DOE/ER/45426--T1

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
77 MASSACHUSETTS AVENUE, ROOM 13-5018
CAMBRIDGE, MASSACHUSETTS 02139-4307

Samuel M. Allen
Professor of Physical Metallurgy
Secretary of the Faculty

Tel: (617) 253-6939
FAX: (617) 258-7874
smallen@mit.edu

June 1, 1998

To: Office of Energy Research
U.S. Department of Energy
Washington, D. C. 20585

Subj: Final Technical Report
"Slip, Twinning, and Transformation in Laves Phases"
Grant No. DE-FG02-90ER45426

Technical Progress Report: August 1, 1990 – January 31, 1997

BACKGROUND

Currently, intermetallic compounds are being studied as potential high-temperature structural materials. Most of these studies are on phases such as Ni_3Al, TiAl, NiAl, and Ti_3Al, which have structures that are crystallographic derivatives of fcc, bcc, or hcp structures. However, most intermetallics have more complex crystal structures, and little is known about their deformation mechanisms and mechanical properties. By far the largest class of such compounds is that of the Laves phases, AB_2 compounds having three different crystal structures: $C15$ (cubic), $C14$ (hexagonal), and $C36$ (dihexagonal). This research program explored room-temperature compressive deformation of two-phase alloys containing substantial amounts of Laves phase, and, by transmission electron microscopy, characterized the deformation-induced defects in these alloys. Our results include: transmission electron microscopy analysis of defect structures to determine deformation mechanisms, use of indentation experiments to gain deeper understanding of deformation mechanisms, systematic study of effects of ternary alloying additions on mechanical properties, and assessment of effects of departure from stoichiometry on phase stability and mechanical properties of Laves phases.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RESULTS

Our research has concentrated on three alloy systems:

1. Two-phase Fe-$ZrFe_2$ alloys
2. Two-phase ternary Ni-Cu-Mg alloys containing $MgNi_2$ and $MgCu_2$ Laves phases
3. Single- and two-phase Ti-$TiCr_2$ alloys, with several ternary additions

We have evaluated microstructures of specimens before and after deformation to characterize the changes and to deduce mechanisms of deformation. Optical microscopy, x-ray and electron diffraction, and conventional and high-resolution TEM have been used in our analyses. In addition to uniaxial compression tests, we have developed the ability to study deformation structures in the vicinity of microhardness indentations; this technique seems to enhance the room-temperature deformability of our alloys, and provides an intriguing variety of microstructural features indicative of significant nonbasal slip in hexagonal Laves phases.

Specific results of this work are summarized below; additional details may be found in the publications appended to this report.

Fe-$ZrFe_2$ Alloys

Two alloys near the Fe-rich eutectic composition were prepared by arc casting, one with 7 at. pct. Zr, one with 10 at. pct. Zr. Optical metallography revealed a fine lamellar eutectic microstructure, with pro-eutectic Fe dendrites in the former alloy and pro-eutectic $ZrFe_2$ particles in the latter. We have done rather extensive studies of the deformation behavior of the 10%-Zr alloy, in uniaxial compression, after an annealing treatment for 48 hours at 1190°C.

Transmission electron microscopy and x-ray and electron diffraction revealed that the Laves phase structure of the annealed specimens is mainly *C*36, but with some *C*15 regions. A high density of stacking faults on the basal planes of the *C*36 phase was present in the as-cast alloy, and also after annealing. After deformation to engineering strains in excess of 45%, x-ray diffraction and TEM showed that the amount of the f.c.c. *C*15 phase increases, and that the *C*15 regions that form are rather free of stacking faults. We have also observed interfaces between *C*36 and *C*15 phases, and these observations are suggestive of a dislocation mechanism for the transformation. Our results provide good evidence that the *C*36 phase is largely retained as a metastable phase on quenching the alloy from the annealing temperature, and that the shape change associated with the $C36 \rightarrow C15$ phase transformation contributes to the room-temperature plasticity of the Laves phase in this two-phase alloy.

Observations of the *C*15 regions in $ZrFe_2$ of deformed specimens show evidence of faulting on different crystallographic variants of the $\{111\}$ planes, providing additional evidence for room-temperature deformation by slip in these complex structures.

Microhardness indentations on a polished specimen have been used to study plastic deformation of hard materials and we have developed a convenient technique for introducing plastic deformation in $ZrFe_2$ using indentations. The technique involves producing an array of 100 or more indentations on a square grid with spacing 100 μm, then using a carefully controlled grinding technique to produce a thin specimen which includes the near-surface region of the sample. Final thinning for TEM observation is accomplished by ion milling. Results of these experiments, on $ZrFe_2$, reveal regions with *extensive* plasticity. While considerable shear is localized on basal planes of the *C*36 phase, there is also extensive shear on planes with traces perpendicular to the basal planes (e.g., prism planes such as $\{11\bar{2}0\}$). The resulting deformed microstructure consists of very well-defined cells, separated by rather intense shear bands. We have identified the slip systems involved in this type of deformation.

Ni,Cu-Mg(Ni,Cu)$_2$ Alloys

Four alloys were prepared spanning compositions between binary Cu-$MgCu_2$ and Ni-$MgNi_2$ alloys. Two of the alloys have the terminal binary compositions, and the remaining two involve varying the amount of the ternary addition. The Laves phase $MgCu_2$ has the *C*15 structure, and the phase $MgNi_2$ has the *C*36 structure. We believe that the mixed ternary Laves phase $Mg(Cu,Ni)_2$ has a stacking fault energy that has a marked composition dependence, consistent with the change of equilibrium crystal structure with alloying. We surveyed the microstructure of all four alloys with optical metallography; extensive TEM study of the Ni-$MgNi_2$ alloy, and TEM surveys of the two ternary alloy compositions.

TEM and electron diffraction examination reveals that the changing Cu:Ni ratio in the ternary alloys results in a systematic change of stacking sequence of close-packed planes, giving rise to stacking sequences at compositions intermediate between $MgCu_2$ and $MgNi_2$ which are periodic, but more complex that those of the terminal *C*15 and *C*36 compositions. Thus, in $MgNi_2$ there is a four-layer sequence AB'A'C… and in $MgCu_2$ there is a three-layer sequence ABC…. At intermediate compositions in the ternary alloy, we have observed a six-layer sequence which can be considered a periodically microtwinned *C*15 structure with stacking ABCACB…. We also have observed a five-layer structure in the ternary alloy.

So far, our deformation study of this system has been confined to the Ni-$MgNi_2$ alloy. The alloy composition is such that the Ni solid solution phase only occupies about 10% of the specimen volume. TEM observations of samples from specimens which had been plastically deformed at room-temperature in uniaxial compression show that deformation occurs by slip on basal planes, prism planes, and pyramidal planes of the *C*36 structure. Stacking faults on prism and pyramidal planes which connect to faults on basal planes are likely to be evidence of significant cross slip in this phase.

We have also studied the microstructure of samples of the Ni-$MgNi_2$ alloy which had been locally deformed by microhardness indentation. In these samples, extensive plastic deformation was observed, similar to that seen in indented samples containing $ZrFe_2$. The microstructure consists of well-defined cells of rather perfect *C*36 structure, demarcated by bands of intense shear on basal planes and on prism planes. Close observation of the *C*36 "blocks" in the deformed specimens shows the periodic faults characteristic of the *C*36 structure, and evidence indicates crystallographic misorientations between the various "blocks." Such microstructures illustrate the extensive plasticity that is possible at room temperature in $MgNi_2$ under the complex loading induced by indentation.

Ti-$TiCr_2$ Alloys

We initially investigated three alloys, prepared by arc casting: Ti-30 at. pct. Cr, Ti-40 at. pct. Cr, and Ti-60 at. pct. Cr. The Ti-Cr phase diagram is very different from the Fe-Zr phase diagram, yielding the possibility of very different morphologies and distributions of the Laves phase in the two alloy systems. Rather than forming from eutectic solidification (like $ZrFe_2$), the $TiCr_2$ Laves phase forms by precipitation from the high-temperature Ti(Cr) b.c.c. solid solution.

In the as-cast condition, neither alloy showed clear-cut Laves-phase particles above the resolution limit of optical microscopy. However, after heat treating the 30% Cr alloy at 950°C and the 40% Cr alloy at 1000°C, a substantial volume fraction of multi-micron Laves-phase particles was seen in both alloys.

An extensive heat treatment study enabled us to gain some control over the phase, size, shape, and volume fraction of the Laves particles in the two-phase alloys. The optical micrographs presented in Figure 3 show two morphologies for the Laves phase particles; they are lath shaped in the 30% Cr alloy, and tend to be more equiaxed in the 40% Cr alloy. The lath-shaped particles in the 30% Cr alloy seem to be twinned lengthwise and to have a preferred orientation within each grain. In the 40% Cr alloy, the particles also contain internal faults. TEM observations demonstrate that the particles contain numerous twins and stacking faults on close-packed planes.

X-ray and electron diffraction were used to identify the Laves phases in samples both before and after heat treatment. The as-cast conditions of the 30% Cr and 40% Cr alloys revealed only single-phase β-Ti(Cr). After many different annealing conditions, only the *C*15 phase of $TiCr_2$ was found. However, in the 60% Cr alloy, the structure seems to vary systematically with heat treatment temperature, consistent with a change of equilibrium structure of $C14 \rightarrow C36 \rightarrow C15$

as the annealing temperature is decreased. Further work is necessary to clarify the equilibrium structure in this system.

5 mm cubes were prepared by spark cutting, and as-cast and heat-treated samples of each alloy were deformed in compression at room temperature. Engineering stress-strain curves were measured. In both the as-cast and the heat-treated conditions, flow stresses were higher for the 40% Cr alloy, which from the equilibrium diagram is expected to contain more Laves phase than the 30% Cr alloy. For each alloy, heat treatment produced a substantial increase in flow stress. The 30% Cr alloy could withstand much higher strains (>26%), whereas the 40% Cr alloy suffered load drops after about 6% strain. The Laves phase in both alloys was severely cracked after the compression tests, and the different volume fractions and morphologies of the phase in the two alloys probably accounts for this difference in strain to fracture of the two-phase macroscopic specimens.

X-ray analysis after deformation showed no signs of a crystal structure change, as expected from the equilibrium diagram. TEM comparisons of typical microstructures in undeformed and deformed specimens revealed an increase in defect structures (i.e., twins, stacking faults) within the Laves phase. Typical microstructures of the *C*15 Laves phase in the Ti - 40% Cr alloy shows twinning on the {111}<112> system likely resulting from both annealing and deformation. However, extensive deformation was not observed, suggesting that alloying may be needed to realize more room-temperature ductility in this alloy system.

An extensive series of new alloys based on the $TiCr_2$ Laves phase were designed to study systematically the effects of departure from stoichiometry, and of site substitution by ternary additions. The alloys were prepared by arc-casting at the Materials Preparation Center of the Ames Laboratory. Two Cr-rich alloys in the two-phase (β-bcc + $TiCr_2$) region were also prepared to complement the work previously done on Ti-rich two-phase alloys. A total of 21 new alloys were made: eight Ti–Cr binaries, four Ti–Cr–V alloys, three Ti–Cr–Fe alloys, three Ti–Cr–Nb alloys, and three Ti–Cr–Mo alloys. An extensive study of the microstructure of these alloys and their response to heat treatment is being completed during Year 2, using primarily optical metallography, x-ray diffraction and electron microprobe analysis.

Uncertainties in the published Ti–Cr phase diagram prompted a careful examination of the binary alloys near the stoichiometric $TiCr_2$ composition. Electron microprobe analysis pinpointed the single-phase $TiCr_2$ field to lie in the range 63.8% Cr to 66.3% Cr at 1300°C ant 64% Cr to 66% Cr at 1000°C. The equilibrium Laves phase in the binary alloys is non-stoichiometric, extending to the Ti-rich compositions. Lattice constant and density measurements suggest that both Cr vacancies and Ti anti-site substitution occur to accommodate off-stoichiometry. All three Laves crystal structures were found to exist at different temperatures within this narrow composition range. The *C*15 structure is stable at 1000°C, the *C*14 structure is stable at 1200°C, and the *C*36 structure is stable at 1300°C. Hardness and fracture toughness values determined by Vickers microhardness indentation were studied as a function of alloy composition. In *C*36 $TiCr_2$ alloys, a hardness maximum occurs as the Ti-rich alloys approach stoichiometry, while the toughness approaches a minimum value of approximately 1 MPa $m^{-1/2}$. This result contrasts with most intermetallics, in which hardness reaches a minimum value at stoichiometry. The hardness and toughness of alloys with the *C*15 structure seem to be superior to values in the same alloy heat treated to retain the *C*36 structure.

Effects of adding Fe, Nb, Mo, and V to $TiCr_2$ have been determined. Fe was found to stabilize the *C*14 structure, while Nb and Mo stabilized the *C*15 structure at 1200°C, and V stabilized the *C*15 structure at 1300°C. The effects of the ternary alloying additions on hardness and toughness were not large. Alloys with Mo and V additions were similar to the binaries; Fe additions were found to lower both hardness and toughness, and V additions raised both slightly. Some of the observed changes can be correlated with site occupancy and observed changes in lattice constants with the alloy additions.

Ti-rich Ti–Cr alloys have been studied and can be heat treated to precipitate $TiCr_2$ particles from a Ti-rich bcc Ti-Cr solid solution phase. In a 30 atomic percent Cr alloy aged at 950°C, the Laves phase particles have a lath morphology, as seen in the accompanying figure. We have used transmission electron microscopy and selected-area electron diffraction analysis to determine the orientation relation: $(101)_\beta \parallel (111)_{C15}$ and $[10\bar{1}]_\beta \parallel [10\bar{1}]_{C15}$. The $TiCr_2$ laths tend to be twinned, with a twin boundary approximately parallel to the midplane of the lath. Reasons for the lath morphology, habit plane, and twinning are under investigation.

SUMMARY

Our work on this project has demonstrated that a variety of room-temperature deformation processes are possible in Laves phases. We have used two methods to advantage to enhance plastic deformation. First, we have for the most part studied deformation in alloys in which the Laves phase exists as discrete second-phase particles in a solid-solution matrix. Second, we have developed a technique for reliably using microhardness indentations to produce localized deformation (with a significant triaxial component to the loading), and to prepare high-quality thin-foil specimens from the deformed regions for examination in the transmission electron microscope.

We have demonstrated that a strain-induced phase transformation from *C*36→*C*15 structures is one mechanism for plastic deformation in $ZrFe_2$, and we have looked at this transformation mechanism is some detail. We have studied the development of two-phase microstructures in $TiCr_2$, and our results show that the *C*15 structure in this alloy deforms by slip and twinning. Our studies of the microstructure after indentation of specimens containing the C36 phases $ZrFe_2$ and $MgNi_2$ indicate that a variety of slip systems are operative in this "dihexagonal" form of the Laves phase.

PUBLICATIONS FROM THE PROJECT*

* reprints removed

James D. Livingston and Ernest L. Hall, "Deformation and Defects in C36 Laves Phases," *Mater. Res. Symp. Proc.* **213**, 443-448 (1991).

Yaping Liu, James D. Livingston and Samuel M. Allen, "Room-Temperature Deformation and Stress-Induced Phase Transformations of Laves Phases in an Fe–10 at. % Zr Alloy", *Electron Microscopy I*, K.H. Kuo and Z.H. Zhai, eds., 5th Asia-Pacific Electron Microscopy Conference, Beijing, China 368–369 (1992).

Yaping Liu, "Room-Temperature Deformation and Stress-Induced Phase Transformations in Laves Phase Fe_2Zr," *Proc. 50th Annual Meeting of the Electron Microscopy Society of America*, G.W. Bailey, J. Bentley and J.A. Small, eds., San Francisco Press (1992).

James D. Livingston, "Laves Phase Superalloys?," *Phys. Stat. Sol.* (a) 131, 415-423 (1992).

Yaping Liu, James D. Livingston and Samuel M. Allen, "Room-Temperature Deformation and Stress-Induced Phase Transformations of Laves Phases in Fe-10 at. % Zr Alloy," *Metall. Trans.* **23A** 3303-3308 (1992).

Katherine C. Chen, Samuel M. Allen, and James D. Livingston, "Morphology, Deformation, and Defect Structures of $TiCr_2$ Alloys," *High-Temperature Intermetallic Alloys V*, Materials Research Society Symposium Proceedings Vol. 288, pp. 373–378. I. Baker, R. Darolia, J.D. Whittenberger and M.H. Yoo, eds., Materials Research Society, Pittsburgh, PA, 1993.

Yaping Liu, Samuel M. Allen, and James D. Livingston, "Deformation Mechanisms in a Laves Phase," *High-Temperature Intermetallic Alloys V*, Materials Research Society Symposium Proceedings Vol. 288, pp. 279–284. I. Baker, R. Darolia, J.D. Whittenberger and M.H. Yoo, eds., Materials Research Society, Pittsburgh, PA, 1993.

Katherine C. Chen, Samuel M. Allen, and James D. Livingston, "Stoichiometry and Alloying Effects on the Phase Stability and Mechanical Properties of TiCr2-Base Laves Phase Alloys," *High-Temperature Intermetallic Alloys VI*, Materials Research Society Symposium Proceedings Vol. 364, pp. 1401–1406. J. Horton, I Baker, S. Hanada, R.D. Noebe and D.S. Schwartz, eds., Materials Research Society, Pittsburgh, PA, 1995.

Yaping Liu, Samuel M. Allen, and James D. Livingston, "An Investigation of Fe_3Zr Phase," *Scripta Metallurgica et Materialia* **32**, 1129–1132 (1995).

Yaping Liu, Samuel M. Allen, and James D. Livingston, "Deformation of Two C36 Laves Phases by Microhardness Indentation at Room Temperature," *Metallurgical and Materials Transactions* **26A**, 1107–1112 (1995).

Yaping Liu, Samuel M. Allen, and James D. Livingston, "Defect Structures and Nonbasal Slip of C36 Laves Phase $MgNi_2$ in a Two-Phase Alloy," *Metallurgical and Materials Transactions* **26A**, 1441–1447 (1995).

Katherine C. Chen, Samuel M. Allen, and James D. Livingston, "Assessment of the Compositional Influences on the Toughness of $TiCr_2$-Base Laves Phase Alloys," *High-Temperature Ordered Intermetallic Alloys VII*, Materials Research Society Symposium

---

* Copies of these publications are provided as an attachment.

Proceedings. C.C. Koch, N.S. Stoloff, C.T. Liu and A Wanner, eds., Materials Research Society, Pittsburgh, PA, accepted for publication, 1997.

Yaping Liu, Samuel M. Allen, and James D. Livingston, "Defect Structures and Nonbasal Slip of *C*36 Laves Phase $MgNi_2$ in a Two-Phase Alloy," *Metallurgical and Materials Transactions* **26A**, 1441–1447 (1995).

Katherine C. Chen, Samuel M. Allen, and James D. Livingston, "Microstructures of Two-Phase Ti–Cr Alloys Containing the TiCr2 Laves Phase Intermetallic," *Journal of Materials Research* **12**, 1472–1480 (1997).

Katherine C. Chen, Samuel M. Allen, and James D. Livingston, "Factors Affecting the Room Temperature Mechanical Properties of TiCr2-Base Laves Phase Alloys," Journal of Materials Science and Engineering A 242, 162–172 (1998).

STUDENTS

Two graduate students worked on this program, and as a result of their research achievements, received doctoral degrees. Both students joined the project in the fall semester 1990.

Yaping Liu was a graduate student from the People's Republic of China, who, prior to joining the project, worked for Prof. Allen on a study of the defect structure and cyclic deformation behavior of single-crystal NiAl, for which Liu received his Master's Degree in Materials Science and Engineering from MIT in September 1990. He passed the General Examination for the Doctorate in Metallurgy in February 1991. Liu held an appointment as a Research Assistant on this research grant. He had responsibility for the research on Fe-Zr alloys, and the Cu-Ni-Mg alloys. Mr. Liu contributed extensively to microstructural analysis Laves phases by high-resolution electron microscopy. He also developed the technique for TEM specimen preparation of samples in which deformation was introduced by microhardness indentations. Mr. Liu completed his Ph.D. degree in August 1993. While still a graduate student, Mr. Liu received the TMS Outstanding Student Paper Contest Award for his paper "Room-Temperature Deformation and Stress-Induced Phase Transformations of Laves Phases in Fe-10 at. % Zr Alloy," awarded by The Minerals, Metals, and Materials Society. Dr. Liu worked in MIT's Center for Materials Science and Engineering for three years as Post Doctoral Associate and Research Associate, and is currently an employee of Micrion Corporation in Peabody, MA.

Katherine C. Chen came to MIT after receiving bachelor's degrees from Michigan State University in Materials Science and Engineering and in Chemistry in June 1990. For the first three years of her graduate program, Ms. Chen held a DOD Fellowship, and subsequently she was supported as a Research Assistant on this program. She was responsible for the research on Ti-Cr alloys. Kathy passed the General Examination for the Doctorate in Materials Science in September 1992, and completed the Ph.D. degree in June 1996. She worked as a Post Doctoral Associate on this program through September 1996, then took a position at Los Alamos National Laboratory, where she is continuing research on Laves phases.

Sincerely,

Samuel M. Allen

Samuel M. Allen
Professor of Physical Metallurgy