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Misfit strain affecting the lamellar microstructure in $NbSi_2/MoSi_2$ duplex crystals

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Abstract

The effect of including an additional element, like Re, Cr, V, Zr or Ir, in $(Mo_{0.85}Nb_{0.15})Si_2$ crystals, carried out with the aim of improving the thermal stability of the fine lamellar microstructures of the crystals, was examined with the help of first-principles calculations. The addition improved the thermal stability of the microstructures at 1400 °C in all cases, and the effect was especially significant in crystals containing Cr and Zr additives. Quantitative evaluation by Moiré fringe analysis revealed that the misfit strain at the interfaces in crystals with added Cr and Zr was smaller than those in crystals with other elements added. The reduced misfit strain resulted in the suppression of the rapid growth of the $C11_b$ phase precipitates that did not possess the variant orientation relationship with the C40 matrix, and hence the thermal stability of the fine lamellar microstructures improved. The results further revealed that the ratio of the atomic size of the additive element to that of Mo, which is the main constituent element in the $C11_b$ phase, is an important factor that controlled the misfit strain at the lamellar interface by the result of Cr addition. However, the addition of Zr was found to result in a significant improvement in the thermal stability of the lamellar microstructure, despite the markedly larger atomic radius of Zr compared with that of Mo. This indicates that there may be other factors, in addition to the atomic radius of the additive, contributing to the thermal stability.

Keywords: Transition-metal silicides; Microstructure; Misfit strain; Lamella; Thermal stability

1. Introduction

1.1. Background

Emissions of CO_2, which is considered to induce the greenhouse effect, have increased over recent years, and the reduction of CO_2 emissions is a pressing environmental challenge globally. The improvement of heat efficiencies in combustion systems, and specifically in electric power plants, is a realistic and reasonable stratagem to address this issue. The improvement in heat efficiency can usually be realized by incrementing the temperature at which the turbine operates. Therefore, the development of new refractory materials, more advanced than the currently used Ni-based superalloys, is essential. Transition metal disilicides are promising ultrahigh-temperature structural materials that can potentially replace conventional materials in turbines, to achieve high operating temperatures [1–12]. However, for practical applications, the low-temperature fracture toughness and high-temperature strength above 1200 °C of these materials, specifically in the monolithic form, are inadequate. To overcome this limitation, Nakano et al. have developed $C11_b$-$MoSi_2$/C40-$NbSi_2$ composite crystals with fine lamellar microstructures [13,14]. These duplex crystals showed superior high-temperature mechanical properties [15] and improved low-temperature fracture toughness [16,17]. For the practical application of these crystals, high thermal stability of the $C11_b$/C40 lamellar structure is required, which enables

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their use in high temperatures for extended periods of time. In specimens of ternary $(Mo_{0.85}Nb_{0.15})Si_2$ duplex crystals annealed for short durations, a large part of the microstructure is composed of fine lamellae [14]. However, small amounts of $C11_b$ phases precipitated with coarse grain sizes also coexist in the microstructure, and their rapid growth collapses the fine lamellar microstructure when the specimens are annealed at 1400 °C for more than 168 h [14]. Therefore, for the practical application of $MoSi_2/NbSi_2$ composite crystals as ultrahigh-temperature structural materials, it is essential to improve the thermal stability of their microstructures.

1.2. Strategy to improve the thermal stability of lamellar microstructure

In our previous study [14], we clarified that the origin of the formation of lamellar microstructures and their orientation relationships in $(Mo_{0.85}Nb_{0.15})Si_2$ crystals are closely related to the characteristics of the crystal structures. The unit cells of the constituent $C11_b$-$MoSi_2$ and C40-$NbSi_2$ phases composing the lamellae are different; tetragonal in $C11_b$ and hexagonal lattices in C40, respectively. However, they have the "common plane", i.e. $\{1\,1\,0\}$ of the $C11_b$ and $(0\,0\,0\,1)$ of the C40, on which the atomic arrangements were almost identical except for a slight lattice distortion [14,18], and only the stacking sequences of the "common plane" are different in them; twofold in $C11_b$ and threefold in C40, respectively. Therefore, the precipitation of the $C11_b$ phase in the C40 matrix during annealing occurred as their common planes aligned parallel to each other at the lamellar interfaces, and hence, the crystals exhibited distinct crystallographic orientation relationships of $(0\,0\,0\,1)_{C40}//\{1\,1\,0\}_{C11b}$ and $\langle\bar{1}\,2\,\bar{1}\,0\rangle_{C40}//\langle 1\,\bar{1}\,0\rangle_{C11b}$. On the common plane, the $[1\,1\,0]$ axis in the $C11_b$ structure and the $[0\,0\,0\,1]$ axis in the C40 structure possessed twofold and sixfold rotation symmetries, respectively. As a result, three variants of the $C11_b$ phase, referred to as variant 1 (V1), variant 2 (V2) and variant 3 (V3) were produced from the C40 single crystals, as represented below [14]:

$$V1:\ (0\,0\,0\,1)_{C40}//(1\,1\,0)_{C11_b},\quad [\bar{1}\,2\,\bar{1}\,0]_{C40}//[1\,\bar{1}\,0]_{C11_b},\quad [1\,0\,\bar{1}\,0]_{C40}//[0\,0\,1]_{C11_b} \tag{1}$$

$$V2:\ (0\,0\,0\,1)_{C40}//(1\,1\,0)_{C11_b},\quad [2\,\bar{1}\,\bar{1}\,0]_{C40}//[1\,\bar{1}\,0]_{C11_b},\quad [0\,\bar{1}\,1\,0]_{C40}//[0\,0\,1]_{C11_b} \tag{2}$$

$$V3:\ (0\,0\,0\,1)_{C40}//(1\,1\,0)_{C11_b},\quad [\bar{1}\,\bar{1}\,2\,0]_{C40}//[1\,\bar{1}\,0]_{C11_b},\quad [\bar{1}\,1\,0\,0]_{C40}//[0\,0\,1]_{C11_b} \tag{3}$$

Hereafter, we will term these orientation relationships as variant orientation relationships. At the $C11_b$/C40 interfaces in the lamellar microstructure of $(Mo_{0.85}Nb_{0.15})Si_2$, the density of misfit dislocation was low, and Moiré fringes were observed in the TEM [14,19]. This suggests that the transformation from C40 to $C11_b$ proceeded smoothly at the interface, maintaining the above-mentioned crystallographic relationship. However, annealing over longer durations (for 168 h) largely degraded the stability of the lamellar structure. During the transformation, whilst maintaining the distinct orientation relationship described above, an internal residual strain locally accumulated at the interface. This strain, as evidenced during in-depth experimentation, is thought to be the driving force that led to the rapid growth of grains in the $C11_b$ phase, in which the variant orientation relationship described above was absent. Hence, according to this assumption, it is necessary to modify the lattice mismatch to reduce the internal strain at the interface in order to improve the thermal stability of the fine lamellar microstructure.

In our strategy, we have attempted to accomplish this reduction in the lattice misfit by incorporating minute amounts of an additive element. In a previous study, we examined the effect of Cr addition to $(Mo_{0.85}Nb_{0.15})Si_2$ crystals [20], and confirmed that the thermal stability of the fine lamellar microstructure was actually improved with the segregation of Cr at the lamellar interfaces. To obtain a more comprehensive understanding of the effect of adding alloying elements to the microstructure with the viewpoint of reducing the misfit strain at the lamellar interfaces, in this study, we prepared various quaternary silicide crystals, i.e. $C11_b$-$MoSi_2$/C40-$NbSi_2$ duplex crystals, containing Re, V, Zr or Ir. Some of these added elements were selected with the help of computational analysis by first-principles calculations. By comparing the variations caused in the microstructure by annealing and by quantitatively evaluating the lattice misfit at the vicinity of the lamellar interfaces, the factors that contributed to the improvement in the thermal stability of the fine lamellar microstructures in $(Mo_{0.85}Nb_{0.15})Si_2$ duplex silicide crystals were examined.

2. Material and methods

Master ingots of $(Mo_{0.85}Nb_{0.15})_{0.97}X_{0.03}Si_2$, where X = Re, Cr, V, Zr or Ir, were prepared by melting high-purity raw materials in a plasma arc furnace. It can be inferred from the chemical formulae that 3% of the parent transition metal atoms (Mo, Nb) were substituted with the additive transition metal elements to control the microstructure. Hereafter, we will denote these quaternary $(Mo_{0.85}Nb_{0.15})_{0.97}X_{0.03}Si_2$ crystals as X-containing crystals. Single crystals composed of C40 single-phase were grown using the floating-zone (FZ) method at a growth rate of 2.5 mm h^{-1} under the flow of high-purity argon. The single crystals obtained were placed in a quartz tube and annealed at 1400 °C for 168 h or 336 h to develop aligned lamellar microstructures comprising C40-$NbSi_2$ and $C11_b$-$MoSi_2$ phases. The microstructures were observed with an optical microscope (OM, OLYMPUS BX51M) and a scanning electron microscope (SEM, JEOL JEM-6500F). In addition, the crystal orientation relationship between the C40 and $C11_b$ phases was examined by analyzing the electron backscatter diffraction pattern (EBSD, software: TSL instruments K.K.) obtained in the SEM at a measured step