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Theoretical and Experimental Studies on the C15 Intermetallic Compound NbCr₂

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ABSTRACT

The electronic structure and total energy of the C15 NbCr₂ have been calculated using the linear muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA). The total energy vs. volume curve, band structure, density of states and Fermi surface were obtained. The calculated results were used to examine several features of the C15 phase, including the elastic properties, phase formation and stability, and solubility of the C15 phase. The theoretical results are compared to experimental studies on the C15 NbCr₂ phase. For example, the elastic moduli, phase stability, and homogeneity range have been characterized with a variety of experimental techniques. Comparison of the experimental and theoretical results will be discussed.

INTRODUCTION

Most investigations on intermetallic compounds as potential high temperature structural materials focus on simple and ordered forms of fcc, bcc or hcp. However, most intermetallics have more complex structures and Laves phases constitute the single largest group. Some of AB₂ Laves phase compounds exhibit high melting temperatures, high strength and excellent oxidation resistance (1-3). In particular, experimental investigations on NbCr₂-based alloys demonstrate attractive features and properties for high temperature applications (4-5). In order to optimize the materials properties, the goal is to understand these experimental results and obtain additional information which is difficult to access by experiments. The achievement of this goal depends strongly on a thorough understanding of the electronic and mechanical properties of the material, and this can be accomplished by a combination of first-principle calculations and comprehensive experimental work (6). In this paper, first-principle calculations on the total energy and electronic structure of C15 NbCr₂ are compared to experimental results.

CALCULATION METHOD AND EXPERIMENTAL PROCEDURES

In the first-principle calculation, the total energy and the electronic structure of the C15 NbCr₂ were calculated using an all electron, self-consistent, linear muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA). The basis set included s, p and d orbitals for each site. The self-consistent iterations used 14 points in reciprocal **k** space along Γ -X direction in the irreducible Brillouin zone (IBZ). The total energy and the electronic band structure were determined at 372 independent **k** points within the IBZ. The valence states were treated in a semi-relativistic scheme (7), and the spin-orbit coupling term was neglected for the

early transition metal elements (Group IVA-VA). The core states were treated fully relativistically. The exchange and correlation potential used in the calculation was the von Barth-Hedin local density formalism (8).

In the experiments, alloy preparation consisted of arc-melting Nb(99.8%) and Cr (99.99%) approximately 15 times in an evacuated (10^{-3} Pa) and purged Ar environment. The ingots were heat-treated in an evacuated and purged high purity Ar environment at 1400 °C for 100 hrs. and cooled at 1 °C/min. After arc-melting and heat-treatment, the ingots contained 20 ppm O₂ and 40 ppm N₂ as determined by inert gas fusion analysis. For quenching studies, the samples were equilibrated at a specified temperature in a vertical vacuum furnace (under identical conditions to the heat-treatment) and dropped into a brine solution. After processing, alloy compositions were determined with elemental-standard-based energy-dispersive spectroscopy (EDS). X-ray diffraction (XRD) with Cu K α radiation was used to measure the lattice parameter. The room-temperature isotropic elastic moduli and the Poisson's ratio of C15 NbCr₂ were measured by resonant ultrasound spectroscopy (RUS) technique(9).

RESULTS AND DISCUSSION

The total energy vs. volume curve for C15 NbCr₂ is shown in Fig. 1. The theoretical equilibrium lattice constant corresponding to the total energy minimum is 0.7125 nm. The bulk modulus of C15 NbCr₂ obtained from Fig. 1 is 250 GPa. Fig. 2 shows the detailed features of the band structure near the Fermi level and the X-point of the IBZ. There is a double degeneracy of electron energy levels with a linear dispersion relationship in the vicinity of the X-point, which is related to the special symmetry (Fd3m) of the C15 structure (9). However, we can see from Fig. 4 that the Fermi surface does not pass through the X-point of IBZ exactly, but passes near the X-point so that there is a very large energy gap, $\Delta\varepsilon=96$ mRy, between the double degeneracy point and the Fermi level. This means that the electronic contribution to the shear modulus, c_{44}^e , of C15 NbCr₂ should be normal, i.e., c_{44}^e decrease with increasing temperature (9-10), not as other C15 Laves phases, e.g. HfV₂ and ZrV₂. Therefore, it can be concluded that the temperature dependence of the shear modulus of C15 NbCr₂ is normal, i.e., the shear modulus decreases with increasing temperature.

Fig. 1 E-V curve for C15 NbCr₂.

Fig. 2 The detailed band structure of C15 NbCr₂ near the Fermi level and the X-point of IBZ.

The total density of state and d-projected density of states on both Nb and Cr sites are shown in Fig. 3. It can be found that the density of states at the Fermi level, $N(E_f)$ is low, resulting in a weak electron-phonon coupling in this system. This also indicates that the Poisson's ratio of this compound is not very high (11).

Fig. 3 (a) Total density of states, (b) d-projected density of states on Nb sites, and (c) d-projected density of states on Cr sites.

A $\langle 001 \rangle$ section of the Fermi surface of C15 NbCr₂ is shown in Fig. 4. It can be seen from Fig. 4 that there is not substantial Fermi surface nesting in this system. Due to the lack of the combination of a large $N(E_f)$ and the Fermi surface nesting, there is no electron-phonon interaction-induced structural instability in C15 NbCr₂. In addition, because of the normal elastic properties, there is no structural instability in C15 NbCr₂ induced by shear modulus softening either. Therefore, it could be concluded that C15 NbCr₂ is structurally stable, unless C15 $\rightarrow$ C14 transformation at a high temperature due to thermal activation.

Fig. 4 Fermi surface of C15 NbCr₂.

The LMTO.ASA calculations also indicate that there is no substantial charge transfer in the formation of C15 NbCr₂. This may results in a relatively larger solubility in C15 NbCr₂ than other C15 line compounds, in which there are large Madelung potential energies due to a large

charge transfer. This also indicates that the geometry factor plays an important role in the solubility and defect mechanism.

The Nb-Cr phase diagram (Fig. 5) indicates that the NbCr₂ intermetallic phase melts congruently at ~1730°C. Upon solidification, the C14 Laves phase forms from the melt, and at temperature below ~1585°C, the C15 Laves phase is the stable phase. An evaluation of the arc-cast NbCr₂ solidification microstructure supports this phase diagram. The arc-cast microstructure indicates faulted equiaxed grains in the stoicheometric alloy (12). The faulted microstructure results from the C14 to C15 transformation process.

Fig. 5 The most recent assesment of the Nb-Cr phase diagram.

X-ray diffraction of the stoicheometric composition illustrates both the C14 and C15 phase in the arc-cast structure (Fig. 6). In addition, indication of a C36 phase is also present. The amount of the C14 and C36 phase is dependent upon the location of XRD sample with respect to the arc-cast alloy. For example, in the lower section of the ingot, more of the hexagonal phases are present, probably due to the higher cooling rates in this portion of the ingot. After heat treatment, (1400°C, 100hrs.), only the C15 phase is detectable. Thermal analysis of arc-cast NbCr₂ has indicated that the hexagonal phases are metastable phases that are retained with the cooling rates associated with arc-casting, and the C36 phase may be an intermetallic phase in the C14 → C15 transformation. The alloy with composition of 67.1 at.% Cr was used to examine the C15 lattice parameter through regression techniques. The lattice parameters for the arc-cast C15 alloy is $a=0.6995$ nm. The heat treated C15 alloy had $a=0.6991$ nm.

Fig. 6 XRD traces of NbCr₂: (a) arc-cast (middle of ingot), (b) arc-cast (top corner of ingot) and (c) heat treated at 1400 °C for 100 hrs and solw cooled at 1 °C/min.

The Nb-Cr phase diagram also illustrates a relatively wide homogeneity range for the NbCr₂ phase at higher temperatures. The maximum solubility range has been defined to be 61.8-69.2 at.%Cr for the Laves phase field. Although over 360 binary Laves phases have been determined, less than 25% have a defined range of homogeneity, with the majority of Laves phases existing as line compounds. The NbCr₂ phase is one of the few phases exhibiting off-stoichiometric solubility. A simple explanation for the observed solubility in the NbCr₂ phase can be determined through geometric considerations of atom sizes in the Laves phase. For example, Laves phases exist between the elemental metallic diameter ratios (D_A/D_B) 1.05 to 1.68, with the ideal ratio being ~1.225 (13). The C15 Laves phases exhibiting a defined homogeneity range generally exist between D_A/D_B ratios of 1.1 to 1.35. This diameter ratio range corresponds to a contraction limit between the size of the elemental metallic atoms and the size of atoms within the Laves phase lattice (d_A and d_B for the A and B atoms, respectively). The percent contraction of the A atoms and B atoms forming the Laves phase can be described as $S_A = 100(D_A - d_A)/D_A$ and $S_B = 100(D_B - d_B)/D_B$, respectively. By examining all known binary Laves phases, the phases can exhibit solubility when $S_A + 2S_B$ is between 0% and 15%. For NbCr₂, $S_A + 2S_B$ is equal to ~4%.

The room-temperature bulk modulus measured from RUS is 229.4 GPa, which is 8% less than the calculated value by LMTO.ASA. This error is reasonable because LMTO.ASA calculates the zero-temperature properties with the local-density-approximation and the elastic moduli of C15 NbCr₂ decrease with increasing temperature, as mentioned above. The room-temperature Young's modulus measured from RUS is 214.1 GPa, which is close to the previous published values measured by micro-indentation mechanical properties probe (14-15). The room-temperature shear modulus is 79.6 GPa. The room-temperature Poisson's ratio is 0.34, which is normal but not very high, as predicted by LMTO.ASA calculations.

CONCLUSIONS

- (1) C15 NbCr₂ phase has a lattice parameter 0.6991 nm by XRD and 0.7125 nm by LMTO.ASA. They are in an excellent agreement.
- (2) There is no phase softening-induced structure instability in NbCr₂ due to the lack of a large N(E_f) and the Fermi surface nesting. Therefore, the C15 structure of NbCr₂ is structurally stable, unless C15 → C14 transformation at a high temperature due to thermal activation.
- (3) The relatively large solubility of C15 NbCr₂ is found and it is partially due to the very small Madelung potential energy, resulting from a very small charge transfer in the formation of the compound.
- (4) For C15 NbCr₂, the room-temperature bulk, Young's and shear moduli and the Poisson's ratio are B=229.4 GPa, Y=214.1 GPa, G=79.6 GPa and ν=0.34, respectively. The LMTO.ASA yields B=250 GPa. The first-principle calculation results also indicates that the temperature dependence of elastic moduli of C15 NbCr₂ is normal, i.e., they decrease with increasing temperature.

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