Available online at www.sciencedirect.com

SciVerse ScienceDirect

www.elsevier.com/locate/matchar

Mechanical characterization of a novel nanocrystalline coating: First-principles calculations and nanoindentation

Daohui Lai[a], *Jiang Xu*[a,b,*], *Zong-Han Xie*[b], *Daryoush Habibi*[b], *Paul Munroe*[c]

[a]*Department of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing 210016, PR China*

[b]*School of Engineering, Edith Cowan University, Joondalup, WA6027, Australia*

[c]*School of Materials Science and Engineering, University of New South Wales, NSW 2052, Australia*

ARTICLE DATA

Article history:
Received 14 October 2011
Received in revised form
29 February 2012
Accepted 5 March 2012

Keywords:
Transition metal silicides
First-principles
Nanocrystalline materials
Mechanical Properties

ABSTRACT

A nanostructured $MoSi_2$ coating with the average grain size of 5 nm and a strong (111) preferred orientation, was synthesized potentially for jet engine hot-zone components against volcanic ash damage. The high hardness of the resulting coating was predicted using first-principles calculations and found to agree well with the experimental data determined by nanoindentation. We also found that the softening and subsequent breaking of the Mo—Si bonds were responsible for the failure of this nanostructured coating under tensile loading.

1. Introduction

Ten million travelers were affected by the recent eruption of Eyjafjallajökull volcano in Iceland, causing the economic loss about 2 billion euros [1]. A new study revealed that the particles of volcanic ash that dispersed over Europe remained sharp and abrasive even after a few weeks of abrasion in stirred water suspension [2]. As a result, these particles could crash planes by damaging thermal barrier coatings used to insulate metallic parts of jet engines from high operating temperature. Therefore, great effort is being made to design and test novel coatings that are resistant to volcanic ash damage [3]. Of the potential candidates, molybdenum disilicide ($MoSi_2$) is thought to be particularly attractive, because of its low density, high melting point and strength retention at high temperatures [4–6]. According to the Mo—Si phase diagram, the crystal structure of molybdenum disilicide ($MoSi_2$) is dimorphous: the phase with the hexagonal C40 structure is stable between the melting point (2030 °C) and 1900°C and the other phase, with the body-centered tetragonal $C11_b$ structure, appears below this temperature. Compared with the $C1l_b$ structure, the hexagonal C40-structure has higher crystallographic symmetry and a lower stacking fault free energy, suggesting that C40-structured $MoSi_2$ would be more ductile than the $C11_b$-structured phase [7,8]. First-principles calculations have also revea'led that the weakness of the Si—Mo bonds along the [001] direction and the Si—Si bonds within the (001) plane promotes shear deformation in the hexagonal phase, which in turn enhances ductility [9]. However, an in-depth understanding of mechanical behavior of the C40-structured $MoSi_2$ has been hindered by the difficulty in obtaining pure crystalline samples. This partly stems from the fact that the C40-structured $MoSi_2$ phase is a metastable phase,

* *Corresponding author at:* Nanjing University of Aeronautics and Astronautics, Department of Material Science and Engineering, 29 Yudao Street, Nanjing 210016, PR China. Tel.: +86 2552112626.
E-mail address: xujiang73@nuaa.edu.cn (J. Xu).

1044-5803/$ – see front matter © 2012 Published by Elsevier Inc.
doi:10.1016/j.matchar.2012.03.003

with respect to $C11_b$-structured $MoSi_2$ at temperatures below the congruent melting point [10]. Consequently, the $MoSi_2$ with hexagonal C40-type structure has been synthesized under non-equilibrium conditions through processes such as ball-milling or thin film deposition [11–13]. In the present study, the C40-structured $MoSi_2$ coating was synthesized on a Ti–6Al–4V alloy substrate by a double cathode glow discharge technique and the resulting coating was found to have an average grain size of 5 nm and a strong (111) preferred orientation. Nanoindentation was then used to measure its hardness, which was found to be in good agreement with the theoretical prediction built upon first-principles calculations and size-effect calculations.

2. Experimental

The hexagonal C40-structured $MoSi_2$ nanocrystalline coating was engineered onto Ti–6A1–4V alloy substrates by a double cathode glow discharge technique using a $Mo_{25}Si_{75}$ target. Inside the chamber, one cathode is used as the target, and the other is as the substrate, as described in our previous papers [14,15]. The glow discharge sputtering conditions are given as follows: base pressure, 4×10^{-4} Pa; target electrode bias voltage, −900 V; substrate bias voltage, −300 V; substrate temperature, 800 °C; working pressure, 35 Pa; parallel distance between the source electrode and the substrate, 15 mm and treatment time of 3 hours. The sputtering targets are fabricated from ball-milled Mo (99.99% purity) and Si powders (99.99% purity) by employing cold compacting technology under a pressure of 600 MPa. Substrate discs, 40 mm in diameter and 3 mm in thickness, were cut from Ti–6A1–4V alloy rod (0.003%N, 0.010% C and 0.074% O). Prior to coating deposition, the substrate was ground using SiC grinding papers of 400, 800, 1200 grades and finally, polished using diamond paste.

Phase composition of the as-deposited coating was characterized with X-ray diffractometry (XRD, D8ADVANCE) operated at 35 kV and 40 mA. X-ray data were collected using a 0.1° step scan with a count time of 1 s. The microstructure of the as-deposited coating was examined using scanning electron microscopy (SEM, Quanta200, FEI Company) with an X-ray energy dispersive spectroscopy (EDS, EDAX Inc.) analyzer attachment and field emission transmission electron microscopy (FEGTEM, Philips CM 200, Eindhoven, Netherlands). Plan-view samples for TEM observation were prepared using single-jet electrochemical polishing technique from the untreated side of the substrate. The hardness of the as-deposited coating was measured by the nanoindentation tester (NHT) equipped with a Berkovich tip. This system, developed by CSEM Instruments, comprises two distinct components: a measuring head for performing nanoindentations and an optical microscope for selecting a specific sample site prior to indentation, and for checking the location of the imprint after indentation. Fused silica was used as a standard sample for the initial tip calibration. The indentation was worked by driving the indenter at a constant loading rate of 40 mN/min into the materials with the maximum applied load of 20 mN. The standard analysis procedure proposed by Oliver and Pharr [16] was used to determine the hardness of the specimens from the unloading curve. After nanoindentation, the topography of the indents was immediately examined by the attached atomic force microscope (AFM).

3. Results and Discussion

Fig. 1(a) shows typical XRD patterns obtained from the as-deposited coating. The diffractions peaks occur at 2θ angles of 41.36° and 60.31°, corresponding to reflections from the (111) and (104) planes of the hexagonal C40-structured $MoSi_2$ (the space groups of $P6_222$). The intensity of the (111) peak is significantly higher than that of standard hexagonal C40-structured $MoSi_2$ given in the JCPDS card file (No. 81-0167), indicating that the coating has a strong (111) preferred orientation. The cross-sectional SEM image (Fig. 1(b)) reveals that the as-deposited coating exhibits a compact columnar microstructure, with thickness of about 15 μm, and is well bonded to the substrate without any visible defects. Energy dispersive X-ray spectrometry (EDS), performed in the SEM, indicates that across the thickness of the as-deposited coating the Si/Mo atomic ratio is about 2, indicating that the as-deposited coating is composed of a single $MoSi_2$ phase. A plan-view TEM bright-field image of the as-deposited coating is shown in Fig. 1(c) with corresponding selected area electron diffraction (SAED) pattern. The microstructure of the as-deposited coating consists of nearly rounded grains with an average grain size ~5 nm. The high intensity of the (111) diffraction ring provides further evidence that the as-deposited coating has a strong (111) oriented texture (the inset in Fig. 1(c)). Fig. 1(d) shows a high-resolution electron microscopy (HRTEM) image of the as-deposited coating. The measured fringe spacings of the crystallites marked by circles are all equal to 2.18 Å, which corresponds to the inter-planar distance for the (111) lattice plane of hexagonal C40-structured $MoSi_2$.

A typical nanoindentation load–displacement curve and AFM morphologies of nanoindentation imprints for the as-deposited coating are shown in Fig. 2(a) and (b). The average nanoindentation hardness of the as-deposited coating was measured to be 23 GPa, which is 2.26 times greater than the theoretical hardness of C40-structured $MoSi_2$ (10.15 GPa) derived from the first-principles calculations by Qiao et al. [9]. In general, values for the theoretical hardness are calculated from a perfect crystal with infinite homogeneous lattice and this represents an upper limit to the strength of a solid material. Therefore, an intriguing question arises, i.e., why here the measured hardness of C40-structured $MoSi_2$ nanocrystalline coating is appreciably higher than the theoretical one? To address this question, we present a new approach to predicting the hardness of C40-structured $MoSi_2$ nanocrystalline coating by coupling anisotropy in strengths of atomic bonds with the crystallite size effect. The procedure of the hardness calculations includes three key steps: a) determination of the yield strength of C40-structured $MoSi_2$ from the first-principles strain–stress analysis, b) linkage of the yield strength with the hardness of bulk materials, and c) calculation of the hardness of C40-structured $MoSi_2$ nanocrystalline by factoring in size-induced effects.

The first-principles calculations were performed within the generalized-gradient approximation (GGA) of the Perdew–Berke–Ernzerhof (PBE) [17] for the exchange-correlation functional as implemented in the CASTEP code [18]. Ultrasoft pseudo-potentials represented in reciprocal space were used to describe electron–ion interactions. According to our convergence tests, a plane-wave cutoff energy of 350 eV and a $7\times7\times4$ k-points