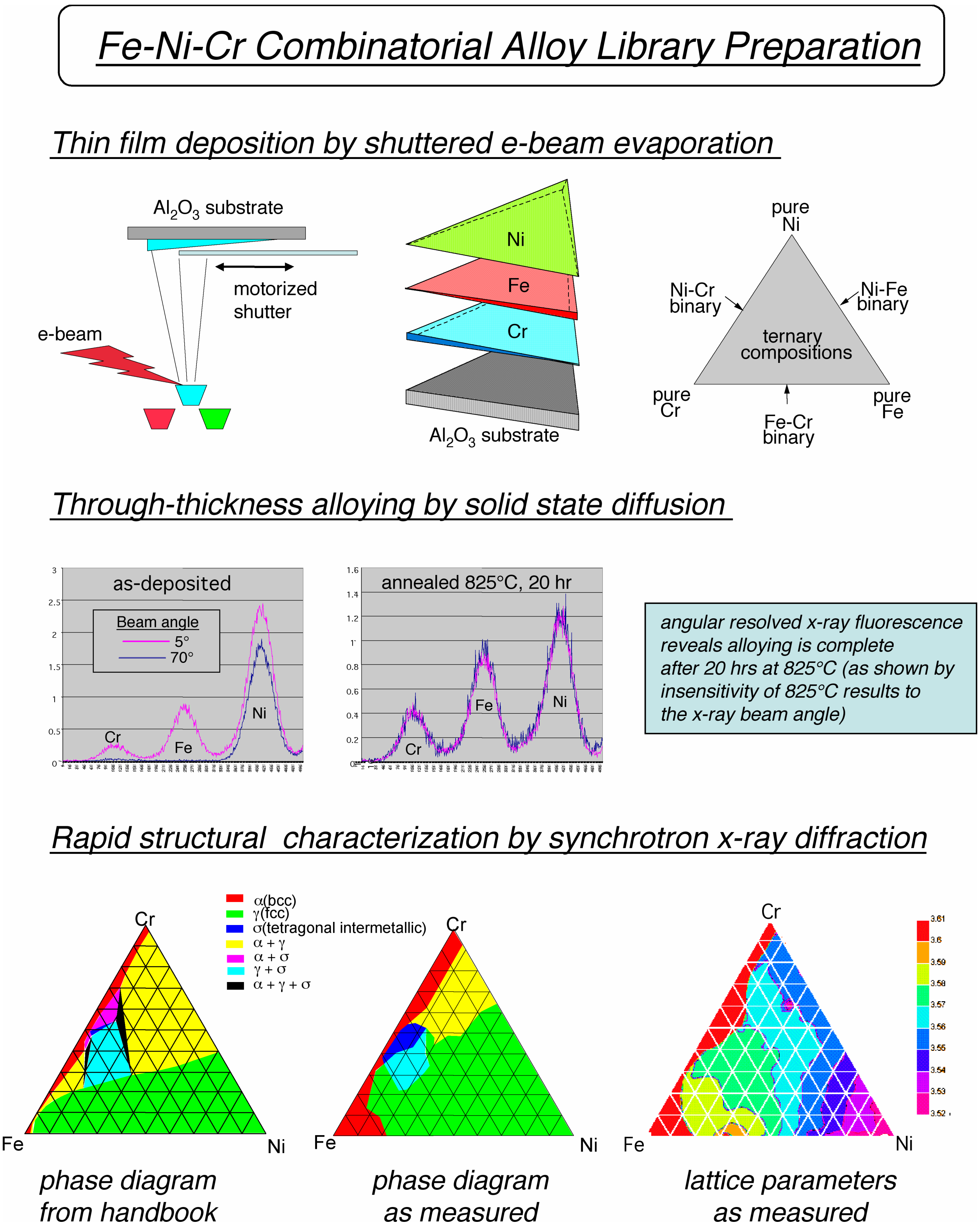
Most of the work in this program is conducted by graduate students working on their dissertations. As such, the technology will be made readily available to a wide cross-section of potential end users through publication in the open literature. In addition, the direct interaction with the industrial partners provides a natural means for the technology to be transferred to an important end user. The ternary elements being investigated here form the basis of the important H-series alloys that are of interest to our industrial partners.

12. **Patents, publications, presentations:** (Please list number and reference, if applicable.)

• A paper entitled "Rapid Structural Characterization of Ternary Phase Diagrams Using Synchrotron Radiation" has been submitted to *Journal of Materials Research*.

• An abstract for a presentation entitled "Preparation of ternary alloy libraries for high-throughput screening of material properties by means of thick film deposition and interdiffusion: benefits and limitations" has been submitted for the Annual Meeting of the American Vacuum Society, Baltimore, MD, November 2003. Papers from this conference will also be published in an archival journal.

Highlight


Fe-Ni-Cr Combinatorial Alloy Library Preparation
Thin film deposition by shuttered e-beam evaporation
Al_2O_3 substrate
motorized shutter
e-beam
Ni
Fe
Cr
Al_2O_3 substrate
pure Ni
Ni-Cr binary
Ni-Fe binary
ternary compositions
pure Cr
pure Fe
Fe-Cr binary
Through-thickness alloying by solid state diffusion
as-deposited
Beam angle
5°
70°
Cr
Fe
Ni
annealed 825°C, 20 hr
Cr
Fe
Ni
angular resolved x-ray fluorescence reveals alloying is complete after 20 hrs at 825°C (as shown by insensitivity of 825°C results to the x-ray beam angle)
Rapid structural characterization by synchrotron x-ray diffraction
α(bcc)
γ(fcc)
σ(tetragonal intermetallic)
α + γ
α + σ
γ + σ
α + γ + σ
Cr
Fe
Ni
phase diagram from handbook
phase diagram as measured
lattice parameters as measured