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Yield stress anomaly controlled by the phase stability in $NbSi_2$ single crystals

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Effects of alloying elements on the deformation behavior of C40-$NbSi_2$ were examined. Yield stress anomaly (YSA), caused by the formation of a dragging atmosphere around dislocations, was found to be controlled by two factors. Dragging atmospheres were considered to be formed by point defects such as vacancies at 900–1200 °C and by substitutional elements at higher temperatures. Variation in YSA depended on the phase stability at higher temperatures. The magnitude of the YSA could be enhanced by increasing the stability of the $C11_b$-phase in C40-$NbSi_2$.

Keywords: Transition metal silicides; Dislocation; Plastic deformation; Refractory metals; Yield stress anomaly

In the context of developing ultrahigh temperature structural materials capable of withstanding temperatures above 1400 °C, $C11_b$-$MoSi_2$-based transition-metal silicide alloys have received significant attention [1–3]. In the $MoSi_2$-based silicide alloys, C40-$NbSi_2$ is a promising candidate for use as the strengthening phase [4–11]. It is known that transition-metal disilicides exhibit three typical crystal structures, $C11_b$, C40 and C54, which are closely related to one another. Although their unit cells are different, with $C11_b$, C40, and C54 exhibiting tetragonal, hexagonal, and orthorhombic structures, respectively, all three structures commonly possess similar atomic planes on which Si atoms are hexagonally arranged around transition metal atoms. These are the (1 1 0), (0 0 0 1) and (0 0 1) planes in the $C11_b$, C40 and C54 structures, respectively. The structures essentially differ only in the stacking sequences of the atomic layers. The $C11_b$, C40 and C54 structures are based on two, three- and fourfold stacking sequences of atomic layers, respectively [5,6]. This similarity in the crystal structures is assumed to strongly affect the plastic deformation behavior of C40-$NbSi_2$. In $NbSi_2$, only the (0 0 0 1) basal slip is dominantly operative, and the critical resolved shear stress (CRSS) is known to increase with increasing temperature at around 1400 °C; the so-called yield stress anomaly (YSA) appears at high temperatures [5,6,12,13]. We previously found that adding small amounts of Mo and W into $NbSi_2$ strongly enhanced the YSA behavior [6]. Further, peculiar plastic deformation behaviors, like the appearance of significant serration on the stress–strain curve and negative strain rate dependence of flow stress, were found to occur during YSA [6]. The operative $a/3\langle 2\bar{1}\bar{1}0\rangle$ superdislocation in $NbSi_2$ is known to dissociate into two partial dislocations on the basal plane following the equation [5,12]:

$$a/3\langle 2\bar{1}\bar{1}0\rangle \rightarrow a/6\langle 2\bar{1}\bar{1}0\rangle + \mathrm{SISF} + a/6\langle 2\bar{1}\bar{1}0\rangle \qquad (1)$$

In this equation, SISF represents the superlattice intrinsic stacking fault. From this evidence, we proposed that the Suzuki effect, which involves the formation of a dragging atmosphere around the SISF and $a/6\langle 2\bar{1}\bar{1}0\rangle$ partial dislocations, is the origin for the YSA behavior [6]. However, the material that forms the atmosphere around the SISF and dislocations is yet to be clearly characterized and understood. We pointed out that the small amount of substitutional elements which stabilize the $C11_b$ elements, such as Mo and W, are the most plausible candidates to cause the above-mentioned effect, because the atomic arrangements around the SISF in the C40 structure are locally identical to the four layers in the $C11_b$ structure owing to the crystal structure similarity described above. However, the influence of point defects such as vacancies [14] cannot be completely ruled out, because binary $NbSi_2$, without $C11_b$

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stabilizing elements, also shows YSA, although the magnitude of the YSA is rather small. In this study, 10 $NbSi_2$-based ternary single crystals with various alloying elements were prepared and, by comparing their plastic deformation behaviors, the factor controlling the YSA was systematically elucidated.

In our experiments, 10 master ingots, with compositions of $(Nb_{0.97}X_{0.03})Si_2$ (X = Mo, W, Re, Cr, Ti, or Fe), $(Nb_{0.90}Y_{0.10})Si_2$ (Y = Mo, W, or Ta) and $Nb(Si_{0.97}Al_{0.03})_2$, were prepared by melting high-purity raw materials in a plasma arc furnace. Hereinafter, we will denote $(Nb_{0.97}X_{0.03})Si_2$ as 3X crystal. Hence, for example, $(Nb_{0.97}Mo_{0.03})Si_2$ will be denoted as 3Mo crystal. The elements added were classified into four groups, depending on their crystal structures in the binary XSi_2 silicide. Mo, W and Re, which stabilize the $C11_b$ structure, comprised group I. It is noteworthy that a recent report clarified that $ReSi_2$ exhibits a higher-order $C11_b$ structure, in which the structural vacancies are arranged in the specific lattice sites with a composition of $ReSi_{1.75}$ [15]. Cr and Ta, which stabilize the C40 structure, as in the case of $NbSi_2$, were included in group II. Ti, which stabilizes the C54 structure, was in group III. Although Al substituted Si but not Nb sites, Al was also classed in group III. Fe was classified as a group IV element. Although $FeSi_2$ exhibits two crystal structures, depending on the temperature, both structures are unrelated to C40-$NbSi_2$. An important feature of the high-temperature β-$FeSi_2$ phase is that, unlike the other dicilisides, it possesses a wide solubility range in nonstoichiometric compositions [16]. Thus, addition of Fe might be expected to increase the structural vacancies in $NbSi_2$. Single crystals with C40 structure were grown using the floating-zone method at a growth rate of 5 mm h^{-1} under the flow of high-purity argon. Variations in the lattice constants of the crystals caused by the addition of various elements were analyzed by X-ray diffraction (XRD) to evaluate the changes in the stability of C40-phase in the crystals caused by the addition of the elements [6]. Compression tests were conducted using approximately 2 mm × 2 mm × 5 mm specimens. The loading axis was set at 45° from the (0001) on the $[01\bar{1}0]$ zone axis, where the Schmid factor of the primary $(0001)[2\bar{1}\bar{1}0]$ slip was 0.5. Compression tests were conducted in a vacuum at a temperature in the range of 500–1700 °C and at a nominal strain rate of $1.67 \times 10^{-4}\ s^{-1}$. Two-face slip trace analyses were conducted after the tests to confirm that only the (0001) basal slip was operative in all the crystals.

Figure 1 shows the temperature dependence of CRSS for the $(0001)[2\bar{1}\bar{1}0]$ slip (τ_y), which was estimated from the yield stress (σ_y) as $\tau_y = 0.5 \times \sigma_y$. The addition of the third element varied the curve profiles at all temperature regions. In particular, the magnitudes of YSA with peak temperatures in the range of 1300–1600 °C varied significantly depending on the third element species. The effects of the third element on the deformation behavior at intermediate and high temperatures taking place before and during the occurrence of YSA, respectively, will be discussed individually.

To elucidate the typical deformation behavior at intermediate temperatures, we chose to focus on the behavior at 900 °C. The CRSS of $(Nb, X)Si_2$ crystals showed a rapid decrease with increasing temperature at low temperatures. However, at around 900 °C, the temperature dependence of CRSS showed a plateau in all the crystals except 3Fe. It is worth mentioning here that the absolute value of the CRSS at this plateau region differed for different crystals, and the strengthening effect caused by the third element addition depended on the atomic species. The magnitude of strengthening could not be explained on the basis of the variation in the stability of the C40 phase, as will be described later; instead, the effect of solid solution hardening is expected to be the controlling factor. In the classical model developed by Fleischer [17,18], the atomic size mismatch (lattice mismatch) parameter, $\varepsilon_r = 1/r \cdot dr/dc$ (with r and c denoting the atomic radius and solute concentration, respectively), and the modulus mismatch parameter, $\varepsilon_G = 1/G \cdot dG/dc$ (where G is the shear modulus), are considered to affect the magnitude of solid solution strengthening by inducing the misfit strain ε according to the following equation:

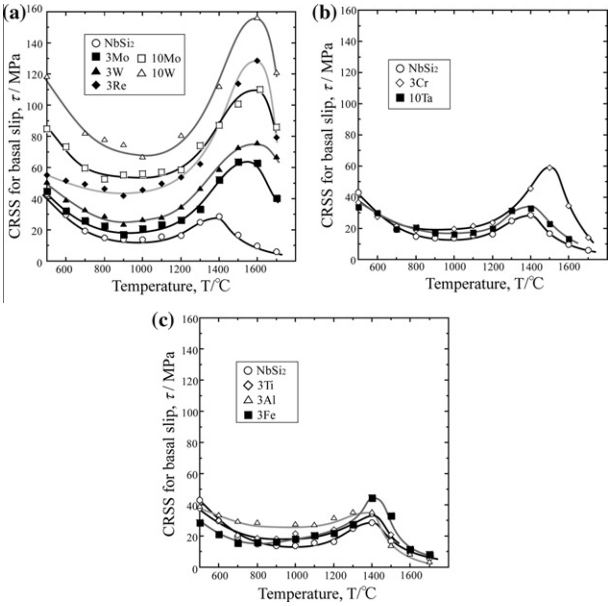

Figure 1. Variations in temperature dependence of CRSS for $(0001)[2\bar{1}\bar{1}0]$ basal slip due to the addition of various third elements. Effects of adding (a) Mo, W and Re (group I); (b) Cr and Ta (group II); and (c) Ti, Al (group III) and Fe (group IV).

$$\varepsilon = |\varepsilon_{G'} - \beta\varepsilon_r| \tag{2}$$

In this equation, $\varepsilon'_G = \varepsilon_G/(1 + 0.5|\varepsilon_G|)$, and β is a constant related to the character of operative dislocation. As the mixed dislocation with its Burgers vector inclined at 60° to the dislocation line is dominantly operative in $NbSi_2$ [6], β is assumed to take the value of 12 [18]. According to this model, the magnitude of solid solution strengthening Δτ is proportional to $\varepsilon^{3/2} \cdot c^{1/2}$. Table 1 lists the r (metallic radius) and G values of the substitutional elements added. Using these values, the relationship between the solid solution strengthening parameter, $\varepsilon^{3/2} \cdot c^{1/2}$, and the actual stress increment value Δτ measured by the experiments described here as $\Delta\tau = \tau_{(Nb,\ X)Si2} - \tau_{NbSi2}$ at 900 °C was examined, and is shown in Figure 2. Δτ tended to increase when $\varepsilon^{3/2} \cdot c^{1/2}$ values increased, although the data points were somewhat scattered. This suggested that the strengthening at 900 °C was governed mainly by the conventional