Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 56 (2008) 4984–4992
Acta MATERIALIA
www.elsevier.com/locate/actamat

First-principles density functional theory study of phase transformations in $NbCr_2$ and $TaCr_2$

Olena Vedmedenko [a], Frohmut Rösch [a], Christian Elsässer [b,*]

[a] Institute for Theoretical and Applied Physics, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany
[b] Fraunhofer Institute for Mechanics of Materials IWM, Wöhlerstr. 11, 79108 Freiburg, Germany

Received 18 April 2008; received in revised form 9 June 2008; accepted 9 June 2008
Available online 12 July 2008

Abstract

Hexagonal to cubic phase transformations in the intermetallic Laves-phase compounds $NbCr_2$ and $TaCr_2$ have been studied systematically using the synchroshear deformation mechanism and first-principles density functional theory (DFT). The DFT results provide a quantitative description of the activation energy profiles during the deformation process. By means of these profiles we discuss several transformation possibilities and propose explanations for recent experimental data. In particular it is shown that the synchroshear deformation mechanism should prevail in the two Laves phases studied. Furthermore, the activation energy barriers for $TaCr_2$ are about 17% larger than those for $NbCr_2$. We discuss how this may lead to the experimentally observed, significantly slower transformation kinetics of $TaCr_2$, compared to $NbCr_2$. Both the observation of fine-scale twins and the origin for the twin formation can also be understood from the activation energy profiles.

Keywords: Intermetallic Laves phases; Interfaces (twin boundaries, stacking faults); Mechanical properties (slip, synchroshear); Phase transformations; Density functional theory (DFT)

1. Introduction

$NbCr_2$ and $TaCr_2$ are two intermetallic Laves-phase compounds exhibiting a high melting temperature, a low mass density, a high oxidation resistance and strong intrinsic resistance to creep deformation – features that are all useful for high-temperature applications [1]. Despite these attractive properties the Laves phases are not yet widely exploited materials in industrial technology. The main reason for this is their pronounced brittleness at low temperatures. This obstacle has evoked an upsurge of research interest in the deformation properties of the Laves phases.

In a number of studies on this subject the phase transformation from the hexagonal C14 phase at high temperature to the cubic C15 phase at low temperature has been investigated experimentally. The characteristic tendencies are a rapid C14–C15 transformation during cooling of $NbCr_2$ and a sluggish transformation of other Laves phases such as $TaCr_2$, $TiCr_2$ or $HfCr_2$ [2]. In the present study, we compare $NbCr_2$ with $TaCr_2$, the latter as a representative of Laves phases showing this kind of reluctant C14–C15 transformation. The critical transformation temperatures of the two compounds are significantly different ($T_{NbCr_2} = 1600\ K \ll T_{TaCr_2} = 1923\ K$ [2]) in spite of the close similarity of their crystallographic and electronic properties. The reasons for this contradiction have not been identified unambiguously so far.

Another interesting subject broadly discussed in the literature is the observation of a large number of fine-scale twins in as-cast single-phase $NbCr_2$ [3–5]. The high volume fraction of these twins in strained samples could not been explained by a Schmid factor analysis [5]. It has been suggested [3] that the twin phases in as-cast compounds arise from a solidified C14 phase rather than from C15. However, to our knowledge, a systematic theoretical investiga-

---

* Corresponding author. Tel.: +49 761 5142286.
E-mail address: christian.elsaesser@iwm.fraunhofer.de (C. Elsässer).

1359-6454/$34.00 © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2008.06.014

tion of this phenomenon, namely by quantitative first-principles density functional theory (DFT) calculations has not yet been performed.

The C14–C15 transformation is suggested to be carried out by means of a synchroshear deformation mechanism [6]. What appears to be the first direct experimental observation of a synchroshear deformation on the atomic length scale has been published recently [7]. In the present theoretical investigation, we confirm the energetic preference of synchroshear by quantitative DFT results, and then we use this mechanism for step-by-step modeling of deformation processes in the Laves phases.

The aim of the present investigation is a systematic description of the C14–C15 transformation in $NbCr_2$ and $TaCr_2$ from first principles and an explanation of the experimental results referred to above. Towards this end we performed DFT calculations for atomistic supercell models of planar defect configurations along various transformation paths by means of the mixed-basis pseudopotential (MBPP) method [8–12] (cf., e.g., Ref. [13] for DFT calculations and atomistic simulations of deformation paths for structural transformations of the transition metal W, or Ref. [14] for a DFT study of a B3 (zincblende) to B1 (rocksalt) transformation of the binary III–V semiconductor AlN).

The paper is organized as follows. Section 2 gives a concise description of the computational MBPP method. In Section 3, the crystal-structure models of the Laves phases and the atomistic transformation configurations for the deformation mechanisms are described and discussed. In Section 4, we explore the synchroshear transformation between the C14-phase and the C15-phase single crystals of $NbCr_2$ and $TaCr_2$ via two stacking-fault configurations. Alternative synchroshear-transformation options for the two compounds are studied in Section 5.

2. Computational method

The first-principles DFT calculations of total energies and atomic forces in the present study are based on the local-density approximation (LDA) for exchange and correlation [15–18]. The interactions of the valence electrons with the atomic nuclei and the core electrons are described by means of optimally smooth, norm-conserving ionic pseudopotentials. These were constructed according to the recipe of Vanderbilt [19] from all-electron, free-atom valence-electron states for reference configurations of Nb ($[Kr]4d^{3.6}5s^{0.6}5p^{0.8}$), Ta ($[Xe]5d^{3.6}6s^{0.6}6p^{0.8}$) and Cr ($[Ar]3d^{4.6}4s^{0.6}4p^{0.8}$). The valence-electron Bloch states were expanded on a mixed basis of plane waves, limited by a kinetic energy of $E_{pw} = 12$ Rydberg, and atom-centered numerical orbitals with d symmetry (angular momentum $l = 2$) and confined within non-overlapping spheres of radii $r_{lo} = 2.8$ Bohr for Nb and Ta, and 2.2 Bohr for Cr. (The basis-set parameters are given in atomic units: 1 Rydberg = 13.606 eV, 1 Bohr = 0.529 Å.) Brillouin-zone integrations in the calculations of total energies were made by sampling on a $4 \times 4 \times 2$ $\boldsymbol{k}$-point mesh [20] and Gaussian broadening of 0.004 Rydberg [21] for a hexagonal supercell containing 12 formula units of $NbCr_2$ or $TaCr_2$. This supercell allows the description of both C14-phase and C15-phase single crystals, and all synchroshear-transformation configurations between them (cf. Fig. 5 in Section 3). The above values for the plane-wave cut-off energy E_{pw} and the $\boldsymbol{k}$-point sampling mesh were calibrated by extensive convergence tests [22,23] to yield sufficiently accurate numerical total-energy differences for the various synchroshear configurations investigated in this work.

3. Crystal structures and deformation mechanisms

Three single-crystal structures of low energy are known for the Laves phases: C14, C15 and C36 (e.g., Ref. [24]). C14 and C36 have hexagonal symmetries, C15 has cubic symmetry. These structures only differ by the stacking order of atomic quadruple layers. Altogether there are six different quadruple layers which are conveniently called X, X', Y, Y', Z and Z' according to a commonly used notation for Laves phases (e.g., Ref. [2]). A schematic side view of such a quadruple layer (perpendicular to the hexagonal [0 0 0 1] or cubic [1 1 1] stacking direction) is shown in Fig. 1.

Top views (parallel to the stacking direction) of quadruple layers in the supercell used for the DFT calculations are given in Fig. 2. The supercell shape and size is indicated by

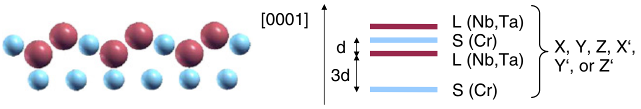

Fig. 1. The side view (perpendicular to the stacking direction) of a quadruple layer. The large (dark red) spheres indicate the larger atoms (Nb or Ta), the small (light blue) spheres the smaller atoms (Cr). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

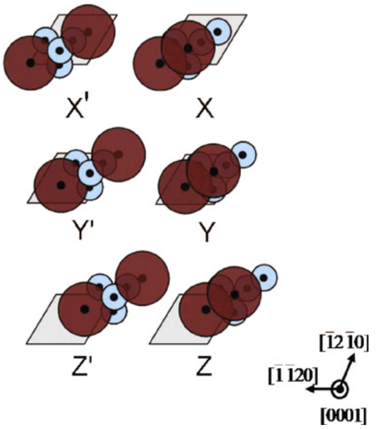

Fig. 2. Top view (along the stacking direction [0 0 0 1]) of the six different quadruple layers. The shaded parallelogram indicates the size and shape of the supercell. The large (dark red) circles indicate the larger atoms (Nb or Ta), the small (light blue) circles the smaller atoms (Cr). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)