Intermetallics 38 (2013) 116–125

Contents lists available at SciVerse ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Ab initio studies of Mo-based alloys: Mechanical, elastic, and vibrational properties

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ARTICLE INFO

Article history:
Received 30 October 2012
Received in revised form
30 January 2013
Accepted 2 March 2013
Available online 28 March 2013

Keywords:
A. Molybdenum silicides
B. Elastic properties
E. Mechanical properties, theory
E. Ab initio calculations

ABSTRACT

Mo-based alloys hold great potential as structural materials for applications at ultra-high temperatures. In order to reliably predict mechanical and thermodynamic properties of Mo-based alloys, the Mo–Si–B model system is studied using first-principles density functional theory methods. Specifically, five intermetallic compounds $MoSi_2$, Mo_5Si_3, Mo_3Si, Mo_5SiB_2 and Mo_2B are chosen, and their equilibrium lattice parameters, elastic properties, phonon spectra, and thermodynamic properties are calculated and compared, most of them for the first time. It is shown that for the calculated properties where the measured data are available, the predicted results are in very good agreement with available experiments, thus validate our computational methodologies. Our comprehensive and systematic calculations reveal many interesting and previously unknown features in the mechanical and vibrational properties of these alloys in relation to their structure and composition. It is shown that boron in the Mo–Si–B system enhances elastic and bulk properties without compromising ductility. $MoSi_2$, which has the largest Si concentration, also has the largest elastic anisotropy compared with the other four crystals.

1. Introduction

Fossil fuels represent a critical component in an overall energy development and utilization strategy with tremendous economic and environmental implications. To reduce the environmental impact from coal-fired power plants, the efficiency of coal gasification processes must be improved. New technologies using hydrogen turbines or oxy-fuel turbines improve the efficiency of coal gasification, but also require that the structural materials of critical components operate at temperatures as high as 1750 °C. Also, the fuel efficiency of jet engine and other industrial gas turbines depends critically on the operating temperature of the airfoil materials. High melting temperature, high tensile strength, sufficient ductility at low temperatures to allow easy processing, and high oxidation and creep resistance are the most crucial properties that structural materials must possess to be used in the hot section of jet engine and industrial gas turbines. Current materials used in these applications are primarily the Ni-based super alloys that have already reached their ultimate performance limit [1,2]. It is unlikely that they will meet the urgent need for applications with increased efficiency while simultaneously addressing environmental concerns. Advanced materials play a critical role in the development of new technologies that will significantly improve the performance of coal-based power plants at elevated temperatures and in a corrosive environment. New materials that are efficient, light weight, oxidation resistant, have high fracture toughness, and provide good creep performance at temperatures above 1350 °C are needed.

The new materials envisioned are likely to be complex both in structure and composition and may contain defects and microstructures. A pure experimental trial and error approach would be impractical and expensive. Accurately and carefully designed computational simulations using *ab initio* methods can provide reliable and predictive results. Developing advanced structural materials that can function at ultrahigh temperatures and in a hostile environment that consists of water vapor, O_2, H_2, CO, CH_4, etc. is not an easy task. An expected life-time of over 20 or 30 years makes the materials development even more challenging. From a design point of view, one has to consider the balance between mechanical properties and oxidation resistance. Mechanical properties include ductility at low temperatures for easy processing, fracture toughness to tolerate cracks and crack propagation, high strength at high temperatures, creep resistance and fatigue

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0966-9795/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.intermet.2013.03.002

tolerance. Mo and Nb based alloys are of great interest because they usually have very a high melting temperature and they satisfy many such requirements for high temperature applications [1–4]. (Mo has a melting point of 2623 °C.) Both Mo and Nb metals are poor in oxidation resistance. However, their alloys with Si and B appear to be more promising [1–3,5,6]. Further improvements in the oxidation resistance of Mo–Si–B systems can be achieved through aluminum pack cementation coating [7] and pre-oxidation at 1150 °C [8]. The Mo-rich portion of the Mo–Si–B ternary system consists of a Mo solid solution (Mo_{ss}) that has a bcc structure, a ternary compound Mo_5SiB_2 (T2 phase), and binary Mo–B and Mo–Si compounds (see Fig. 1). Manipulation of the phase relationship and the microstructure in the Mo-rich Mo–Si–B offers tremendous opportunities for balancing mechanical properties and chemical stability against oxidation. For example, Schneibel et al. [9] shows that the combination of three phases of Mo_{ss}, Mo_3Si, and T_2 offers just such a promising balance. Alloying strategies for extending possible combinations of phases in the Mo–Si–B system have been pursued by various researchers in order to seek improved performance [7,10,11]. These compounds usually have much stronger inter-atomic bonding and provide exceptional oxidation resistance than the Mo metal. In addition, formation of coherent adhesive glassy scale on the metal surface that involves Si and B offers further protection to the base metal from oxidation. Consequently, Mo–Si–B alloys and those with other transition metals have been studied extensively by experimentalists [11–21]. Using a computational approach to accelerate new materials design for high temperatures performance is significant and urgent. The present study is the first step toward fundamental understanding of the mechanical and thermodynamic properties of Mo–Si–B based alloys at the electronic level. Validation of computational methodologies allows us to not only predict the mechanical properties as a function of temperature and pressure, but also to conduct future multi-axial tensile experiments on supercomputers, and to address the issue of how elastic anisotropy contributes to the failure behavior of these materials.

In this paper, we report a comprehensive study of elastic, vibrational and thermodynamic properties of five crystals, $MoSi_2$, Mo_5Si_3 (T1 phase), Mo_3Si, Mo_5SiB_2 (T2 phase), and Mo_2B based on density functional theory (DFT). These crystals are ordered according to the concentration of Si and/or B atoms so as to ascertain if there is any particular trend in physical properties based on Si and B concentration. Of these five crystals, only Mo_3Si has a body centered cubic structure, the rest have body centered tetragonal symmetry. The crystal parameters of the five crystals are listed in Table 1 and illustrated in the ball and stick diagrams in Fig. 2. In the following section, we outline the methods used in the calculations. This is followed by the presentation of calculated results and their discussions. A brief summary and conclusions are presented in the last section. These results provide the necessary insights and background for further in-depth simulations on composite models of varying compositions, and in modeling microstructures and defects.

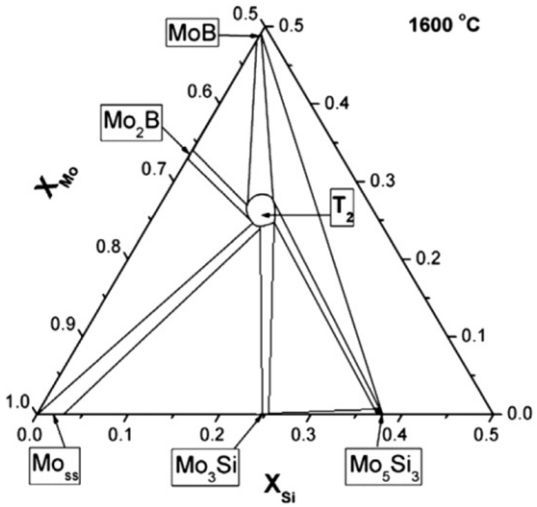

Fig. 1. Phase diagram of the Mo–Si–B ternary system (From reference 18).

2. Computational methods

The density functional theory (DFT) based Vienna *ab initio* simulation package (VASP) [22–24] is the primary tool in our calculations along with other specific packages including the *G*(P,T) package that employs VASP to compute phonon, thermodynamic and mechanical properties. VASP uses plane waves as the basis set and the interactions between electrons and positive ions are described by using pseudo-potentials [25,26] or projector augmented wave (PAW) [27,28] potentials. VASP is efficient and accurate for geometry optimization and force related calculations. For structural relaxation to the minimum total energy while allowing changes in volume, cell shape, and ionic positions, we used an energy cutoff of 700 eV, a highly stringent electronic convergence limit of 10^{-7} eV, and an ionic convergence limit of 10^{-5} eV/Å. As initial atomic positions of these Mo–Si–B systems are fairly accurate, we used quasi-Newton algorithm for ionic relaxation. For elastic tensor calculations, an even higher accuracy is desirable; hence an even smaller electronic convergence of 10^{-9} eV was used. For all calculations, we used the PAW potential with the generalized gradient approximation (GGA-PBE) [29,30] since it is considered to be more accurate than other potentials. Because the alloys in the Mo–Si–B systems are metallic, we used method of Methfessel-Paxton smearing scheme and large k-point meshes of $11 \times 11 \times 5$, $5 \times 5 \times 9$, $11 \times 11 \times 11$, $9 \times 9 \times 9$, and $9 \times 9 \times 9$ for the five crystals $MoSi_2$, Mo_5Si_3, Mo_3Si, Mo_5SiB_2 and Mo_2B respectively which are sufficiently large.

2.1. Elastic properties at zero temperature

The calculation of elastic and mechanical properties of a crystal is based on the strain-stress analysis of its equilibrium structure [31]. In this scheme, a small deformation, usually −1% (compression) and +1% (expansion) is applied to each independent strain element of the fully optimized structure. The atomic positions of the strained structure are optimized using VASP while keeping the volume and shape of the structure fixed. The six components of the stress tensor (σ_i) (i = xx, yy, zz, yz, zx, xy) are calculated for each applied strain (ε_i). From the set of stress vs. strain data, the elastic tensor C_{ij} is evaluated using the usual linear elastic theory (Hook's law):

$$\sigma_{ij} = \sum_{i,j} C_{ij}\varepsilon_j \tag{1}$$

From the calculated C_{ij} (or equivalently, the compliance tensor S_{ij}), the parameters describing the bulk mechanical properties (bulk modulus (K), shear modulus (G), Young's modulus (E), and Poisson's ratio (η)) are evaluated using the Voigt–Reuss–Hill (VRH) approximation [32–34]. The Voigt approximation [32] is based on the uniform strain in the structure giving the upper limit expressed in terms of the elastic coefficients C_{ij}.

$$K_{\text{Voigt}} = 1/9(C_{11} + C_{22} + C_{33}) + 2/9(C_{12} + C_{13} + C_{23})$$