High pressure study and electronic structure of NiAI and Ni₃AI compounds

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Abstract

Nickel aluminide intermetallic compounds, mainly NiAl and Ni₃Al, have been considered as promising high-temperature structural materials because of their high melting points, low densities and good oxidation resistance. Ni-Al intermetallics are potential candidates as heat shields in chambers and gas turbines, however, these materials suffer from brittleness. The Thermodynamic properties with advance first-principles approach where predicting the structural and physicals properties of the NiAl and Ni3Al compounds.

This study presents the room temperature crystallographic, metallurgical, and electronic properties of the Ni₃Al and NiAl compound, as a function of pressure. Both x-ray diffraction (XRD) measurements and full potential linearized augmented plane wave (LAPW) calculations were applied. No phase transition was observed in the XRD measurements up to a pressure of ~30 GPa. The Holzapfel equation was used to fit the volume-pressure curve to the equation-of-state. The bulk modulus (B₀) at ambient pressure was calculated from the X-Ray data, sound-velocity and density measurements, and from the LAPW calculations.

Keywords: High pressure, Iridium, electronic structure, LAPW.

1. Introduction

The Aluminum - Nickel phase diagram as shown by Robertson [1].Is a rich one and includes five different compositions. Most of these compositions are not stoichiometric, Al_3Ni_2 , $AlNi_1$, Al_3Ni_2 , $AlNi_3Ni_5$ and $AlNi_3$. The AlNi can accommodate the structure even with a $\pm 7\%$ variation of the composites while the $AlNi_3$ can accommodate $\pm 1\%$. Nickel aluminide intermetallic compounds, mainly NiAl and Ni₃Al, have been considered as promising high-temperature structural materials because of their high melting points, low densities and good oxidation resistance. However, these materials suffer from brittleness. A lot of cracks can be identified while preparing these samples. In this work we looked at the thermodynamic properties of NiAl and Ni₃Al, namely the change of volume and structure as a function of pressure. The Pm3m (221) cubic structure AuCu₃ type and Pm3m (221) cubic structure CsCl type for the Ni₃Al and NiAl, respectively, are well known.

The inter-metallic compounds that we checked in this system, shown in figure 1 [1], have relatively high melting points, 1638° C and 1385° C for NiAl and Ni₃Al, respectively. The present study has three goals, (a) preparing of well characterized and homogeneous

samples; (b) studying mechanical and physical properties of this compound, at ambient and high pressures; (c) determining the electronic structure and explaining the special mechanical and physical properties of this compound, using theoretical DFT full potential linearized augmented plane wave (LAPW) calculations.



Figure 1: The hafnium-iridium phase diagram as shown by Robertson [1]. The Ni_3Al with the fcc structure and the NiAl with the bcc structure are shown in the top left and right, respectively.

2. Experimental Details

2.1 Samples preparation

Samples with Ni₃Al and NiAl with stoichiometric composition were prepared by arcmelting under argon atmosphere, from high purity Ni 99.5% and Al 99.95% lumps. Annealing of the sample took place in an evacuated quartz tube at 850° C for 4 days. The sample dimensions for high pressure measurements were about 50µm in height and 100µm in diameter in the diamond-anvil cell with 500µm culets.

2.2 Samples characterization

High pressure application

The pressure (up to 17.9 and 27.7 GPa) was applied via a diamond anvil cell and the experiments were conducted using a polychromatic X-ray beam. A Merrill-Bassett type diamond anvil cell (DAC) and a "Tel-Aviv"-type DAC [2] were used. The pressure was measured utilizing the fluorescence of the Ruby technique [3].

Si oil was used as a pressure medium in the $250\mu m$ cavity diameter stainless steel gasket. The pressure distribution inside the sampling volume was checked at different regions of the sample chamber and was determined to vary by less than 5%. Typical data collection time was around 10 minutes.

Microstructure

The microstructures were examined by scanning electron microscopy (SEM) and the phases analyzed by energy dispersive spectroscopy (EDS) to determine their chemical compositions.

X-ray

X-ray diffraction pattern of the Ni₃Al and NiAl samples taken at ambient pressure was taken to ensure the right composition and structure. The measurement was carried out using Cu-K_{α 1} radiation with a Ni filter and SiO₂ monochromator, in the angle range of 2 Θ =20-120°, step size of 0.02° and measurement duration of 6 sec for a step.

The high-pressure energy dispersive X-ray diffraction studies at the X17-C beamline of the National Synchrotron Light Source (NSLS) were performed [4]. The energy dispersive data (NSLS) was collected with a Ge detector at a fixed Bragg angle $(2\theta=12^{\circ})$. The high-pressure X-ray powder diffraction measurements were taken at discrete pressure steps in the range of 0 -27.7 GPa. The data was collected by the EDS technique, using the white beam of the superconducting wiggler at the X17-C, NSLS. Typical data collection time was about 10 minutes.

In the lower range of the High-Pressure range, Angle dispersive measurements were carried out in the transmission configuration with the Image plate technique.

In all cases Rietveld analysis of the data [5] was performed using a commercial software package [6] in order to confirm the unit cell parameters and crystallographic structure.

Mechanical properties

The Micro hardness microscope with a diamond-pyramid, loaded at 1N (~100 gr_f) for 15 sec, yielded an indentation proportional to the sample hardness. Vickers micro hardness tests of the Ni₃Al and NiAl phases were carried out on both as cast and annealed samples. The calibration sample was stainless steel standard block of for the high range.

The elastic moduli measurements that were carried out with the sound-velocity technique are not fully reliable since the samples had a lot of cracks and voids [7].

3. Results

The optical micrograph depicted in figure 2 indicates that no extra phase exists in the bulk sample. The SEM and optical pictures of the Ni₃Al and NiAl sample indicate a single phase. EDS analysis revealed no impurities, as can be seen in the graph depicted in figure 3. The EDS calculations were done with the energy Ni and Al lines. The energy spectrum was taken in the range of 0-20KeV and the ZAF [8] calculation yields the atomic ratio of 74.76% of Ni and 25.24% of Al, as expected 3:1 and 47.00% and 53.00% as expected 1:1, for Ni₃Al and NiAl, respectively. This measurement confirms that there are no losses of any of the constituent elements.





<u>50 µm</u>

Figure 2: The morphology of the Ni₃Al (left) and NiAl (right) annealed samples, no evidence of a second phase exists.



Figure 3: EDS analysis indicates the stoichiometric ratio and the purity of the samples NiAl and Ni₃Al.

X-Ray mapping indicates and confirms the homogeneity of the sample; it is a 2D map of the Al and Ni elements concentration.

Extra oxidization on the surface sample was removed by polishing with a $1\mu m$ abrasive before loading to the high-pressure cell.

Figure 4 is an X-ray diffraction spectrum of Ni₃Al and NiAl at ambient conditions. Rietveld analysis of the data confirms an isotropic single Pm3m (221) cubic structure AuCu₃ type and single Pm3m (221) cubic structure CsCl type with the unit cell parameters of a=3.572(5) Å, and a=2.887(5) Å for the Ni₃Al and NiAl, respectively. Those parameters are in the error region of the values that were reported by Wilde [9] and Baker [10]. This pattern confirms that neither Ni-Al nor Ni or Al traces exist in the annealed sample.



<u>Figure 4:</u> X-ray powder diffraction pattern of the treated Ni₃Al and NiAl samples, taken with Cu-K_{α 1} radiation at ambient pressure.

The high-pressure X-ray powder diffraction data was converted to angle dispersive data, and then Rietveld analyses were preformed.

$$E * d = \frac{6.1993}{Sin\Theta} = K$$
, since $\lambda = \frac{hc}{Ve} = \frac{12,400}{V}$ (1)

$$2\varphi = 2 * Sin^{-1} \left[\frac{E(KeV) * 1.54056 \text{\AA}}{2 * \text{E} * d} \right]$$
(2)

Where Θ is the EDS detector angle, during the measurement, and 2φ is the calculated peak angle corresponding to $\lambda=1.54056\text{\AA}$ (Cu K α radiation).

The X-ray powder diffraction pattern of the treated Ni_3Al and NiAl samples as a function of pressure are depicted in figures 5 and 6. The graphs are shown as a function of the d- spacing and were fitted with Rietveld analysis. An example of this kind of fitting is shown in figure 7, for the NiAl sample at 9.5 GPa.



Figure 5: X-ray EDS powder diffraction of Ni₃Al as a function of pressure. Typical data collection time was around 10 minutes.



<u>Figure 6:</u> X-ray EDS powder diffraction of NiAl as a function of pressure. Typical data collection time was around 10 minutes.

All of the refined results indicate a single cubic Ni_3Al phase which crystallizes in the AuCu₃ type or single cubic NiAl phase which crystallizes in the CsCl type, respectively, figure 1. No x-ray fluorescence in addition to the crystalline lines spectra at the various pressures is indicated, since those lines are in a very low energy state. Each spectrum (representing a distinct pressure) was elevated just to show the tendency. The Miller indexes of the various peaks and the fluorescence lines are indicated at the top of the figure. The spectra structure crystal lines are pressure dependent as the crystal shrinks, while the X-ray fluorescence lines are fixed in energy and can be used for the internal emerge calibrator (not in the 2 Θ presented range).

As pressure increases the cell parameter, a, shrinks monotonically with no phase change.



<u>Figure 7:</u> X-ray powder diffraction pattern of the NiAl sample at 9.5 GPa. Rietveld analysis was preformed. The line is the best fit for the data in circles, and the difference between, is depicted at the bottom of the graph. (This is EDS data which was converted to angle dispersive data).

The relationship between pressure and volume change for both materials was determined by the Vinet equation of state (EOS) [11]:

$$P(V) = 3B_0 \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} \left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right) \exp^{\left(\frac{3}{2}(B_0^{'}-1)\left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right)\right)}$$
(3)

1))

Where B_0 is the isothermal bulk modulus at room temperature and ambient pressure, and B_0' is the partial derivative of the isothermal bulk modulus against pressure under the same conditions. This constitutive relationship was shown to be universally valid for all solids

under a wide range of pressure values [11]. Any attempts to fit the data to other EOS formalism, like Holzapfel [12] or Birch [13] gave the same results. No hysteresis was observed for the volume data while increasing or decreasing pressure. From the results of the fit, a volume contraction of $V/V_0=0.87$ at 27.6 GPa, and a bulk modulus value of $B_0=165\pm5$ GPa was derived for a fixed $B_0'=4$. It is clear from the comparison between the equation-of-state of NiAl and the equation-of-state Ni₃Al that the first composite is a bit harder then the other. It looks like we didn't have enough data points in the low range to be able to leave B_0' as a free parameter.



<u>Figure 8.</u> The volume-pressure curve derived from the X-ray high-pressure diffraction Rietveld refinement for the Ni₃Al sample with the modified Holzapfel Equation fit to the experimental data [12].



<u>Figure 9.</u> The volume-pressure curve derived from the X-ray high-pressure diffraction Rietveld refinement for the Ni_3Al sample with the modified Holzapfel Equation fit to the experimental data [12].

4. Calculation

The density of state (DOS) of NiAl and Ni₃Al was calculated for $0.9 \le V/V_0 \le 1.05$ using the full potential linearized plane wave (LAPW) method, as embodied in the WIEN97 code [14]. The unit cell in these calculations is divided into two parts, the atomic spheres and the interstitial region. The wave functions inside the atomic spheres are described by atomic like functions, while in the interstitial region plane waves are used [15]. Exchange and correlation effects are treated within the density functional theory, using the generalized gradient approximation (GGA) [16], where not only the local density, but also its gradient determines the magnitude of the effect. The value of V_{zz} in these calculations is given by an integral of the charge density $\rho(r)$ over the unit cell,

$$V_{ZZ} = \int \rho(r) \frac{2P_2(\cos\theta)}{r^3} dr, \qquad (4)$$

where P_2 is the second-order Legendre polynomial. In most cases, the charge asymmetry inside the atomic sphere, where the V_{zz} value is being calculated, determines more than 90% of the V_{zz} value. Inside this sphere, the contribution to V_{zz} can be further divided into s-d, p-p and d-d components, so that the physical origin of the efg can be analyzed [16]. The aluminum atom in both compounds is located at the (1a) 0 0 0 site, while the nickel atom is located at the (1b) $\frac{1}{2}$ $\frac{1}{2}$ and (3c) 0 $\frac{1}{2}$ $\frac{1}{2}$ sites, for NiAl and Ni₃Al respectively. The 1a and 1b sites are symmetric, resulting in a zero V_{zz} value, while the (3c) site is symmetric only in the xy plain, resulting in a nonzero V_{zz} value which is depicted in figure 10 for $0.9 \le V/V_0 \le 1.05$.



The total density of states (DOS) in NiAl and Ni₃Al is plotted in figure 11 as a function of energy for $0.9 \le V/V_0 \le 1.05$. The main feature of the DOS is determined by the Ni 3d-electrons distribution, starting from -2.5 and -3.5 eV up to E_{Fermi} , with a DOS value of 0.5 and 6 states per eV at E_{Fermi} , for NiAl and Ni₃Al, respectively. In both compounds, as V/V_0

decreases from 1.05 to 0.9, the DOS is shifted down in energy by about 1 eV.



Figure 11: Total DOS of: (a) NiAl and (b) Ni₃Al, calculated for V/V₀ values of 0.9, 0.95, 1 and 1.05.

Based on the total electronic DOS at the Fermi level calculated for 0 K $(N(E_{Fermi}^0))$, the band contribution (γ_{band}) to the value of the electronic specific heat coefficient (γ) can be evaluated using the following equation,

$$\gamma_{band} = \frac{\pi^2 k_B^2}{3} N(E_{Fermi}^0) \tag{5}$$

where k_B is the Boltzmann constant. This equation serves as a link between band structure calculations and electronic specific heat measurements [17].

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