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To: Dr. Joseph Darby
U.S. Department of Energy
Energy Research, ER-64
Washington, DC 20545

Subj.: Technical Progress Report for Grant DE-FG02-90ER45426, "Slip, Twinning and Transformation in Laves Phases," for the period August 1, 1990 - July 31, 1993

INTRODUCTION

Intermetallic compounds are currently 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). An earlier DOE-sponsored study entitled "Deformation and Defects in Laves Phases" explored the high-temperature deformation of cubic and hexagonal Laves phases, room-temperature deformation of two-phase V-Hf-Nb alloys containing substantial amounts of Laves phase, and, by TEM, the deformation-induced defects in these alloys. The present study builds on these earlier results, and has as its general goal an improved understanding of the factors influencing ductility and toughness of Laves phases, particularly at room temperature.

Like most intermetallics, Laves phases show brittle behavior when loaded in tension at ambient temperatures. Possible reasons for brittleness of intermetallics are many [1,2]. For polycrystalline specimens with hexagonal crystal structures having large unit cells, a likely contributor to brittle behavior is limited slip on nonbasal planes. One objective of this study has been to determine the extent of nonbasal slip in hexagonal Laves phases. Laves phases are also known to deform by twinning, and another goal of the research has been to study the relative contributions of slip and twinning to deformation. The close structural relationship between the three Laves structures allows for a possible complex shear transformation mechanism from one structure to another [3]. Because more than one structure often appears in different regions of an equilibrium diagram for a specific alloy system, deformation-induced phase transformations between these crystal structures also comprise possible deformation mechanisms for Laves phases. Thus, we have studied deformation-induced changes in crystal structure in this project. Nearly all of our experiments have explored the deformation behavior in two-phase alloys in which the Laves phase coexists with a more ductile f.c.c. or b.c.c. solid solution phase, with the aim of inducing greater plasticity in the Laves phase, and of toughening the alloys.

RESULTS TO DATE

Our research has concentrated on three alloy systems:

1. Two-phase Ti-$TiCr_2$ alloys
2. Two-phase Fe-$ZrFe_2$ alloys
3. Two-phase ternary Ni-Cu-Mg alloys containing $MgNi_2$ and $MgCu_2$ Laves phases

We have done microstructural evaluation 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.

Some 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 C36, but with some C15 regions. A high density of stacking faults on the basal planes of the C36 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. C15 phase increases, and that the C15 regions that form are rather free of stacking faults. We have also observed interfaces between C36 and C15 phases, and these observations are suggestive of a dislocation mechanism for the transformation, as seen in Figure 1. Our results provide good evidence that the C36 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→C15 phase transformation contributes to the room-temperature plasticity of the Laves phase in this two-phase alloy.

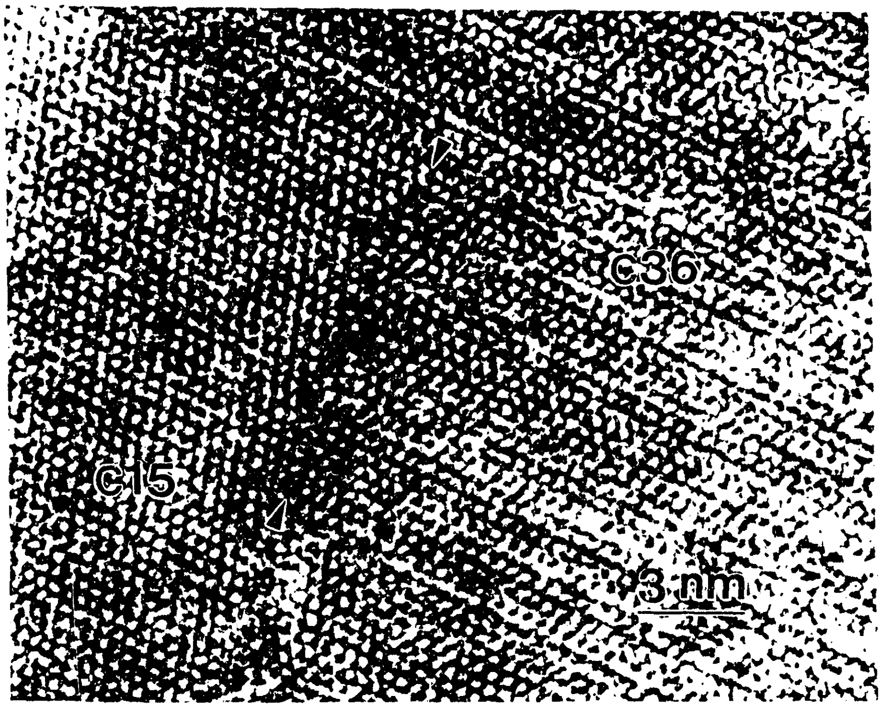


Figure 1. Transmission electron micrograph of Fe-10 Zr alloy, showing microstructure of Laves phase $ZrFe_2$ after room-temperature compressive deformation. A transformation interface between C36 and C15 phases is clearly visible between the arrows.

Observations of the C15 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.

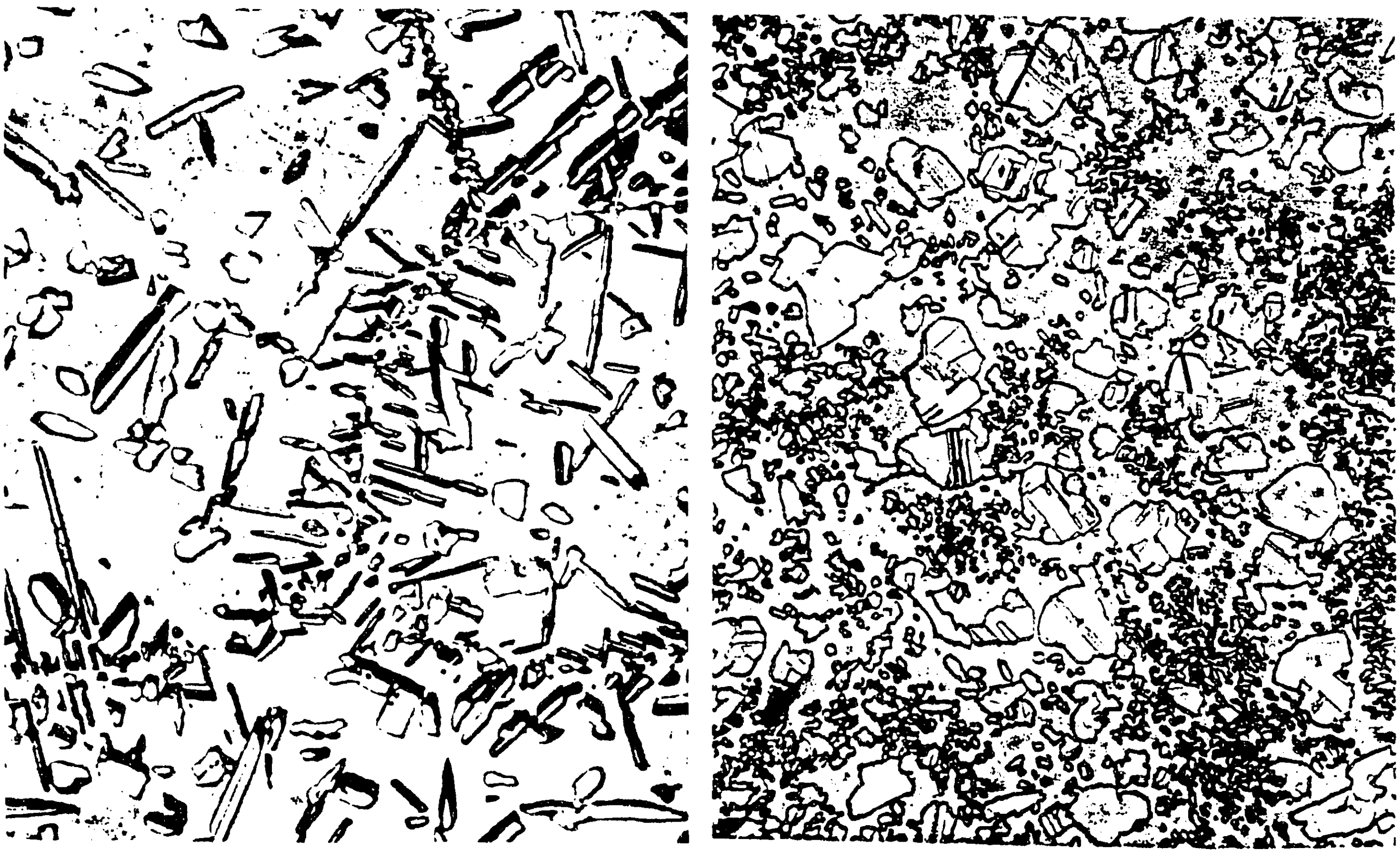
Microhardness indentations on a polished specimen have been used to study plastic deformation of hard materials, and we have developed a convenient technique for introducing plastic deformation in $ZrFe_2$ using indentations. The technique involves producing an array of 100 or more indentations on a 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. Preliminary results of these experiments, on $ZrFe_2$, reveal regions with extensive plasticity, as shown in Figure 2. While considerable shear is localized on basal planes of the C36 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 are in the process of careful identification of the slip systems involved in this type of deformation, and ultimately hope to be able to correlate deformation structure with distance and orientation relative to the microhardness indentations (i.e., stress state).

Figure 2. Transmission electron micrograph of Laves phase near microhardness indentation in Fe-10 Zr alloy. The individual cells are bounded by basal and prism planes, and seem to have significant misorientations with neighboring cells.

Ti-$TiCr_2$ Alloys

We have 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, as shown in Figs. 3(a) and 3(b).



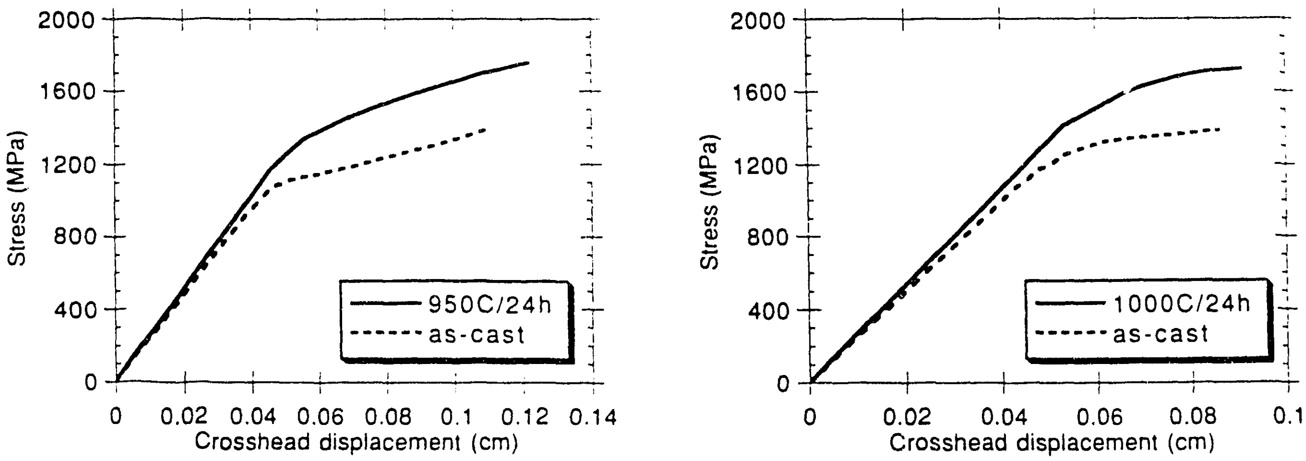
(a) (b)

Figure 3. (a) Optical micrograph of Ti-30 Cr alloy after annealing at 950°C. (b) Ti-40 Cr alloy after annealing at 1000°C. Both micrographs at 660X.

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 C15 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→C36→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 are presented in Figs. 4 (a) and 4(b). 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



(a) (b)

Figure 4. (a) Engineering stress vs. crosshead displacement for Ti-30 Cr alloy containing approx. 17 volume % Laves phase. The total strain was about 26%. (b) Deformation behavior of Ti-40 Cr alloy containing about 39 volume % of Laves phase. Total strain was 6%. Crosshead speed in all tests was 0.001 in/min, loading was uniaxial compression.

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. A typical microstructure of the C15 Laves phase in the Ti - 40% Cr alloy is shown in Figure 5. Twinning on the {111}<112> system seemed to result from both annealing and deformation. However, extensive deformation was not encountered, suggesting that alloying may be needed to realize more room-temperature ductility in this alloy system.

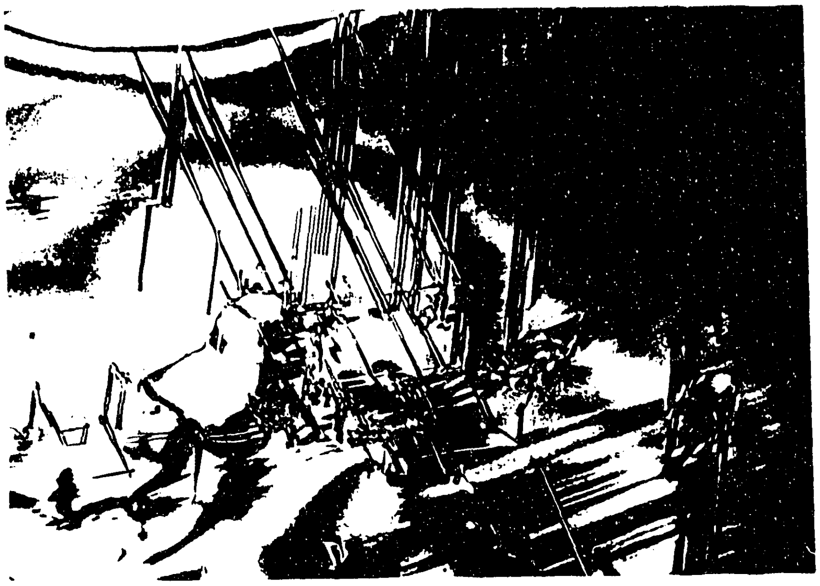


Figure 5. Transmission electron micrograph of defect structures in compressed sample of Ti - 40% Cr alloy containing C15 Laves phase. Magnification 20,000X.

<u>Ni,Cu-Mg(Ni,Cu)$_2$ Alloys</u>

Four alloys have been prepared which span 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 C15 structure, and the phase $MgNi_2$ has the C36 structure. We expect 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. Our work to date has involved a survey of 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 C15 and C36 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 C15 structure with stacking ABCACB..., shown in Figure 6. We also have observed a five-layer structure in the ternary alloy.

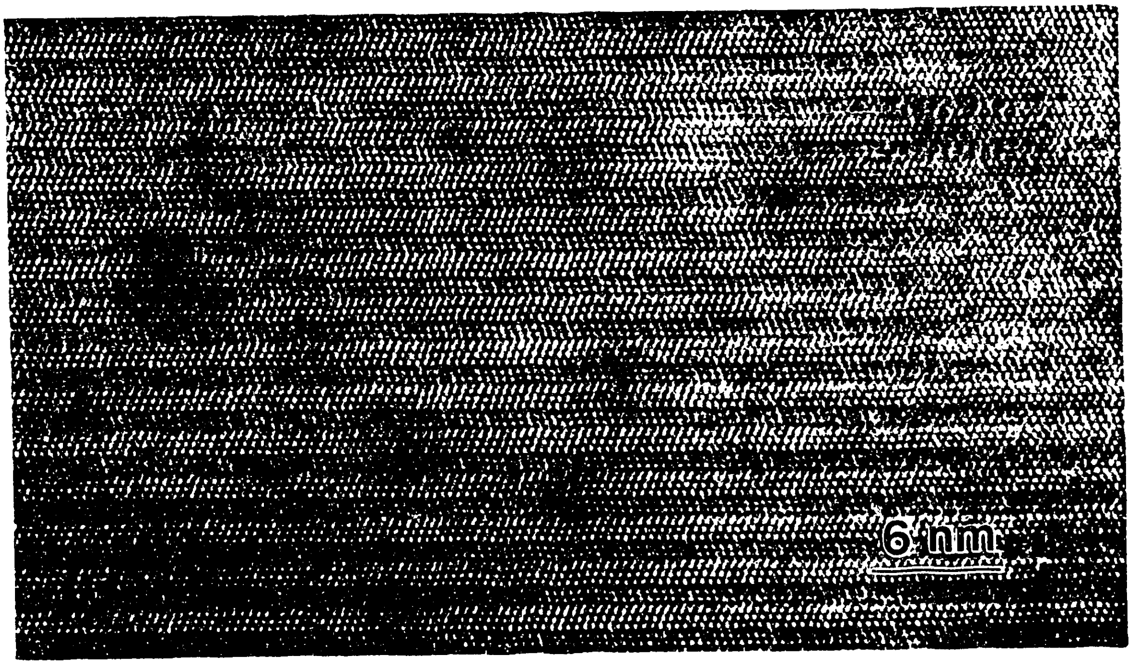


Figure 6. High-resolution transmission electron micrograph of Laves phase with six-layer stacking sequence in Cu - 57 at. % Ni - 15 at. % Mg alloy.

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 C36 structure. Examples of some of these features are seen in Figure 7. 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.

Figure 7. Transmission electron micrograph of Laves phase $MgNi_2$ after uniaxial compression. Stacking faults and slip bands are seen on nonbasal planes, indicative of a variety of slip systems 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 C36 structure, demarcated by bands of intense shear on basal planes and on prism planes. Figure 8 is a typical microstructure. Close observation of the C36 "blocks" in both Figures 2 and 8 shows the periodic faults characteristic of the C36 structure, and it can be seen that misorientations are apparent between the various "blocks." This microstructure illustrates the extensive plasticity that is possible at room temperature in $MgNi_2$ under the complex loading induced by indentation.

Figure 8. Transmission electron micrograph of Laves phase $MgNi_2$ after deformation by microhardness intentation. Shear bands on basal and prism planes give rise to a cell structure, similar to that observed in $ZrFe_2$ (Figure 2).

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 for examination in the transmission electron microscope.

We have demonstrated that a strain-induced phase transformation from C36→C15 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 C15 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 $MgNi_2$ indicates that a variety of slip systems are operative in this "dihexagonal" form of the Laves phase.

The remaining months of this program will be devoted to quantitative analyses of many of the defect structures that we have observed, to determine specific Burger's vectors and slip planes which are operative in the different alloys, and to begin to understand the extent of common behavior among the various Laves phases which we have studied.

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PUBLICATIONS FROM THE PRESENT PROJECT*

Katherine C. Chen, Samuel M. Allen and James D. Livingston, "Morphology, Deformation, and Defect Structures of $TiCr_2$ Alloys," *High-Temperature Intermetallic Alloys-V*, Proceedings of Fall 1992 Materials Research Society Meeting, Boston, MA, accepted for publication.

Yaping Liu, Samuel M. Allen and James D. Livingston, "Deformation Mechanisms in a Laves Phase," *High-Temperature Intermetallic Alloys-V*, Proceedings of Fall 1992 Materials Research Society Meeting, Boston, MA, accepted for publication.

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).

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).

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

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

* Copies of these publications are provided as an attachment to this Progress Report

STUDENTS

There are two graduate students working on this program, both of whom joined the project in the fall semester 1990.

Yaping Liu is a fifth-year 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 holds an appointment as a Research Assistant. He has responsibility for the research on Fe-Zr alloys, and the Cu-Ni-Mg alloys. Mr. Liu has contributed extensively to our microstructural analysis by high-resolution electron microscopy. He also developed the technique for TEM specimen preparation of samples in which deformation was introduced by microhardness indentations. We expect Mr. Liu to complete his Ph.D. degree by September, 1993. Recently, Mr. Liu learned that he will be honored at the Annual Meeting of The Minerals, Metals and Materials Society, as he has been selected as a TMS Outstanding Student Paper Contest Award recipient for his paper "Room-Temperature Deformation and Stress-Induced Phase Transformations of Laves Phases in Fe-10 at. % Zr Alloy."

Kathy Chen is a third-year graduate student who received bachelor's degrees from Michigan State University in Materials Science and Engineering and in Chemistry in June 1990. Kathy is responsible for the research on Ti-Cr alloys. She holds a three-year DOD Fellowship, and therefore has contributed her time to this project at no cost. Her DOD Fellowship support ends August 31, 1993. Kathy passed the General Examination for the Doctorate in Materials Science in September 1992, and expects to complete the Ph.D. degree in June, 1995.

Sincerely,

Samuel M. Allen

Samuel M. Allen
Professor of Physical Metallurgy

James D. Livingston

James D. Livingston
Senior Lecturer

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