Intermetallics 54 (2014) 232–241

Contents lists available at ScienceDirect

Intermetallics

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

Mechanisms of Cr segregation to $C11_b/C40$ lamellar interface in $(Mo,Nb)Si_2$ duplex silicide: A phase-field study to bridge experimental and first-principles investigations

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ARTICLE INFO

Article history:
Received 12 March 2014
Received in revised form
24 May 2014
Accepted 27 May 2014
Available online 16 July 2014

Keywords:
A. Intermetallics
B. Alloy design
D. Interfaces
E. Phase field modeling
G. Energy systems

ABSTRACT

Cr segregation at lamellar interfaces in the $MoSi_2/NbSi_2$ duplex silicide was examined using a newly developed phase-field model to elucidate the mechanism of interfacial segregation, which is believed to improve the thermal stability of lamellar structures as well as creep resistance. This is because lamellar structures can improve the high-temperature strength, and the stabilization of the lamellar structures improves creep resistance. The model takes into account the segregation energy determined using first-principles calculations to reflect the chemical interaction between the solute atoms and the interface, in addition to the elastic interaction. Cr segregation occurs at the interface when the segregation energy is considered, whereas no segregation occurs in the case where only the elastic interaction is considered. However, the extent of segregation was much smaller than that observed experimentally when the segregation energy was evaluated using first-principles calculations without considering lattice vibrations (i.e., the calculations were performed for 0 K). A simulation that took into consideration the segregation energy with the lattice vibrations at 1673 K resulted in segregation similar to that observed experimentally, where the Cr-added $MoSi_2/NbSi_2$ duplex silicide was equilibrated at 1673 K, namely, the temperature at which the segregation energy was calculated. Thus, it was revealed that the solute-interface chemical interaction and its temperature dependence are responsible for the interfacial segregation of Cr. These results suggest that the segregation energy needs to be taken into account in the search for more effective additive elements for improving the thermal stability of lamellar structures as well as the creep resistance.

1. Introduction

Owing to its high melting temperature, low density, and good thermal-conductivity [1], $MoSi_2$ with a $C11_b$-structure (Fig. 1a) has attracted attention as a refractory material for gas power generation systems, which involve at ultrahigh-temperatures, where Ni-based superalloys cannot withstand. Monolithic $MoSi_2$ exhibits good plastic deformability at low temperatures, owing to the operation of several slip systems. However, its fracture toughness at low temperatures and strength at high temperatures are insufficient [2–5]. There have been many studies aiming to improve the mechanical properties of $MoSi_2$ by forming composites with other materials. For instance, $MoSi_2$–based composites with ceramics such as Al_2O_3 and SiC exhibit improved high-temperature strengths. However, they exhibit poor thermal shock resistance and low-temperature toughness [6,7]. As another approach, reinforcing $MoSi_2$ by combining it with another silicide has been receiving attention [8–10]. Disilicides with $C40$-structure (Fig. 1b) are attractive for reinforcing the $MoSi_2$ matrix, as they exhibit anomalous strengthening and higher strength than does $MoSi_2$ [11–14]. Recently, Nakano et al. [9,10] developed $MoSi_2/NbSi_2$ duplex crystals with fine and well-oriented lamellar microstructures as a new promising candidate material to

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http://dx.doi.org/10.1016/j.intermet.2014.05.019
0966-9795/

overcome the above-mentioned problems. The highly oriented lamellar composed of a $C11_b$-type Mo-rich phase and a $C40$-type Nb-rich phase, could be developed in the alloy, which had a nominal composition of $Mo_{0.85}Nb_{0.15}Si_2$, by unidirectional solidification using the floating-zone-melting method. This involved the growth of the $C40$ phase single crystals and subsequent annealing at the dual-phase temperatures. The obtained duplex crystals with oriented lamella exhibited superior high-temperature mechanical properties [15] and improved low-temperature fracture toughness [16,17]. The lamellar structure was relatively thermally stable [10]. However, the lamellar structure coarsened and collapsed after prolonged annealing. Thus, the thermal stability of the lamellar structure needs to be improved further in order for the composite to be suitable for practical use. It was recently found that additive elements such as Cr and Zr drastically improve the thermal stability of lamellar structures in the $MoSi_2/NbSi_2$ duplex silicide [18,19]. For instance, the lamellae in the $(Mo_{0.85}Nb_{0.15})_{0.97}Cr_{0.03}Si_2$ alloy remain well defined for more than 336 h. It is believed that the improvement in the thermal stability of the lamellar structure is due to the decrease in the lattice misfit at the $C11_b/C40$ lamellar interface resulting from Cr segregation. That Cr segregation at the interface has already been proved through scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) [18]. It has been suggested that Cr segregation changes the value of the lattice parameter in the vicinity of the lamellar interface, thus reducing the lattice misfit and improving the planarity and thermal stability of the lamellar structures [19]. However, the suggested mechanism of Cr segregation at the $C11_b/C40$ interface has not yet been proven. Further, the quantitative relationship between the extent of Cr segregation and the change in the lattice misfit remains unclear. In addition, it remains to be clarified whether Cr is the most suitable additive element for stabilizing the lamellar structure in $MoSi_2/NbSi_2$.

The phase-field method is a versatile technique for simulating the microstructural evolution and interfacial segregation in various materials on the basis of thermodynamics and the diffuse interface concept. Thus far, we have applied the phase-field method to study the microstructural evolution and segregation at interfaces such as stacking faults [20], twin boundaries [21], and antiphase boundaries [22]. In particular, this method has been used for quantitative investigations of interfacial segregation, which are difficult to be performed experimentally. The objective of this study was to elucidate the factors dominating the mechanism of interfacial segregation of additive elements in $MoSi_2/NbSi_2$ duplex silicide by using the phase-field method.

2. Method

2.1. Phase-field model

As illustrated in Fig. 1a and b, both the $C11_b$ tetragonal structure and the $C40$ hexagonal structure consist of two sublattices, that is, a transition metal (TM) sublattice (represented by the red spheres) and a Si sublattice (blue spheres). Although a small number of Si atoms can occupy the TM sites, this number is negligibly small [23]. Therefore, for the sake of simplicity, it is assumed that no antisite atoms are formed, that is, Si atoms cannot occupy the TM sites and *vice versa*. The $C11_b$ and $C40$ structures may appear quite different from one another, but the atomic arrangement within an atomic layer on the (110) plane of the $C11_b$ phase and that on the (0001) plane of the $C40$ phase are nearly identical (Fig. 1c, d). The difference between the two crystal structures is in the sequence of the stacking layers. That is to say, the $C11_b$ structure exhibits ACAC-type stacking whereas the $C40$ structure shows ABDABD-type stacking. Coherent lamellar interfaces are formed parallel to the $(110)_{C11b}$ and $(0001)_{C40}$ planes [10,24]. Six types of lamellar interfaces with different interconnecting layers can be formed. A previous study based on first-principles calculations had indicated that the interface with the stacking sequence of … DABDAB|ACAC …. has the lowest interfacial energy.

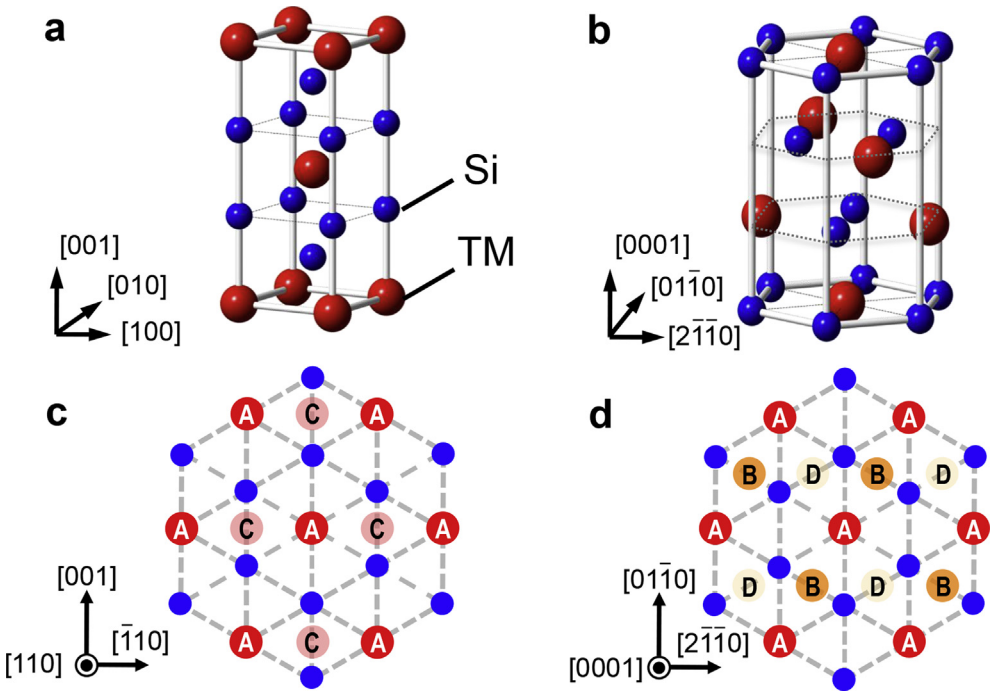

Fig. 1. Unit cells of (a) $C11_b$-structure and (b) $C40$-structure. Large balls show transition metals (Mo or Nb atoms) and small ones show Si atoms. Atomic arrangements on (c) (110)-plane of $C11_b$-phase and (d) (0001)-plane of $C40$-phase, which are parallel to the $C11_b/C40$ lamellar interface.