

The effect of pressure on the structure of NiAl₂O₄

Itzhak Halevy^{1,4}, Danut Dragoi¹, Ersan Üstündag^{1,5}, Alan F Yue¹,
Elizabeth H Arredondo², Jingzhu Hu³ and Maddury S Somayazulu³

¹ Department of Materials Science, California Institute of Technology, Pasadena, CA 91125, USA

² Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

³ Geophysical Laboratory of Carnegie Institution of Washington, Washington, DC 20015, USA

E-mail: ersan@caltech.edu.

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Abstract

NiAl₂O₄ is known to transform from a normal spinel, (Ni²⁺)[Al₂³⁺]O₄, to an inverse spinel, (Al³⁺)[Ni²⁺ Al³⁺]O₄, and vice versa. In this process, the larger Ni²⁺ ions which occupy the tetrahedral (8a) sites in normal spinel move to the octahedral (16d) sites in inverse spinel while half of the smaller Al³⁺ ions move in the opposite direction. The extent of this move is measured by the disorder or inversion parameter, *I* (the fraction of tetrahedral sites occupied by the Al ions; *I* = 0 for normal spinel and *I* = 1 for inverse spinel). Previous studies suggest that the lattice constant of spinel can decrease as the disorder parameter increases to better accommodate the Ni ions. *In situ* neutron diffraction studies performed by us indicate that this process is also occurring during the reduction of NiAl₂O₄ to Ni and Al₂O₃. It is possible that the compressive residual stresses generated during reduction play a role in the structural evolution of NiAl₂O₄.

To systematically investigate the effect of pressure on the structure of NiAl₂O₄, x-ray diffraction studies at the X17 beamline of the National Synchrotron Light Source were performed. The pressure (up to 35 GPa) was applied via a diamond anvil cell and the experiments were conducted using a polychromatic x-ray beam. By comparing the relative intensities of certain spinel reflections that are sensitive to cationic disorder, a trend toward inverse spinel as a function of pressure was observed. The results are presented in comparison to previous studies on this material.

(Some figures in this article are in colour only in the electronic version)

⁴ Permanent address: Physics Department, Negev Nuclear Research Centre, PO Box 9001, 84190 Beer-Sheva, Israel.

⁵ Author to whom any correspondence should be addressed.

1. Introduction

A general formula for 2–3 oxide spinels is AB_2O_4 , where A and B are divalent and trivalent cations, respectively [1, 2]. In *normal* spinel the divalent cations occupy 8 tetrahedral interstices (8a) and the trivalent cations sit in 16 octahedral (16d) sites. The structure in this case is denoted as AB_2O_4 . In *inverse* spinel, $(B)[AB]O_4$, all 8 divalent cations together with 8 trivalent ones occupy 16 octahedral positions while the remaining 8 trivalent cations move to 8 tetrahedral sites. In spinel structure, the oxygen ions occupy the 32e sites and are arranged in an almost cubic close-packed manner. The unit cell contains eight formula units and has the cubic space group $Fd\bar{3}m$. Many spinels, including $NiAl_2O_4$, have structures that fall in between the two extremes. The changes in the cationic sublattice are quantified by the disorder or inversion parameter, I (the fraction of tetrahedral sites occupied by the trivalent ions). In other words, $I = 0$ for normal spinel and $I = 1$ for inverse spinel. Usually at high temperatures, spinels tend towards the completely random distribution where $I = 2/3$, i.e., $(A_{1/3}B_{2/3})[A_{2/3}B_{4/3}]O_4$.

The relative ease with which its cationic sublattice can be modified (due to fast cationic self-diffusion) has led to many structural studies on $NiAl_2O_4$. Here the two most recent ones are cited: [1, 2]. The reader is referred to [2] for a more detailed review. Almost all of these studies used x-ray powder diffraction (XRD) for structure analysis. Specimens were usually annealed at high temperatures and then quenched to room temperature assuming that the high-temperature structure would be conserved ('frozen in'). These studies showed that Ni spinel tended to become less inverse at higher temperatures approaching the 'random' case with $I = 2/3$. They also noticed relationships between the inversion, oxygen and lattice parameters. Specifically, the lattice parameter decreased as the inversion parameter increased. A similar inverse relationship was also observed between the inversion and oxygen parameters. These observations can be explained by the fact that the Ni^{2+} ions are much larger than the Al^{3+} ions. As a result, the Ni^{2+} ions can fit 'more easily' in the larger octahedral (16d) sites, and when they move from the smaller tetrahedral (8a) sites into the 16d sites (as spinel becomes more inverse), the lattice relaxes, leading to decreases in the oxygen and lattice parameters.

2. Neutron powder diffraction results

Our interest in the structure of Ni spinel was motivated by our previous studies of its reduction to Ni and Al_2O_3 [3–5]. This reaction is accompanied by a volume shrinkage (up to 18%) and can lead to residual stress generation. In previous neutron powder diffraction (NPD) work [3–5], this reaction was monitored *in situ* to elucidate the evolution of strains and phases. It was seen that substantial changes in the spinel lattice constant could occur in some specimens (figure 1(a)) pointing to the possibility of significant residual strain/stress generation during reduction. The NPD specimens were cylinders in which the progress of the reaction from the surface inward would lead to an enclosed unreduced $NiAl_2O_4$ region surrounded by a Ni– Al_2O_3 composite layer. The shrinkage of this outside layer (combined with the constraint imposed on it by the unreduced spinel in the middle) could lead to compressive stresses/strains in the spinel. The data shown in figure 1(a) seemed to support this hypothesis since a progressively increasing compressive 'strain' was measured in the spinel.

Unfortunately, a second observation obtained from the NPD data complicated the above interpretation. As shown in figure 1(b), the Rietveld refinement of the NPD data yielded a progressive transformation of $NiAl_2O_4$ towards inverse spinel. The equilibrium value of I was measured to be around 0.8 at 1200 °C in previous studies [1, 2]. $I = 0.8$ was approximately the value obtained at the beginning of the reduction (figure 1(b)); however, its later change towards 1.0 seemed to be related to the reduction reaction, and more specifically the conceivable

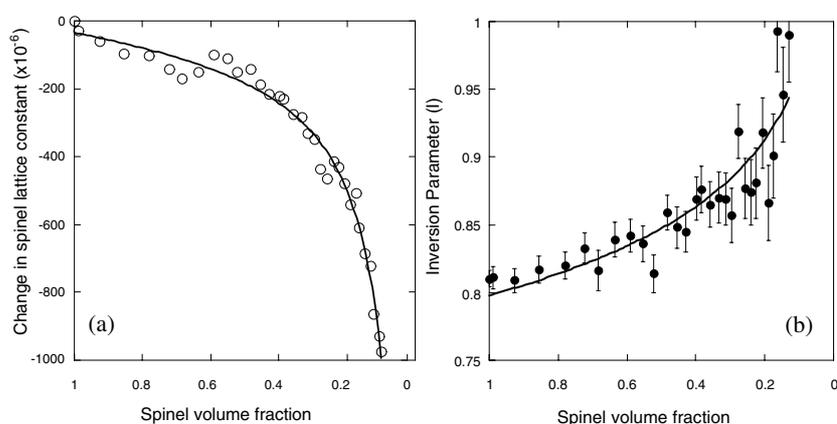


Figure 1. *In situ* NPD results from the reduction of Ni spinel at 1200 °C [3–5]. (a) The evolution of the spinel lattice parameter as a function of unreduced spinel volume fraction (and rough reduction time); (b) the change in the inversion parameter of spinel. Fitting curves are added to both plots to guide the eye.

compressive stresses generated during its progress. To clarify the effect of pressure on the structure of NiAl₂O₄, several high-pressure experiments were conducted using a diamond anvil cell and employing XRD. Some preliminary results are presented and discussed in this article.

3. Experimental procedure

NiAl₂O₄ was processed by reacting stoichiometric mixtures of Al₂O₃ and NiO in air at 1550 °C for 48 h. The partly sintered compacts were ground to powder, which was then sieved to –325 mesh size (<44 μm). The samples were stoichiometric within the experimental error (as determined by electron microprobe analysis). There was no significant loss of Ni during the high-temperature annealing. To attain the equilibrium structure of spinel, the powders were annealed again at various temperatures following the guidelines given in the literature [2]. After annealing, the samples were pulled out of the furnace quickly to induce a fast cooldown to room temperature (within several minutes). In this article, the results obtained from the NiAl₂O₄ powders annealed at 1100 °C for 60 h are reported. To confirm that the 1100 °C structure was maintained after cooldown, room temperature XRD measurements were performed using a Siemens D500 diffractometer with Cu Kα radiation. The data were analysed using a Rietveld code [6]. The inversion parameter obtained from Rietveld analysis ($I \sim 0.82$) was reasonably close to the value reported in the literature [1, 2] for 1100 °C anneals (~ 0.81). It should be noted that anneals conducted at temperatures below 800 °C yield an I -value of close to 1.0 [1, 2].

High-pressure (quasi-hydrostatic) XRD experiments were carried out in a ‘Tel-Aviv’-type diamond anvil cell with 600 μm culets. The pressure calibration was done with ruby and platinum while Si oil was the pressure medium in a 250 μm diameter stainless steel gasket. These experiments were conducted in ambient temperature at the X17C beamline of the National Synchrotron Light Source (NSLS). In this process, energy dispersive (EDS) data generated by a polychromatic x-ray beam were collected with a Ge detector at a fixed Bragg angle ($2\theta = 13^\circ$). The pressure distribution inside the sampling volume was checked and was determined as varying by less than 5%. Typical data collection time was around 5 min.

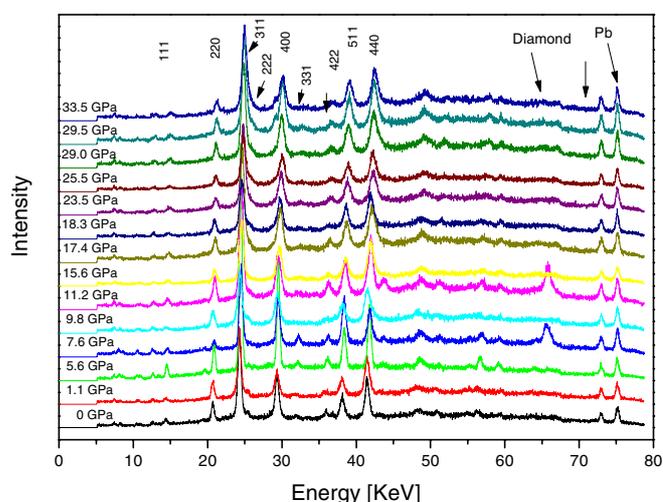


Figure 2. The effect of pressure on the EDS x-ray pattern of NiAl_2O_4 at ambient temperature. Major spinel reflections are indexed. A systematic shift towards higher energy (i.e., lower d -spacing) is observed in NiAl_2O_4 due to the compression of its lattice.

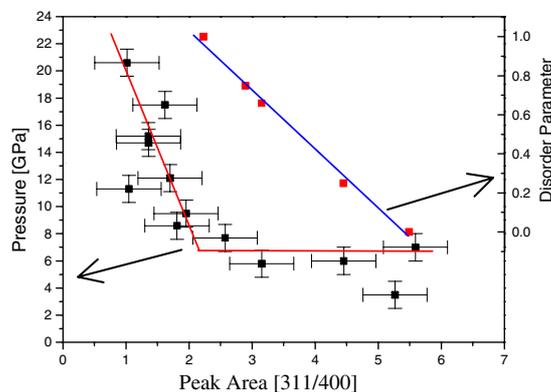


Figure 3. The variation of the relative intensities of the (311) and (400) reflections of NiAl_2O_4 as a function of pressure. The lines were added to the experimental data to guide the eye. The ‘Crystallographica’ prediction is shown on the right axis.

4. Results and discussion

The pressure/x-ray energy data of the NiAl_2O_4 spinel are shown in figure 2 for the range of 0–33.5 GPa. Note that the escape peaks are ignored in these patterns. They usually occur at energies about 9.8 keV lower than the original peak in each case.

The data shown in figure 2 are currently being analysed with the Rietveld method. In the meantime, single-peak fitting was performed on some reflections of Ni spinel. Of these, (400) is insensitive to changes in the cationic sublattice, while (311) is the most sensitive. This was determined by simulating spinel diffraction patterns as a function of I using commercial software (Crystallographica) and the results are shown in figure 3. A comparison of the relative intensities of these two reflections (figure 3) as revealed by the experimental data shows that there is systematic change towards inverse spinel as a function of applied pressure. This

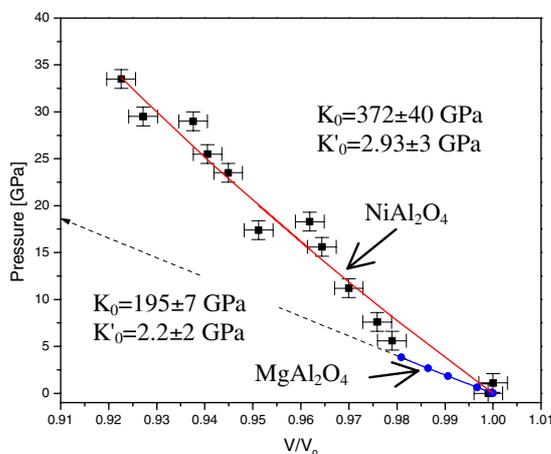


Figure 4. The pressure–unit-cell-volume relationship for NiAl₂O₄. A Birch–Murnaghan equation of state was fitted to the data. The MgAl₂O₄ data [9] were added for comparison.

change seems to stop around 10 GPa at which point the spinel is likely to be fully inverse. A further confirmation of this observation will only be possible after the Rietveld refinement is completed and will be reported in a future publication.

This is the first time that the effect of pressure on the cationic partitioning in NiAl₂O₄ has been studied experimentally. Preliminary data (figure 3) suggest that NiAl₂O₄ can transform under pressure and become an inverse spinel. The only other similar study on NiAl₂O₄ was a theoretical investigation using interionic potential calculations [7]. It showed that the inversion parameter of NiAl₂O₄ could indeed increase under pressure. For instance, this study predicted that at 25 °C, $I = 0.992$ at ambient pressure and $I = 1.0$ at 10 GPa. Similarly, I was calculated to increase from 0.827 (ambient pressure) to 0.857 (10 GPa) at 1100 °C [7]. Our preliminary results then seem to confirm the NPD observations (figure 1) in that the structural evolution during the reduction of NiAl₂O₄ is probably due to compressive residual stresses generated during reduction.

Another result of the high-pressure experiments is the equation of state of NiAl₂O₄. The pressure–volume curve shown in figure 4 allows the calculation of the bulk modulus of this material using the Birch–Murnaghan analysis [8]. The pressure–volume curve (figure 4) shows about 8% reduction in unit-cell volume at 33.5 GPa. Fitting the dependence of the unit-cell volume, V , on pressure to a Birch–Murnaghan equation of state yielded the zero-pressure bulk modulus, $K_0 = 372 \pm 40$ GPa and the pressure derivative for the bulk modulus, $K'_0 = 2.9 \pm 3$. The K_0 -value compares favourably with the results of ultrasonic measurements of the elastic constants of NiAl₂O₄ using solid polycrystalline samples. These measurements produced a Young's modulus of about 345 GPa and a Poisson's ratio of about 0.36. There is some uncertainty in these values since the exact amount of porosity in the samples could not be determined to a high precision. Nevertheless, the bulk modulus obtained from the ultrasonic data is about 410 GPa, approximately in the same range as given by the high-pressure data. It is interesting to note that a similar high-pressure experiment on the more common MgAl₂O₄ spinel produced a much lower value for the zero-pressure bulk modulus of that material ($K_0 \sim 195$ GPa) [9].

5. Conclusions

The preliminary results of high-pressure XRD experiments conducted at NSLS using a diamond anvil cell suggest that pressure forces NiAl_2O_4 spinel to become more inverse. At a pressure of ~ 10 GPa the change ceases, probably because the NiAl_2O_4 structure is already fully inverse. These observations were obtained by comparing the relative intensities of the (311) and (400) reflections of NiAl_2O_4 . The former is the reflection most sensitive to changes in the cationic sublattice of NiAl_2O_4 , while the latter is completely insensitive to these. A more quantitative description of the effect of pressure on the NiAl_2O_4 structure is expected after the completion of the Rietveld analyses of the EDS XRD data. The preliminary results, however, do support the previous NPD results in that the reduction of NiAl_2O_4 seems to generate compressive residual stresses which cause its transformation to a more inverse spinel. The other important conclusion of the present study is that no other pressure-induced phase transformations are present in NiAl_2O_4 at pressures up to 34 GPa. Finally, the bulk modulus of NiAl_2O_4 was also calculated from the high-pressure data using a Birch–Murnaghan analysis and its value (~ 370 GPa) was found to be similar to that obtained by independent ultrasonic measurements on solid specimens.

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