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Mechanical and electrochemical properties of Al alloyed $D8_m$-Ta_5Si_3 nanocrystalline coatings

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ABSTRACT

In this work, the structural stability, mechanical properties and electronic structure of β-Ta_5Si_3 with different Al additions were first predicted by first-principles density functional calculations. The binary and ternary β-Ta_5Si_3 are thermodynamically and mechanically stable, but their thermodynamic stability slightly decreases with Al additions. The elastic constants, bulk modulus (B), shear modulus (G) and Young's modulus (E) of Al-alloyed β-Ta_5Si_3 were calculated. According to the criteria involving the bulk/shear modulus (B/G ratio) and Poisson's ratio, the $D8_m$-structured ternary Ta_5Si_3, where two Si^{4a} atoms are replaced by two Al atoms, shows improved ductility. Based on the theoretical analysis, the β-$Ta_5(Si_{0.83}Al_{0.17})_3$ nanocrystalline coating was deposited onto polished Ti-6Al-4V alloy substrates by double cathode glow discharge plasma method. The phase constitution, microstructure and composition of the coating were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) including energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM). The as-deposited coating was composed of nearly rounded $D8_m$-β-Ta_5Si_3 grains with an average size of ~4 nm and exhibited strong (002) and (400) preferred orientation. After Al alloying, the hardness and the compressive residual stress of the β-Ta_5Si_3 decreased, and the contact damage resistance and adhesion strength increased. The electrochemical corrosion properties of the β-$Ta_5(Si_{0.83}Al_{0.17})_3$ nanocrystalline coating were compared to the binary β-Ta_5Si_3 coating and Ti-6Al-4V in 3.5 wt% NaCl solution by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. It was shown that the corrosion resistance of the β-Ta_5Si_3 was improved through the substitution of Al for Si.

1. Introduction

Refractory metal silicides (RMS) are regarded as promising candidates as next generation ultrahigh-temperature structural materials. They have attracted significant attention for ultrahigh-temperature structural applications, due to a unique combination of physical and mechanical properties; e.g., excellent oxidation resistance, outstanding thermal stability, high melting points, attractive creep resistance and notable mechanical strength at elevated temperatures [1,2]. Among RMS, Mo and Nb-based silicides have been thoroughly investigated both experimentally and theoretically [3,4]. However, few studies have focused on the Ta–Si system, which is considered to be the most refractory metal silicide.

Similar to the binary phase diagram of the Nb-Si system, there are four stable phases, i.e. $TaSi_2$, Ta_5Si_3, Ta_2Si, and Ta_3Si, presented in the binary Ta-Si phase diagram, with melting points in the range of 2200–2550 °C. Compared with the others transition metal silicides with 5:3 stoichiometry, such as Nb_5Si_3 (2520 °C) [5] and Ti_5Si_3 (2130 °C) [6], Ta_5Si_3 has the highest melting point of 2550 °C and, hence, shows greater potential for applications in harsh environments. Ta_5Si_3 phase is formed by congruent transformations at melting point and exists three prototype structures: a low temperature hexagonal Cr_5B_3 prototype ($D8_1$-structured α-Ta_5Si_3), a high temperature tetragonal W_5Si_3 prototype ($D8_m$-structured β-

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Ta_5Si_3) and a metastable Mn_5Si_3 prototype ($D8_8$-structured Ta_5Si_3) [7].

Tao et al. [8] compared the elastic properties of $D8_1$-structured α-Ta_5Si_3 and $D8_m$-structured β-Ta_5Si_3 using first-principles calculations. According to the Pugh criterion, the brittleness of $D8_1$-structured α-Ta_5Si_3 is higher than that of $D8_m$-structured Ta_5Si_3, which is of utmost concern for practical structural applications. Because such compounds have both high atomic mass and are difficult to machine by traditional processing methods, tantalum silicides are better suited to serve as anti-adhesive wear/anti-corrosion coatings. Generally speaking, the 5:3 type metal silicides with a tetragonal structure have strong anisotropy in the thermal expansion coefficients(CTE), with the ratio of CTE values along the *c* to *a* axes (α_c/α_a) ranging from 1.2 to 2.9 [9]. This is primarily due to the difference in the interatomic bonding strength along different crystallographic axes [10]. That is, for $D8_m$-structured β-Ta_5Si_3, the -Si-Ta-Si- chains along the [100] and [010] directions exhibit strong bonding among the atoms on the (001) plane accompanied by a large anharmonicity along the [001] direction, rendering the thermal expansion along the *a* axis difficult to occur. This large thermal expansion anisotropy leads to residual internal stresses at grain boundaries during high-temperature processing, giving rise to microcracking or grain boundary fracture [11]. In addition, due to its non-cubic structure with low symmetry and highly covalent bonding, monolithic 5:3 type metal silicides exhibit inadequate room-temperature fracture toughness, which is one of the key challenges in their engineering applications.

To address these issues, ternary alloying additions by substitutions for metal and Si atoms have been proved to reduce the anisotropy of thermal expansion and enhance the low temperature toughness of 5:3 type metal silicides [12,13]. The positive effects of substitutional alloying stem mainly from two aspects: the increased symmetry of the crystal structure and the change of the interatomic bonds [14]. Amongst various alloying elements, Al is seen as one of the most effective alloying elements to improve the oxidation resistance and the ductility of metal silicides [15]. It is interesting to note that the substitutional alloying of highly ordered metal silicides is totally different from the alloying of an ordinary random alloy by the additional feature that the added alloying elements may occupy one or more substitution positions, determined by the composition, type of metal silicides and alloying species. Understanding the site occupancy of substitutional elements is important, which influences the electronic structure and hence the mechanical properties of the metal silicides. Unfortunately, to date, studies focused on the influences of ternary alloying additions on the electronic structure, the mechanical behavior and corrosion resistance of $D8_m$ structured β-Ta_5Si_3 are very limited.

Compared to the trial-and-error experimental method, first-principles density functional calculation is a time- and labor-saving approach. It gives a valuable insight into the mechanical properties of a material and, in so doing, it offers an attractive alternative to be use a cost-effective precursor to costly experiment [16]. Therefore, application of the first-principle calculations is helpful for our microscopic understanding of how alloying elements affect the brittle or ductile behavior of the metal silicides. In this work, the mechanical properties of β-Ta_5Si_3 with various concentrations of Al were explored by using first-principle calculations through analysis of a variety of mechanical indicators. It provides a direct guideline for the subsequent experiment. Based on the prediction of optimum Al content, the ternary β-$Ta_5(Si_{1-x}Al_x)_3$ coating was prepared onto Ti-6Al-4V substrates using double cathode glow discharge technique. The mechanical properties and corrosion behavior in 3.5 wt % NaCl solution of the ternary β-$Ta_5(Si_{1-x}Al_x)_3$ coating were investigated and compared to the binary β-Ta_5Si_3 coating.

2. Theoretical and experimental methods

2.1. Calculation parameters

All the first-principles calculations in this study were performed using the Cambridge serial total energy package (CASTEP) code, in which a plane-wave pseudopotential method based on density functional theory (DFT) was employed [17,18]. An exchange correlation functional was implemented by a generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE). The interactions between the ionic cores and the electrons were described by ultrasoft pseudo-potentials. The electronic configurations of Ta, Si and Al atoms were $5d^36s^2$, $3s^23p^2$ and $3s^23p^1$, respectively. After a series of convergence tests, a plane-wave cutoff energy was determined to be 330 eV for both the binary and ternary β-Ta_5Si_3 compounds, which were found to be sufficiently precise for the present study. For the sampling of the Brillouin zone, a $3 \times 3 \times 4$ Monkhorst-Pack grid of k-points was selected for integrations in reciprocal space. During the geometry optimization, the convergence tolerances were as follows: the total energy changes less than 5×10^{-6} eV/atom, maximum ionic Hellmann-Feynman force below 0.01 eV/Å, maximum stress lower than 0.02 GPa and maximum ionic displacement within 5×10^{-4} Å.

Based on the stress-strain approach, the elastic stiffness constants C_{ij} of the tetragonal binary and ternary β-Ta_5Si_3 were calculated by applying small strains to the equilibrium lattice [19]. From the calculated C_{ij} values, mechanical parameters, such as bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (υ), can be evaluated using the Voigt-Reuss-Hill (VRH) approximation method [20]. Fig. 1 shows the crystal structure model of the tetragonal β-Ta_5Si_3 with the *I*4/*mcm* symmetry used for these calculations. As depicted in Fig. 1(a), a β-Ta_5Si_3 unit cell

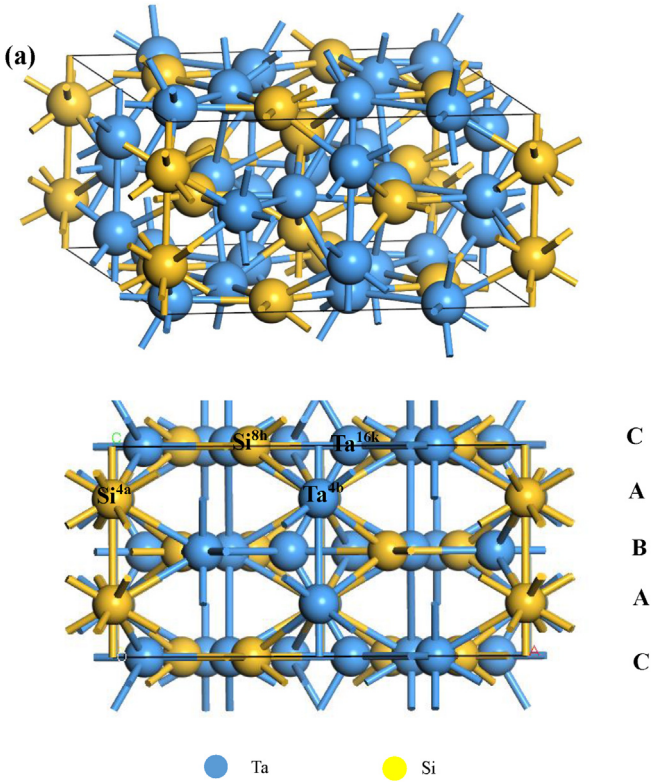

Fig. 1. Crystal structures (a) and atomic arrangement on (010) plane (b) for the D8m-structured β-Ta_5Si_3 crystal structure.