Mechanisms of Deformation in B2 and Ruthenium Aluminides

Final Report
for period
April 1, 1996 – October 31, 2000

Tresa M. Pollock*
Principal Investigator

Carnegie Mellon University
Department of Materials Science and Engineering
5000 Forbes Ave.
Pittsburgh, PA 15213

*Present Address
Department of Materials Science and Engineering
University of Michigan
2300 Hayward, HH Dow 2042
Ann Arbor, MI 48109

Prepared for
THE U.S. DEPARTMENT OF ENERGY
AWARD NO. Grant # DE-FG02-96ER45566

DOE Patent Clearance Granted
Mark P. Dvorscak
(830) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office

Date 8.20.03
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Mechanisms of Deformation in B2 and Ruthenium Aluminides

1.0 Personnel

This research grant provided support for the principal investigator, Professor Tresa Pollock and one Ph.D. student, Dr. David Lu, who successfully completed a Ph.D. thesis in September, 2000. The thesis was entitled “Dislocation Substructures and Mechanical Properties of RuAl-based Intermetallic Compounds”. An additional M.S. Student was supported by this grant: Mr. Khenlak Eow, who completed a thesis entitled “Mechanisms of Deformation in B2 Aluminides”. Other collaborators on this grant included Dr. Vinod Sikka of Oak Ridge National Laboratory (who assisted with some exploratory processing studies on ruthenium aluminides) and Dr. Man Yoo of ORNL who served on the Ph.D. thesis committee of Dr. Lu. Additional Carnegie Mellon collaborators included Professor Marc De Graef and Dr. Xiaoli Shi. Dr. Robert Fleischer of General Electric Corporate Research & Development, Dr. Ron Noebe of the NASA-Lewis Research Center and Dr. Ram Darolia of General Electric Aircraft Engines also donated a portion of the experimental materials for this study.

2.0 Background and Research Objectives

Continued advances in high temperature structural materials are critical to the performance of power generation and transportation systems. Gas turbines and large diesel engines for power generation are two examples of systems whose efficiencies are presently limited by the high temperature materials in their hottest sections. Intermetallics are a promising class of materials for such applications, since they combine generally high melting points with the potential for some degree of tensile ductility (and toughness) essential to reliable performance in service. Intermetallic B2 type aluminides are particularly attractive since they form protective alumina scales that are generally resistant to oxidation and corrosion. They also have the potential for generally ductile behavior with deformation on five independent slip systems. However, the mechanical behavior of B2 aluminides ranges from extremely brittle to generally ductile. The mechanisms responsible for such wide variations in deformation behavior are still not well understood. While many factors may influence tensile ductility, of particular importance are the number of independent slip systems and the intrinsic mobility of dislocations, since these aspects of material behavior are not readily changed by minor variations in composition or processing.

Our research has aimed to establish a link between macroscopic deformation behavior and intrinsic aspects of plastic flow that are likely to limit ductility of B2 aluminides. The approach has been to couple macroscopic measurements of deformation kinetics with electron microscopy studies in order to identify rate-limiting features of deformation and distinguish between extrinsic and intrinsic barriers to deformation. Studies in this program focused on three model B2 aluminides: NiAl, FeAl and RuAl.
3.0 Summary of Research Accomplishments

The results of investigations conducted are summarized in detail in the publications listed in Section 4.0. A total of 16 publications and presentations resulted from this grant. Significant advances in the understanding of deformation mechanisms in B2 aluminides were achieved, with exceptionally interesting results for the ruthenium aluminides systems. Subsequent research has focused only on ruthenium aluminide-based systems. Highlights of the investigations are summarized and publications can be referred to for more details.

3.1 Comparative Analysis of Model B2 Aluminides

The microscopic and macroscopic deformation characteristics of three different B2 aluminides were studied, with the use of FeAl, NiAl and RuAl as "model" systems. As can be seen from Table I, these three aluminides display a range of melting temperatures and elastic properties. FeAl-based materials are known to display a significant amount of tensile ductility if tested in inert environments. NiAl polycrystals tend to have less than 1% tensile ductility at room temperature and commercial purity NiAl single crystals have tensile ductilities of less than 2%. To our knowledge, no tension tests have been reported for RuAl; this is apparently due to the difficulty of processing this very high temperature compound. However, RuAl has been reported by Fleisher and co-workers to possess a relatively high toughness, judged on a qualitative comparative basis to other intermetallics with the use of a chisel and hammer. RuAl also possesses very good oxidation and corrosion resistance, along with a moderate density of 7.95 g/cm³.

Single crystal Fe-40Al-0.2Zr, single crystals and polycrystalline stoichiometric NiAl and polycrystalline RuAl have been investigated. All single crystals were grown by investment casting with a modified Bridgman technique at the General Electric Company. The Fe-40Al-0.2Zr crystals were [001] oriented. The NiAl crystals were primarily investigated in the "soft" [110] orientation, where deformation occurs by glide of <001> type dislocations. Limited comparative experiments were conducted on "hard" <100> crystals which deform by glide of <111> type dislocations. A number of different variants of the NiAl single crystals were examined, including "commercial" purity Bridgman crystals (containing moderate levels of C, O, N and Si in solution), higher purity crystals grown by containerless growth techniques, Fe-microalloyed crystals and pre-strained crystals. None of these variants of the material were qualitatively different in terms of deformation kinetics, compared to the commercial purity (CP) crystal. Polycrystalline NiAl was obtained by extrusion, conducted at the NASA-Lewis Research Center. Due to the high melting point of RuAl, single crystals of this compound have not been grown to date, so only arc melted polycrystalline materials have been examined. Binary RuAl and a number of different ternary RuAl compositions containing, B, Sc, Y or Cr additions were examined.
Table I - Classes of B2 Compounds Studied and Comparison of Selected Properties

| Compound          | Melting Point (°C) | RT Elastic Modulus (GPa) | A, Elastic Anisotropy Ratio | APB Energy (mJ/m²)  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-40Al-0.2Zr</td>
<td>1310 (d)*</td>
<td>180 (a)</td>
<td>3.7 (a)</td>
<td>490 (d)</td>
</tr>
<tr>
<td>NiAl</td>
<td>1638 (d)</td>
<td>193 (c)</td>
<td>3.7 (c)</td>
<td>889 (b)</td>
</tr>
<tr>
<td>RuAl</td>
<td>2060 (d)</td>
<td>267 (f)</td>
<td>1.5 (b)</td>
<td>580 (b)</td>
</tr>
</tbody>
</table>

* The highest temperature at which the B2 ordered phase exists, at Fe-45Al.

Macroscopic deformation kinetics were characterized via strain rate jump experiments over a range of temperature on a large number of samples from each of the three types of aluminides. These strain-rate jump experiments utilized compression specimens and typically consisted of an abrupt increase strain rate imposed by two orders of magnitude, from rates of approximately $10^{-4}$s⁻¹ to $10^{-2}$s⁻¹ after ≈ 2% plastic deformation in a screw-driven Instron machine.

The typical response of each of the three types of materials to a strain rate change at room temperature is shown in Figure 1. All stresses are expressed as net section compressive stresses. Note that arrows mark the point at which the strain rate change is imposed in each experiment. The response of the NiAl material is clearly more rate sensitive than either the Fe-40Al-0.2Zr material or the RuAl. Table II summarizes the results of strain rate change experiments on all three compounds across a range of composition and temperature. From these experiments several activation parameters can be calculated.

First, the shear rate of deformation, $\dot{\gamma}$, can be expressed in the form of an Arrhenius relationship:

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta G(\sigma)}{kT}\right) \tag{1}$$

where $\Delta G(\sigma)$ is the stress-dependent activation energy (activation free enthalpy) required to activate a dislocation past a slip plane barrier. The pre-exponential factor, $\dot{\gamma}_0$, contains a frequency factor for the
activation process. With a strain-rate change, an apparent activation area, $A^*$, which is a measure of the area on the slip plane involved in the saddle point configuration of the dislocation, or an activation volume, $V^*$, is defined as:

$$A^* = \frac{V^*}{b} = \frac{1}{b} \left( \frac{\partial \Delta G}{\partial \tau} \right)_T = \frac{kT}{b} \left( \frac{\partial \ln \gamma'}{\partial \ln \dot{\gamma}} \right)_T$$  \hspace{1cm} (2)

where $b$ is the Burgers vector, $\tau$ is the applied shear stress, $k$ is the Boltzmann constant and $T$ is temperature. Additionally, a rate sensitivity, $m'$, which is related to the activation area, can be calculated from the power-law relationship between stress and strain rate:

$$m' = \frac{\partial \ln \tau}{\partial \ln \dot{\gamma}}$$  \hspace{1cm} (3)

Several features of the macroscopic deformation behavior of these materials are apparent from the results shown in Table II. First, the flow stress of “soft” <110> NiAl crystals is very temperature sensitive, with an increase of approximately 5X when the temperature is decreased from room temperature to -196°C. This is consistent with the relatively high rate sensitivity and suggests that deformation is limited by thermally activated dislocation glide processes in this temperature range. Analysis of these data produced an activation enthalpy of approximately 1.3 eV. The temperature dependence of the flow stress and the rate sensitivities for deformation in polycrystalline NiAl are similar to those observed for the <110> single crystals, indicating that the same processes limit deformation in both forms of the material.

Unlike NiAl, the temperature dependence of the flow stress between liquid nitrogen and room temperatures for RuAl is negligible. The data for the RuAl+0.5%B material actually suggest a slight rise in flow stress from -196°C to room temperature, however this effect may be due to inhomogeneities in the grain size in the arc-melted material. The rate sensitivities for deformation in RuAl and Fe40Al-0.2Zr are both very low compared to NiAl. Similar to ternary substitutional additions in NiAl, the addition of B, Sc, Y or Cr to RuAl has only a minor influence on rate sensitivities.

As the flow stresses increase (as liquid nitrogen temperatures are approached) in <110> NiAl crystals the activation areas decrease to very low levels (<10 $b^2$) for the soft crystals, suggesting a strong short range barrier to dislocation glide at low temperatures. Due to limited amounts of material, activation areas in Fe-40Al-0.2%Zr were measured only at room temperature. Under those conditions, $A^* = 76$ $b^2$, which is about 25% higher than the <110> NiAl crystals. For NiAl and FeAl, activation areas were calculated by
resolving stresses and strains onto the active slip systems. However, as will be discussed further below, due to the multiple types of dislocations observed in the RuAl material, it was only possible to estimate a range of activation areas for this material, using a BCC Taylor factor and evaluating all the possible slip systems. Compared to the soft NiAl material, the activation areas for deformation in RuAl were in the range of 3 to 10 times higher at liquid nitrogen temperatures and up to 3 times higher at room temperature. These factors collectively suggest a higher intrinsic dislocation mobility in RuAl, compared to NiAl, particularly at lower temperatures.

After approximately 2% deformation in all "soft" (<110>, <223> and <123> oriented) NiAl crystals the substructure consisted entirely of <100> type dislocations across the range of temperatures investigated. These dislocations existed in the form of small dipole loops loosely aligned in bands, along with segments

**Figure 1** - Results of room temperature strain rate change experiments in compression for the three different B2 aluminides.
Table II - Results of Strain Rate Change Experiments on Selected Experimental Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Flow Stress at ε = 2% (MPa)</th>
<th>Rate Sensitivity, $m'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl &lt;110&gt;</td>
<td>-196</td>
<td>1083</td>
<td>0.0219</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>231</td>
<td>0.0248</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>219</td>
<td>0.0231</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>174</td>
<td>0.0239</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>173</td>
<td>0.0197</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>133</td>
<td>0.0261</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>130</td>
<td>0.0257</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>115</td>
<td>0.0170</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>124</td>
<td>0.0181</td>
</tr>
<tr>
<td>NiAl Extruded Polycrystalline</td>
<td>-196</td>
<td>925</td>
<td>0.0180</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>325</td>
<td>0.0120</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>335</td>
<td>0.0120</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>246</td>
<td>0.0153</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>246</td>
<td>0.0166</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>153</td>
<td>0.0236</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>155</td>
<td>0.0284</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>98</td>
<td>0.0254</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>101</td>
<td>0.0258</td>
</tr>
<tr>
<td>Fe-40Al-0.2Zr &lt;100&gt;</td>
<td>RT</td>
<td>358</td>
<td>0.0023</td>
</tr>
<tr>
<td>RuAl+0.5%B</td>
<td>-196</td>
<td>430</td>
<td>0.0067</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>448</td>
<td>0.0061</td>
</tr>
<tr>
<td>Ru$<em>{52}$Al$</em>{43}$Sc$_{5}$</td>
<td>-196</td>
<td>445</td>
<td>0.0066</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>410</td>
<td>0.0059</td>
</tr>
<tr>
<td>Ru$<em>{50.5}$Al$</em>{44.5}$Cr$_{5}$</td>
<td>RT</td>
<td>478</td>
<td>0.0078</td>
</tr>
<tr>
<td>Ru$<em>{51}$Al$</em>{49}$Y</td>
<td>RT</td>
<td>450</td>
<td>0.0047</td>
</tr>
</tbody>
</table>
that were mixed in character with a relatively high density of jogs, Figure 2. These features develop due to easy cross slip (and double cross slip) of screw segments, in spite of the fact that they are elastically unstable in the screw orientation. Similar features have recently been observed by several other investigators during in-situ straining experiments and are present in single slip as well as multi-slip orientations. The major difference in the substructure of material deformed at liquid nitrogen temperatures, compared to that deformed at room temperature was a much higher density of dipole loops.

Following deformation of the <100> oriented Fe-40Al-0.2Zr crystals, only <111> type dislocations were observed. Figure 3 shows a typical region after low strain deformation at room temperature, containing two sets of <111> type dislocations. This result was not unexpected, and similar to that observed by a number of other researchers who have examined substructures following deformation of FeAl type alloys.

Figure 2 - Weak beam micrograph of the substructure of NiAl following room temperature deformation, containing small dipole loops and jagged dislocations with a high density of jogs along their length. All dislocations are <100> type.
The substructural features following low temperature deformation of RuAl type compounds are markedly different than either the NiAl or FeAl-based materials. These unusual characteristics of deformation in this B2 system are outlined in the following section.

3.2 Deformation of Ruthenium Aluminides

The aim of this investigation was to characterize in detail the dislocations and operative slip systems in RuAl polycrystals. Deformation at both room temperature and 77 K was studied, in an attempt to detect any major changes in substructure at lower temperature where dislocation mobility might be restricted. Small strain compression experiments were performed and dislocations were analyzed in detail by transmission electron microscopy (TEM). Results of microscopy investigations are compared to image simulations by using the program of Head & Humble. The nominal composition of the compound studied in most detail was RuAl + 0.5%B. Samples were arc-melted into disk shaped ingots approximately 7 cm in diameter and annealed at 1350 °C for 20 hr. low magnification view of the substructure following 2% deformation.

Figure 3 - Fe-40Al-0.2Zr following 2% compressive deformation. Note the presence of two sets of $<111>$ dislocations locally.
Low magnification TEM surveys showed that dislocations in the substructure could generally be characterized as curved and lacking any obvious preferred line direction or alignment with surrounding dislocations at both temperatures. The set of bright field images given in Figure 4(a) to (f) show the

![Image](a) ![Image](b)

![Image](c) ![Image](d)

![Image](e) ![Image](f)

**Figure 4.(a)-(f) Six bright-field micrographs of a region imaged with different diffraction vectors \( \bar{g} \) after 1.3\% deformation at 77 K. The triangle marks a common reference point in each of the micrographs.
substructure for a series of different diffraction vectors after 77 K deformation. The short arrow marks a reference point in each photo. The results of the analysis shown in Figure 4 along with other similar analyses for other regions, indicate that Burgers vectors present are the major types \<100> and \<110>. Additionally, a relatively low density of \<111> type was distributed among \<100> and \<110>, as indicated in Figure 5. Trace analysis was used to determine line directions and slip planes for dislocations marked by A, B and C in Figure 6. Line directions are \[221\], \[223\] and \[43 \bar{3}\], respectively, and these results again suggest that \{110\} planes are the most common slip planes for \<100> and \<110> types of Burgers vectors.

![Figure 5. Burgers vectors identified by g \cdot b analysis are marked beside the dislocations in the same area as shown in Fig. 4. Dislocations A, B and C were selected for analysis of the line directions and slip planes.](image)

A similar analysis was performed for a sample deformed at room temperature. No significant difference in the density or distribution of dislocations was noted for deformation at room temperature, compared to 77 K. The results of the analysis of the Burgers vectors in Figure 6 again show that \<100> and \<110> types are predominant in the sample deformed at room temperature. The line direction of dislocation A is \[\overline{111}\] and the slip plane is (101). Similar analyses conducted on other samples also showed that the \{110\} plane was the most likely slip plane.
Figure 6. Burgers vectors identified by $g \cdot b$ analysis are marked beside the dislocations in a sample after 2% deformation at 298 K. Dislocation A was selected for analysis of the line direction and slip plane.

Some additional interesting features of this boron-containing material were also studied in this program. RuAl-based materials with and without boron additions have been studied (in collaboration with Prof. Marc De Graef). Boron additions have been observed to produce thin, planar precipitates on \{100\} planes in this compound, Figure 7. The precipitates have been shown to be non-conservative substitutional complex faults arising from the substitution of aluminum by boron. These planar precipitates, which are not visible by optical or SEM analysis, interact with gliding dislocations and may be the reason that boron additions result in unusually high work hardening rates in this material. The crystallography of these planar faults has been shown to be related to the crystallography of ternary borides of the type Al$_{n-1}$B$_n$X$_n$.

To summarize, investigations on RuAl-based systems suggest that the behavior of this material is quite different, compared to all other B2 systems. It has a very high melting temperature (2060°C), low temperature sensitivity of the flow stress and low rate sensitivity. Additionally, microscopy studies on deformed polycrystalline RuAl reveal high densities of $<110>$ and $<100>$ dislocations on \{110\} planes, which may indicate five independent slip systems. These factors collectively suggest that RuAl has a high intrinsic deformability compared to all other high temperature B2 aluminides. For these reasons, we are currently investigating the deformation characteristics of this compound in more detail in single crystals as well as with systematic ternary and quaternary additions.
Figure 7 – Bright field images of a boron-induced fault under various diffraction conditions.

4.0 Publications and Presentations*


* Due to a typographical error in the original internal grant award paperwork at Carnegie Mellon some of the above publications acknowledged Grant DE-FG02-95ER45548, rather than DE-FG02-95ER45566, but all research was performed under the grant of the latter number.