Orientation relationships, interface structures, and mechanical properties of directionally solidified MoSi₂/Mo₅Si₃/Mo₅Si₃C composites

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Abstract

The microstructures, orientation relationships, and high-temperature deformation behavior of directionally solidified (DS) ingots of MoSi₂/Mo₅Si₃/Mo₅Si₃C three-phase eutectic composites were investigated. DS three-phase composites exhibit a fine and homogeneous script lamellar microstructure. Mo₅Si₃ and Mo₅Si₃C individually form interconnected networks that extend in the growth direction (GD) of the MoSi₂ matrix and maintain $[1\bar{1}0]_{\text{MoSi}_2}$, $[001]_{\text{Mo}_5\text{Si}_3}$, and $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$ approximately parallel to the GD. High-temperature strength is higher in the DS three-phase composite than in the

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2 binary two-phase counterpart, especially below 1200 °C. This is mainly because of
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4 MoSi₂ matrix refinement and the presence of the strengthening phase Mo₅Si₃C. The
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6 observed orientation relationship between component phases is discussed in relation to
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8 lattice misfits.
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14 Key words: A. transition-metal silicides; B. alloy design; B. mechanical properties; D.
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16 microstructure; D. interfaces
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22 1. Introduction

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24 One of the greatest challenges for improving efficiency in advanced
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26 combustion systems such as gas turbine power plants and aircraft engines is developing
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28 ultra-high temperature materials that drastically increase combustion temperatures
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30 beyond the maximum operating temperatures of current Ni-based superalloys. MoSi₂
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32 with the tetragonal C11_b structure has received considerable attention because of its
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34 attractive properties such as a high melting point (2020 °C), excellent oxidation
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36 resistance, and relatively low density [1-5]. However, poor fracture toughness at room
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38 temperature and insufficient strength at elevated temperatures should be improved for
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40 its practical application as ultra-high temperature structural materials. Extensive efforts
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42 to improve the insufficient mechanical properties of monolithic MoSi₂ have been made
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44 by forming composites with hard ceramics or intermetallics such as SiC, TiC, ZrO₂, and
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46 Mo₅Si₃ [5,6]. Among these composites, MoSi₂/Mo₅Si₃ eutectic composites with high
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48 eutectic temperatures of approximately 1900 °C are expected to have higher probability
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50 for the property improvements of MoSi₂ through interface property control due to the
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52 fine script lamellar microstructure that forms via directional solidification (DS) [7-11].
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2 Recently, we have systematically studied the influences of ternary additions on the
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4 microstructure and mechanical properties of DS $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ eutectic composites. We
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6 have found that their high-temperature mechanical properties are improved through
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8 microstructure refinement and fracture behavior of the $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ interface in the
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10 DS composite can be modified by controlling lattice misfit between MoSi_2 and Mo_5Si_3
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12 as well as interface segregation through ternary alloying [7,8,11]. In addition, we have
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14 found that the DS ternary alloys that contain a small amount of C exhibit a
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16 homogeneous three-phase script lamellar structure composed of MoSi_2 , Mo_5Si_3 , and
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18 $\text{Mo}_5\text{Si}_3\text{C}$ [7,12,13]. Identification of microstructural characteristics and their influence
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20 on mechanical properties in three-phase eutectic composites is important because
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22 MoSi_2 -based composite mechanical property improvement is expected to occur through
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24 control of microstructure and properties of various interfaces between component
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26 phases. This study analyzed microstructures, orientation relationships between
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28 component phases, and mechanical properties of DS ingots of $\text{MoSi}_2/\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$
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30 three-phase eutectic composites. The observed orientation relationship between the
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32 component phases is discussed in relation to the lattice misfits.
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43 2. Experimental

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45 Rod ingots of the ternary alloy with a nominal composition of Mo - 52 at.% Si
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47 - 2 at.% C were prepared by arc melting. DS ingots were grown from the rod ingots by
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49 the optical floating-zone method at a growth rate of 10 mm/h under Ar gas flow.
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51 Microstructures of the DS ingots were examined by scanning electron microscopy
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53 (SEM), electron backscatter diffraction (EBSD) in SEM, transmission electron
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55 microscopy (TEM), and scanning transmission electron microscopy (STEM). The SEM
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examinations were carried out in a JEOL JSM-7001FA electron microscope with a field emission gun (FEG) operated at 15 or 20 kV and a TSL DVC5-type EBSD detector. Thin foils for TEM/STEM observations were cut from the DS ingots, polished mechanically and then Ar ion milled using a JEOL EM-09100IS ion milling machine operated at 6.0 kV for milling and 2.0 kV for finishing. The TEM/STEM analysis was carried out in a JEOL JEM-ARM200F equipped with a cold FEG operated at 200 kV. Lattice parameters of the component phases were determined by powder X-ray diffraction (XRD) with a Rigaku Miniflex II diffractometer operated at 30 kV, 15 mA.

Oriented single crystalline specimens $1.4 \times 1.4 \times 3.5 \text{ mm}^3$ in size were cut from the DS ingots by electro discharge machining (EDM) for compression tests, which were performed along $[1\bar{1}0]_{\text{MoSi}_2}$ nearly parallel to the growth direction (GD) of the DS ingots in the temperature range of 900 to 1400 °C in a vacuum at a nominal strain rate of 10^{-4} s^{-1} .

3. Results

3.1. Microstructures and orientation relationships

DS ingots of $\text{MoSi}_2/\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ three-phase eutectic composites exhibit a fine script lamellar microstructure similar to DS $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ eutectic composites [7,12]. Fig. 1 shows EBSD orientation maps analyzed on one cross-section and two longitudinal sections of the DS three-phase composite. Orientation distributions of the three component phases along the GD of the DS ingot are indicated in Fig. 1. The three regions, namely, blue, green, and red correspond to MoSi_2 , Mo_5Si_3 , and $\text{Mo}_5\text{Si}_3\text{C}$, respectively. Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ phases clearly form individual interconnected

networks extending along the GD in the MoSi_2 matrix and maintain $[1\bar{1}0]_{\text{MoSi}_2}$, $[001]_{\text{Mo}_5\text{Si}_3}$, and $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$ approximately parallel to the GD (Fig. 1(b)). Approximate orientation relationships among three phases determined by the EBSD analysis are summarized as follows (EBSD orientation maps are shown in supplementary material):

$$\begin{aligned} [1\bar{1}0]_{\text{MoSi}_2} // [001]_{\text{Mo}_5\text{Si}_3} // [0001]_{\text{Mo}_5\text{Si}_3\text{C}} \\ [110]_{\text{MoSi}_2} // [1\bar{1}0]_{\text{Mo}_5\text{Si}_3} // [2\bar{3}10]_{\text{Mo}_5\text{Si}_3\text{C}} \\ [001]_{\text{MoSi}_2} // [110]_{\text{Mo}_5\text{Si}_3} // [41\bar{5}0]_{\text{Mo}_5\text{Si}_3\text{C}} \end{aligned} \quad (1).$$

The orientation relationship between MoSi_2 and Mo_5Si_3 is identical with that observed in DS $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ two-phase eutectic composites, described as $(110)_{\text{MoSi}_2} // (1\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ and $[1\bar{1}0]_{\text{MoSi}_2} // [001]_{\text{Mo}_5\text{Si}_3}$ with a minor misalignment of $\sim 2^\circ$ between $[1\bar{1}0]_{\text{MoSi}_2}$ and $[001]_{\text{Mo}_5\text{Si}_3}$ [7,9]. A slight misalignment of $\sim 1^\circ$ is also confirmed between $[2\bar{3}10]_{\text{Mo}_5\text{Si}_3\text{C}}$ and $[110]_{\text{MoSi}_2} // [1\bar{1}0]_{\text{Mo}_5\text{Si}_3}$ by diffraction analysis in TEM as shown in Fig 3. Approximate crystallographic orientations of the three component phases in each section are indicated in Fig. 1. The volume fraction of MoSi_2 , Mo_5Si_3 , and $\text{Mo}_5\text{Si}_3\text{C}$ in the three-phase composite is estimated to have a ratio of $48.3 \pm 1.1 : 26.2 \pm 0.8 : 25.5 \pm 0.7$ based on the phase area fraction data obtained from seven rectangular areas of about $150 \mu\text{m} \times 450 \mu\text{m}$ analyzed by SEM–EBSD. Because Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ have rod-like morphology, no correction is required to estimate the volume fraction from the phase area fraction data.

A typical SEM backscattered electron image observed from a cross-section of the DS three-phase eutectic composite as well as that of the two-phase counterpart is

shown in Fig. 2. The three component phases of MoSi_2 , Mo_5Si_3 , and $\text{Mo}_5\text{Si}_3\text{C}$ appear as dark, light, and medium gray regions, respectively. The Mo_5Si_3 branches in the three-phase composite exhibit rectangular shapes similar to those observed in the two-phase counterpart (Fig. 2). Each $\text{Mo}_5\text{Si}_3\text{C}$ rod form a connection between the neighboring Mo_5Si_3 branches (Fig. 2(a)) and divide the MoSi_2 matrix into smaller regions compared to that in the two-phase composite (Fig. 2(b)). Consequently, the average thickness of the MoSi_2 matrix along two orthogonal directions of $[001]_{\text{MoSi}_2}$ and $[110]_{\text{MoSi}_2}$ is reduced to 4.2 ± 2.0 and 5.6 ± 4.2 μm , respectively, compared with 7.1 ± 8.1 and 6.1 ± 4.6 μm for the binary two-phase counterpart produced at the same growth rate of 10 mm/h. The average thicknesses of the MoSi_2 matrix along $[001]_{\text{MoSi}_2}$ and $[110]_{\text{MoSi}_2}$ are obtained from ~ 100 thickness measurements for each direction using test grids drawn on SEM images of the $(1\bar{1}0)_{\text{MoSi}_2}$ cross-section.

Orientation relationships and interface structures between $\text{Mo}_5\text{Si}_3\text{C}$ and the other two phases were further investigated by TEM and atomic-resolution high-angle annular dark-field (HAADF)-STEM. Fig. 3 shows selected-area electron diffraction (SAED) patterns taken from the $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ and $\text{MoSi}_2/\text{Mo}_5\text{Si}_3\text{C}$ interface regions with the incident beam direction parallel to $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$. As indicated in the SAED pattern taken from the $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interface region (Fig. 3(a)), the diffraction spots of $550_{\text{Mo}_5\text{Si}_3}$ and $41\bar{5}0_{\text{Mo}_5\text{Si}_3\text{C}}$ are very closely located with a minor deviation of $\sim 1^\circ$ around the incident beam direction. Moreover, $\bar{3}30_{\text{Mo}_5\text{Si}_3}$ and $\bar{2}3\bar{1}0_{\text{Mo}_5\text{Si}_3\text{C}}$ have a similar relationship, consistent with the orientation relationship obtained by EBSD analysis. In addition, diffraction spots of $4\bar{2}0_{\text{Mo}_5\text{Si}_3}$ and $3\bar{3}00_{\text{Mo}_5\text{Si}_3\text{C}}$ appear at nearly

the same position with $\sim 0.5^\circ$ deviation around the incident beam direction (Figs. 3(a) and (b)). Thus, the orientation relationship between Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ is slightly better described as

$$(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} // (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}, [001]_{\text{Mo}_5\text{Si}_3} // [0001]_{\text{Mo}_5\text{Si}_3\text{C}} \quad (2).$$

The orientation relationship between MoSi_2 and $\text{Mo}_5\text{Si}_3\text{C}$ described by Eq. (1) is also confirmed by diffraction analysis in TEM as summarized in Figs. 3(c) and (d).

An atomic-resolution HAADF-STEM image of a typical $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interface with a habit plane macroscopically parallel to $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} - (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ is shown in Fig. 4(a). The interface exhibits relatively high coherence (Fig. 4(a)). This is demonstrated by the connection of each black line that corresponds to traces of the $(110)_{\text{Mo}_5\text{Si}_3}$ planes to a black line of a $(10\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ trace at the interface. Schematic illustration of the $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} - (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ interface clearly indicates that atomic columns corresponding to Mo-chain sites in both of the phases ($4b$ and $4d$ sites for Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$, respectively) are periodically shared at the interface (Fig. 4 (c)). This type of interface structure with very high coherence is apparently not observed at any of the $\text{MoSi}_2/\text{Mo}_5\text{Si}_3\text{C}$ interfaces (Fig. 4(b)). Thus, orientation relationships of the $\text{Mo}_5\text{Si}_3\text{C}$ phase with respect to MoSi_2 and Mo_5Si_3 are considered to be selected primarily to form the $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} - (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ interface with relatively high coherence.

3.2. High-temperature deformation behavior

Fig. 5(a) illustrates typical stress–strain curves obtained for $[1\bar{1}0]_{\text{MoSi}_2}$ -oriented specimens of the DS three- and two-phase composites compressed by 2 ~ 4 %

plastic strain. Plastic flow is confirmed above 1000 °C for both the DS three- and two-phase composites. The stress–strain curves exhibit yield drop behavior. Similar yield drop behavior has been frequently observed in compression tests of single crystals of many transition-metal silicides including the [001]-oriented Mo_5Si_3 and [0001]-oriented $\text{Mo}_5\text{Si}_3\text{C}$ [1,14-19]. This implies how difficult it is to activate dislocation sources or introduce new dislocations in these materials. The temperature dependence of the yield stress that corresponds to the flow stress at 0.2% plastic strain is plotted in Fig. 5(b). The temperature dependence curves of the yield stress for MoSi_2 , Mo_5Si_3 , and $\text{Mo}_5\text{Si}_3\text{C}$ single crystals tested along the corresponding loading axis orientations of $\langle 110 \rangle_{\text{MoSi}_2}$, $[001]_{\text{Mo}_5\text{Si}_3}$, and $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$ are also provided in Fig. 5(b) for reference [1,14,15]. The yield stress for the three-phase composites decreases monotonously with increasing temperature in the temperature range of 1000 to 1400 °C. The yield stress at 1000 °C for the three-phase composites is much higher (~64 %) than that for the binary counterparts, while above 1200 °C they are nearly identical. This indicates that the $\text{Mo}_5\text{Si}_3\text{C}$ addition effectively improves yield strength, especially below 1200 °C.

Fig. 6 shows deformation markings observed on two orthogonal side surfaces, namely, $(\bar{1}\bar{1}0)_{\text{MoSi}_2}$ and $(001)_{\text{MoSi}_2}$, of the DS three-phase composites compressed to ~2% plastic strain at 1000 °C. Slip traces are observed in the MoSi_2 matrix on the $(\bar{1}\bar{1}0)_{\text{MoSi}_2}$ surface but not on the $(001)_{\text{MoSi}_2}$ surface. This suggests that the slip directions of the MoSi_2 matrix are parallel to $(001)_{\text{MoSi}_2}$. The $\{011\}\langle 100 \rangle$, $\{010\}\langle 100 \rangle$, $\{023\}\langle 100 \rangle$, and $\{013\}\langle 331 \rangle$ slip systems were reported to operate in compression tests of [110]-oriented MoSi_2 single crystals [1]. Among these possible slip systems, the

observed slip systems in the MoSi_2 matrix of the DS three-phase composites are inferred to be $\{011\}\langle 100\rangle$ slip systems based on the trace analysis. In the Mo_5Si_3 rods, fine slip traces corresponding to $(11\bar{2})_{\text{Mo}_5\text{Si}_3}$, $(\bar{1}12)_{\text{Mo}_5\text{Si}_3}$, and $(\bar{1}\bar{1}\bar{2})_{\text{Mo}_5\text{Si}_3}$ are observed on both of the surfaces. Since the shortest Burgers vector on $\{11\bar{2}\}_{\text{Mo}_5\text{Si}_3}$ is $1/2\langle 111\rangle_{\text{Mo}_5\text{Si}_3}$, the $\{11\bar{2}\}\langle 111\rangle$ slip systems are inferred to operate in Mo_5Si_3 . In contrast to the fine slip traces in the MoSi_2 matrix and the Mo_5Si_3 rods, deformation markings in $\text{Mo}_5\text{Si}_3\text{C}$ are appeared as relatively thick bands sparsely distributed on both of the surfaces. However, it is difficult to identify the deformation modes operating in $\text{Mo}_5\text{Si}_3\text{C}$ from the trace analysis.

4. Discussion

4.1. Orientation relationship among three component phases

Among various interfaces in the DS $\text{MoSi}_2/\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ three-phase composite, one type of $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interface being macroscopically parallel to $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ and $(1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ exhibits relatively high coherence. In general, the orientation relationship between two phases, stable interface structure, and interface properties are all closely related to the lattice misfits between component phases [7,20]. Thus, it is important to consider the relationship between the observed orientation relationship and lattice misfits to understand why the observed orientation relationships are preferentially selected. The $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interfaces form to connect intersections between the $\{110\}_{\text{Mo}_5\text{Si}_3}$ and $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ traces when the interfaces are viewed along the common direction parallel to $[001]_{\text{Mo}_5\text{Si}_3}$ and $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$. Thus, it is reasonable to consider the lattice misfit between $\{110\}_{\text{Mo}_5\text{Si}_3}$ and $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ (misfit A) defined by

the equation

$$\text{Misfit A} = 2 \frac{d_{\{110\} \text{ of Mo}_5\text{Si}_3} - d_{\{1\bar{1}00\} \text{ of Mo}_5\text{Si}_3\text{C}}}{d_{\{110\} \text{ of Mo}_5\text{Si}_3} + d_{\{1\bar{1}00\} \text{ of Mo}_5\text{Si}_3\text{C}}} \quad (3),$$

where $d_{\{hkl\} \text{ of Mo}_5\text{Si}_3}$ and $d_{\{hkl\} \text{ of Mo}_5\text{Si}_3\text{C}}$ correspond to the interplanar distances of $\{hkl\}$ in Mo_5Si_3 and $\{hkl\}$ in $\text{Mo}_5\text{Si}_3\text{C}$, respectively. An additional lattice misfit exists between $(001)_{\text{Mo}_5\text{Si}_3}$ and $(0001)_{\text{Mo}_5\text{Si}_3\text{C}}$ (misfit B) and is estimated as

$$\text{Misfit B} = 2 \frac{d_{(001) \text{ of Mo}_5\text{Si}_3} - d_{(0001) \text{ of Mo}_5\text{Si}_3\text{C}}}{d_{(001) \text{ of Mo}_5\text{Si}_3} + d_{(0001) \text{ of Mo}_5\text{Si}_3\text{C}}} \quad (4).$$

The values of misfits A and B are calculated as 8.0 % and -3.2 %, respectively using the lattice parameters $a_{\text{Mo}_5\text{Si}_3} = 0.966$ nm, $c_{\text{Mo}_5\text{Si}_3} = 0.489$ nm, $a_{\text{Mo}_5\text{Si}_3\text{C}} = 0.728$ nm, and $c_{\text{Mo}_5\text{Si}_3\text{C}} = 0.505$ nm determined from powder XRD data of the ternary composites.

Lattice misfit A with a larger absolute value has a strong influence on the observed orientation relationship. A relatively large misfit such as misfit A can be macroscopically accommodated by tilting one of the two crystals with respect to the other across the interface as in the MoSi_2 and Mo_5Si_3 interface examined in our previous study [7,20]. Fig. 7 schematically illustrates the misfit accommodation. If a tilt with angle ϕ between $(110)_{\text{Mo}_5\text{Si}_3}$ and $(10\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ is introduced keeping $[001]_{\text{Mo}_5\text{Si}_3}$ and $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$ parallel to each other, the lattice misfit A_1 between $(110)_{\text{Mo}_5\text{Si}_3}$ and $(10\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ is completely accommodated on the interfaces labeled OP_1 and OP_1' with interface inclination angles θ_1 and θ_1' , respectively. Because $\text{Mo}_5\text{Si}_3\text{C}$ has a hexagonal lattice, two additional sets of $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$, namely, $(0\bar{1}10)_{\text{Mo}_5\text{Si}_3\text{C}}$ and $(1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$, and one more set of $\{110\}_{\text{Mo}_5\text{Si}_3}$; i.e., $(1\bar{1}0)_{\text{Mo}_5\text{Si}_3}$, for the tetragonal Mo_5Si_3 can be simultaneously considered as illustrated in Fig. 7. The relationship between the tilt angle

φ and the interface inclination angle θ (θ_i and θ_i') for the three sets of $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$, namely, $(10\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ ($i = 1$), $(1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ ($i = 2$), and $(0\bar{1}10)_{\text{Mo}_5\text{Si}_3\text{C}}$ ($i = 3$), with respect to $(110)_{\text{Mo}_5\text{Si}_3}$ defined in Fig. 7 are described by the following equations:

$$\tan \theta_i = \frac{d_1 \cdot \sin \varphi_i}{d_1 \cdot \cos \varphi_i - d_2} \quad (i = 1, 2, \text{ and } 3) \quad (5),$$

$$\tan \theta_i' = \frac{d_1 \cdot \sin \varphi_i}{d_1 \cdot \cos \varphi_i + d_2} \quad (i = 1, 2 \text{ and } 3) \quad (6),$$

where $d_1 = k \cdot d_{\{110\} \text{ of } \text{Mo}_5\text{Si}_3}$, $d_2 = l \cdot d_{\{1\bar{1}00\} \text{ of } \text{Mo}_5\text{Si}_3\text{C}}$ (k, l : positive integers), and $\varphi_i = \varphi$ ($i = 1$), $\varphi + 60^\circ$ ($i = 2$), and $\varphi + 120^\circ$ ($i = 3$). When both k and l are equal to 1, a one-to-one connection between the $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ plane and the $(110)_{\text{Mo}_5\text{Si}_3}$ plane is achieved. When the number k is equal to 1 and the number l is greater than 1, the $(110)_{\text{Mo}_5\text{Si}_3}$ planes coincide with the $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ planes at an interval of l planes and so on. Relationships for the three sets of $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$, namely, $(10\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ ($i = 4$), $(1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ ($i = 5$), and $(0\bar{1}10)_{\text{Mo}_5\text{Si}_3\text{C}}$ ($i = 6$), with respect to $(1\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ are similarly described by the following equations:

$$\tan \theta_i = \frac{d_3 \cdot \sin \varphi_i - d_4}{d_3 \cdot \cos \varphi_i} \quad (i = 4, 5, \text{ and } 6) \quad (7),$$

$$\tan \theta_i' = \frac{d_3 \cdot \sin \varphi_i + d_4}{d_3 \cdot \cos \varphi_i} \quad (i = 4, 5, \text{ and } 6) \quad (8),$$

where $d_3 = m \cdot d_{\{110\} \text{ of } \text{Mo}_5\text{Si}_3}$, $d_4 = n \cdot d_{\{1\bar{1}00\} \text{ of } \text{Mo}_5\text{Si}_3\text{C}}$ (m, n : positive integers), and $\varphi_i = \varphi$ ($i = 4$), $\varphi + 60^\circ$ ($i = 5$), and $\varphi + 120^\circ$ ($i = 6$).

Fig. 8(a) plots the φ - θ relationships for $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ with respect to $(110)_{\text{Mo}_5\text{Si}_3}$, assuming that both k and l are equal to 1. The intersections between two φ - θ

curves correspond to the conditions that two types of lattice misfits are simultaneously accommodated except for cases where one set of $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ is parallel to $(110)_{\text{Mo}_5\text{Si}_3}$; i.e., at the coordinates (φ, θ) of $(0^\circ, 0^\circ)$ and $(60^\circ, 180^\circ)$ seen in Fig. 8(a). In the φ - θ plots with respect to $(110)_{\text{Mo}_5\text{Si}_3}$ shown in Fig. 8(a), four intersections (points (I)–(IV)) exist at the coordinates (φ, θ) of (I): $(2.8^\circ, 32.8^\circ)$, (II): $(9.8^\circ, 69.8^\circ)$, (III): $(50.2^\circ, 110.2^\circ)$, and (IV): $(57.2^\circ, 147.2^\circ)$. Intersections (I) and (IV) are geometrically equivalent with a mirror relationship with respect to the $(110)_{\text{Mo}_5\text{Si}_3}$ plane, and the same holds for intersections (II) and (III). Only intersections (I) and (II) are sufficient for consideration. The repeat distances OP_1 for intersections (I) and (II) are calculated as 1.26 and 0.728 nm ($=a_{\text{Mo}_5\text{Si}_3\text{C}}$), respectively, which suggests that the condition for intersection (II) is preferred because of higher lattice coincidence. The (φ, θ) coordinate $(11.6^\circ, 71.6^\circ)$ for the observed orientation relationship of $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} // (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ is quite close to intersection (II) with a minor deviation of $\sim 2^\circ$.

It is reasonable to simultaneously consider the lattice misfit with respect to the $(1\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ planes in addition to the $(110)_{\text{Mo}_5\text{Si}_3}$ planes discussed previously according to the four-fold symmetry along the $[001]_{\text{Mo}_5\text{Si}_3}$ axis. Various (k, l) and (m, n) pairs of relatively small positive integers are considered since relatively high coherence can be achieved when k, l, m , and n are small (see supplementary material). Figs. 8(b) and (c) plot the φ - θ relationships with respect to the $(1\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ planes for the (m, n) pairs of (1, 1) and (1, 3), respectively. Among various intersections between different curves in Figs. 8(b) and (c), the intersection between the φ - θ_4 and φ - θ_6 curves with the (m, n) pair of (1, 3) has the coordinate $(11.8^\circ, 71.8^\circ)$ and is hereafter referred to as intersection (X).

The experimentally observed (φ, θ) coordinate $(11.6^\circ, 71.6^\circ)$ is located between intersections (II) and (X) with less than 2° deviation. No other points have such a high coincidence of intersections in the tilt angle range between 0° and 30° (see supplementary material). Thus, it can be concluded that the observed orientation relationship of $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} // (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ is selected mainly because it can simultaneously minimize four types of $\{110\}_{\text{Mo}_5\text{Si}_3} - \{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ lattice misfits.

Once the tilt angle φ is fixed, the intersections between the φ - θ curves and the vertical line of the fixed φ provide the interface inclination angles θ with relatively low energies achieved by minimizing at least one of the $\{110\}_{\text{Mo}_5\text{Si}_3} - \{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ lattice misfits. Fig. 8(d) shows the superposed image of Fig. 8(a) and Fig. 8(b) plotted in the tilt angle range from 0° to 30° . In the same way, Fig. 8(e) shows the superposed image of Fig. 8(a) and Fig. 8(c). In addition to the intersections in Figs. 8(a) and (b), there is an intersection between two φ - θ curves, φ - θ_1 and φ - θ_5 located near the observed tilt angle φ of 11.6° in Fig. 8(d). This intersection suggests that the $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interfaces with the macroscopic inclination angle of $\sim 5^\circ$ are stable interfaces with relatively low energy because two types of lattice misfits are minimized simultaneously at the inclination angle. In fact, $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interfaces with the macroscopic inclination angle θ of $\sim 5^\circ$ are also frequently observed (see supplementary material).

A similar analysis can be applied to the $\text{MoSi}_2/\text{Mo}_5\text{Si}_3\text{C}$ interfaces where three types of lattice misfits; i.e., misfit C: $(001)_{\text{MoSi}_2} - \{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$, misfit D: $(110)_{\text{MoSi}_2} - \{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$, and misfit E: $(1\bar{1}0)_{\text{MoSi}_2} - (0002)_{\text{Mo}_5\text{Si}_3\text{C}}$ should be considered. Misfits C and D can be accommodated by tilting one of the crystals with respect to the other. The φ - θ relationships with respect to misfits C and D are also described by Eqs. (5)–(8)

where $d_1 = p \cdot d_{(001) \text{ of MoSi}_2}$, $d_2 = q \cdot d_{\{1\bar{1}00\} \text{ of Mo}_5\text{Si}_3\text{C}}$, $d_3 = r \cdot d_{\{110\} \text{ of MoSi}_2}$, and $d_4 = s \cdot d_{\{1\bar{1}00\} \text{ of Mo}_5\text{Si}_3\text{C}}$ (p , q , r , and s are positive integers). Fig. 9 shows several φ - θ relationships with respect to misfits C and D. One intersection (point (III)) for misfit C is located near the vertical line corresponding to the observed tilt angle φ of 11.6° at the (φ, θ) coordinate $(11.9^\circ, 161.9^\circ)$, when the (p, q) pair is (1, 2) as shown in Fig. 9(b). Two intersections (points (VII) and (VIII)) for misfit D possess tilt angle φ values close to the observed value when the (r, s) pair is equal to (1, 1) (Fig. 9(c)). These results suggest that the interface inclination angles of 161.9° (point (III)), 100.3° (point (VII)), and 71.9° (point (VIII)) are preferentially selected because they possess relatively low interface energies. The macroscopic inclinations of $\sim 72^\circ$ and $\sim 162^\circ$ are actually observed (see supplementary material). Therefore, it is concluded that the preferred interface inclination angles are selected so as to effectively minimize the interface energy related to lattice misfits.

4.2. High-temperature strength

Although the operative deformation modes has not been completely characterized in the present study, all three component phases are confirmed to deform plastically at 1000°C , where the flow stress starts to decrease from the maximum value at $\sim 1\%$ plastic strain. As shown in Fig. 5(b), plastic deformation of Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ single crystals with corresponding loading axis orientation has not been reported so far at 1000°C [14,15]. Moreover, yield stress values for the three- and two-phase eutectic composites are much higher than those of MoSi_2 single crystals at all tested temperatures, especially below 1200°C . Thus, it is reasonable to consider that plastic

deformation starts in the MoSi_2 matrix and then transmits to the Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ rods. As described in section 3.1, the average thickness of the MoSi_2 matrix measured along two orthogonal directions decreases with the existence of the $\text{Mo}_5\text{Si}_3\text{C}$ rods compared with the average thickness in the two-phase counterpart. Therefore, higher yield strength for the three-phase composites is considered to reflect mainly the difference in average thickness of the MoSi_2 matrix and also the difference in stress level that activates dislocation sources in $\text{Mo}_5\text{Si}_3\text{C}$ and Mo_5Si_3 rods.

4. Conclusions

1. DS ingots of the $\text{MoSi}_2/\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ three-phase eutectic composites exhibit a homogeneous script lamellar structure. Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ phases individually form interconnected networks that extend along the GD in the MoSi_2 matrix and maintain $[1\bar{1}0]_{\text{MoSi}_2}$, $[001]_{\text{Mo}_5\text{Si}_3}$, and $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$ approximately parallel to the GD.

2. The three component phases possess a distinct orientation relationship in the DS three-phase eutectic composites. The orientation relationship between Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{C}$ in the DS three-phase eutectic composites is summarized as $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3} // (1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$ and $[001]_{\text{Mo}_5\text{Si}_3} // [0001]_{\text{Mo}_5\text{Si}_3\text{C}}$, whereas that between MoSi_2 and Mo_5Si_3 is $(110)_{\text{MoSi}_2} // (1\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ and $[1\bar{1}0]_{\text{MoSi}_2} // [001]_{\text{Mo}_5\text{Si}_3}$, the latter of which is identical to what is observed in the two-phase counterparts. The orientation relationship of $\text{Mo}_5\text{Si}_3\text{C}$ in the DS three-phase composites is selected to effectively accommodate lattice misfits between $\{110\}_{\text{Mo}_5\text{Si}_3}$ and $\{1\bar{1}00\}_{\text{Mo}_5\text{Si}_3\text{C}}$ at the $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interfaces parallel to $(2\bar{1}0)_{\text{Mo}_5\text{Si}_3}$ and $(1\bar{1}00)_{\text{Mo}_5\text{Si}_3\text{C}}$.

3. High-temperature strength of the DS three-phase eutectic composites is higher than

1
2 that of the binary two-phase counterparts, especially below 1200 °C. This is because of
3
4 the existence of the $\text{Mo}_5\text{Si}_3\text{C}$ phase and the resultant microstructure refinement of the
5
6
7 MoSi_2 matrix.
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9

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Fig1

Fig2

Fig3

Fig4

Fig5

Fig6

Fig7

Mo_5Si_3 - $\text{Mo}_5\text{Si}_3\text{C}$ interface

Fig9

MoSi₂ - Mo₅Si₃C interface

Fig. 1. EBSD orientation maps analyzed for the growth direction (GD) on (a) one cross-section and (b,c) two longitudinal sections of the DS $\text{MoSi}_2/\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ three-phase eutectic composite. Blue, green, and red regions correspond to MoSi_2 , Mo_5Si_3 , and $\text{Mo}_5\text{Si}_3\text{C}$, respectively.

Fig. 2. SEM backscattered electron image observed on a cross-section of (a) three-phase and (b) two-phase DS eutectic composites.

Fig. 3. Experimental SAED patterns taken from (a) $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ and (c) $\text{MoSi}_2/\text{Mo}_5\text{Si}_3\text{C}$ interface regions. (b) and (d) are corresponding schematic illustrations for (a) and (c), respectively. Solid circles and open squares in the schematics indicate diffraction spots from $\text{Mo}_5\text{Si}_3\text{C}$, and Mo_5Si_3 (b) or MoSi_2 (d), respectively.

Fig. 4. Atomic-resolution HAADF-STEM images of (a) $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ and (b) $\text{MoSi}_2/\text{Mo}_5\text{Si}_3\text{C}$ interfaces. Black arrows in (a) indicate the positions of some traces of the $(110)_{\text{Mo}_5\text{Si}_3}$ planes and the $(10\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ planes. (c) Schematic illustration of the $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interface shown in (a). Only the atomic columns of Mo are indicated in (c).

Fig. 5. (a) Stress-strain curves of the DS three-phase (2 at.%C) and two-phase (binary) eutectic composites tested in compression along $[1\bar{1}0]_{\text{MoSi}_2}$ parallel to the growth direction. (b) Temperature dependence of yield stress of the DS composites.

Fig. 6. Deformation markings observed on (a) $(\bar{1}\bar{1}0)_{\text{MoSi}_2} // (\bar{1}10)_{\text{Mo}_5\text{Si}_3} // (\bar{2}3\bar{1}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ and (c) $(001)_{\text{MoSi}_2} // (110)_{\text{Mo}_5\text{Si}_3} // (41\bar{5}0)_{\text{Mo}_5\text{Si}_3\text{C}}$ of the DS three-phase composite deformed at 1000 °C. (b) and (d) the schematic illustrations of the phase distribution and some typical slip traces in (a) and (c), respectively.

Fig. 7. Schematic illustrations of the misfit accommodation by tilting $\text{Mo}_5\text{Si}_3\text{C}$ about $[0001]_{\text{Mo}_5\text{Si}_3\text{C}}$ by the tilt angle ϕ with respect to the other component phases. Dashed and dashed-and-dotted lines correspond to the misfit-accommodated interfaces.

Fig. 8. Interface inclination angle θ as a function of tilt angle ϕ for the $\text{Mo}_5\text{Si}_3/\text{Mo}_5\text{Si}_3\text{C}$ interfaces. Chain and dotted lines indicate the observed tilt angle ϕ and inclination angles θ , respectively.

Fig. 9. Interface inclination angle θ as a function of tilt angle φ for the $\text{MoSi}_2/\text{Mo}_5\text{Si}_3\text{C}$ interfaces. Chain and dotted lines indicate the observed tilt angle φ and inclination angles θ , respectively.