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Effects of Alloying Elements Hf, Sn, Ta, Zr, Dy and Ho on the Microstructure and Mechanical Properties of Nb-Nb₅Si₃ Alloy: Postprint

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Abstract

This work comprehensively reviews research conducted by the authors over the past several years on the effects of Hf content on Ni-16Si, Hf and Sn on Ni-20Ti-5Cr-3Al-18Si, Zr content on Ni-22Ti-16Si, Ta content on Nb-22Ti-16Si-7Cr-3Al, and rare earth elements Dy and Ho on Ni-23Ti-10Ta-2Cr-18Si and Ni-22Ti-16Si-7Cr-3Al-3Ta-2Hf alloys, focusing on their microstructure and mechanical properties. The addition of alloying elements Hf, Zr, Sn+Hf, Ta, Dy, and Ho to Nb-Si binary or multicomponent alloy systems significantly improves their room-temperature and high-temperature yield strength, ductility, and fracture toughness. The enhancement in strength is associated with solid solution strengthening by the alloying elements, while the improvement in ductility and toughness is related to factors such as microstructural refinement and an increased number of solid solution (Nb, Ti)_{ss} particles exceeding the critical size.

Full Text

Preamble

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Effects of Alloying Elements Hf, Sn, Ta, Zr, Dy, and Ho on Microstructure and Mechanical Properties of Nb-Nb₅Si₃ Alloys

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Abstract

This paper reviews the research works on effects of alloying elements on the microstructure and mechanical properties of Nb-Si alloys conducted by the authors in recent years, including the effects of Hf on Nb-16Si, Hf and Sn on Nb-20Ti-5Cr-3Al-18Si, Zr on Nb-22Ti-16Si, Ta on Nb-22Ti-16Si-7Cr-3Al, and rare earth elements Dy and Ho on Nb-23Ti-10Ta-2Cr-18Si and Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf, respectively. The addition of elements Hf, Zr, Sn+Hf, Ta, Dy, and Ho to Nb-Si binary or multi-component systems significantly enhances room- and high-temperature strength, plasticity, and fracture toughness. The strength enhancement is related to solid solution strengthening by the alloying elements, while the improvement in plasticity and toughness is associated with microstructural refinement and an increased number of (Nb, Ti)_{ss} particles exceeding the critical size.

KEY WORDS Nb₅Si₃, alloying element, microstructure, mechanical property

Introduction

The intermetallic compound Nb₅Si₃ offers promising potential as a next-generation high-temperature structural material for turbine blades operating at 1200–1400 °C, owing to its high melting point (2520 °C), low density (7.16 g/cm³), and excellent high-temperature strength. However, its complex crystal structure and extremely low room-temperature plasticity have hindered practical applications. Introducing a ductile Nb phase to fabricate Nb/Nb₅Si₃ in-situ composites significantly improves room-temperature plasticity and fracture toughness, but at the expense of high-temperature strength. Consequently, researchers have employed various approaches to achieve an optimal balance between room-temperature plasticity and high-temperature strength, with alloying being the most common method. Extensive studies have been conducted on alloying with Ti, Cr, Al, Mo, W, and V, yielding some beneficial results, though not yet reaching the required strength-toughness levels for practical applications.

Hf is an alloying element that can toughen the Nb solid solution (Nb_{ss}) without increasing its ductile-to-brittle transition temperature, while also reducing the pest sensitivity of Nb/Nb₅Si₃ alloys. Sn addition can eliminate the pest phenomenon in the 750–950 °C range. However, few studies have investigated the combined effects of Hf and Sn on Nb/Nb₅Si₃ alloys. Ta, belonging to the same VB group as Nb, can potentially strengthen Nb_{ss} through solid solution strengthening, thereby improving the high-temperature strength of Nb/Nb₅Si₃ alloys. The effects of rare earth elements Dy and Ho on the microstructure and mechanical properties of Nb/Nb₅Si₃ in-situ composites have not been reported

to date. Additionally, the influence of Zr element and directional solidification processes has rarely been investigated.

Accordingly, our research group has systematically studied the effects of Hf content on Nb-16Si, Hf and Sn on Nb-20Ti-5Cr-3Al-18Si, Zr content on Nb-22Ti-16Si, Ta content on Nb-22Ti-16Si-7Cr-3Al, and rare earth elements Dy and Ho on Nb-23Ti-10Ta-2Cr-18Si and Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf (at%) alloys, aiming to identify approaches for simultaneously enhancing the strength and toughness of (Nb, Ti)_{ss}/(Nb, Ti)₅Si₃ alloys. This paper provides a comprehensive review of these research efforts. In all studies, button ingots were prepared as test samples. High-purity elemental raw materials were melted in an arc furnace with a non-consumable tungsten electrode under Ar atmosphere, with at least five remelting cycles to ensure compositional homogeneity. Since the weight loss of the ingots was less than 0.5%, the actual composition was considered consistent with the nominal composition. Compression samples measuring 4 mm × 4 mm × 6 mm and other test specimens were cut from the lower central portion of the ingots using wire electrical discharge machining. For directional solidification samples, master alloys were melted in a 1 kg non-consumable tungsten electrode arc furnace and directionally solidified in an optical floating zone furnace at growth rates of 6.9 and 12 mm/h under Ar atmosphere to produce rods with a diameter of 8 mm and height of 70 mm; various specimens were then cut from the center of these rods. Phase identification and microstructural observation were performed using a D/Max-2500CC X-ray diffractometer (XRD) and an S-3400 scanning electron microscope (SEM). The chemical compositions of various phases were analyzed using an EPMA-1610 electron probe microanalyzer (EPMA). A JEM-2010 transmission electron microscope (TEM) was employed to identify new phases and conduct high-resolution structural observations. Room- and high-temperature compressive properties were tested on a Gleeble-1500 electro-servo thermal simulation testing machine.

1.1 Effects on Microstructure

Backscattered electron (BSE) images of Nb-16Si alloys with different Hf contents are shown in [Figure 1: see original paper][10]. Based on XRD and EPMA analysis results, the white phase is Nb_{ss} and the dark gray phase is Nb₃Si. In Hf-containing alloys, bright white particulate phases appear at phase boundaries with a chemical composition (at%) of 30.2Hf-1.9Nb-67.9O (Table 1 [10]), where Hf:O = 1:2, indicating that the bright white phase is HfO₂. Table 1 also shows that the Hf content in Nb₃Si is higher than in Nb_{ss}. The microstructure primarily consists of primary Nb_{ss} dendrites and fine Nb_{ss}/Nb₃Si eutectic. Hf addition significantly alters the microstructural morphology; as Hf content increases, the eutectic composition shifts toward lower Nb content, resulting in reduced eutectic cell quantity and obvious microstructural refinement characterized by increased primary Nb_{ss} particles and decreased eutectic cell size. When Hf content reaches 7%, the composition approaches the eutectic point, causing the eutectic cells to nearly disappear (Fig. 1d).

1.2 Effects on Fracture Toughness

The fracture toughness of Nb-16Si alloys with different Hf contents is presented in [Figure 2: see original paper][10]. The results show that fracture toughness increases with Hf content, rising from $5.6 \text{ MPa} \cdot \text{m}^{1/2}$ to $8.5 \text{ MPa} \cdot \text{m}^{1/2}$. This enhancement is closely related to microstructural changes. With increasing Hf content, the fine eutectic structure decreases while primary Nbss particles increase. Crack propagation observations (Fig. 3 [Figure 3: see original paper][10]) reveal that when cracks encounter larger primary Nbss phases, crack bridging and deflection are commonly observed, whereas cracks can propagate directly through the eutectic structure. Literature reports indicate that Nbss thickness exceeding a critical size can effectively hinder crack propagation, consistent with our observations. Since the Nbss particle size is larger than the critical size, cracks can be bridged and deflected, absorbing significant energy. In contrast, Nbss phases in the eutectic structure are smaller than the critical size and cannot prevent crack propagation, allowing cracks to pass straight through the eutectic. Hf-containing alloys contain more Nbss phases exceeding the critical size than binary Nb-Si alloys without Hf. Furthermore, Hf addition itself can improve the plasticity of Nbss; like Ti, Hf is one of the few elements that can enhance the plasticity and toughness of Nbss by reducing the Peierls-Nabarro energy barrier, thereby benefiting the overall toughness of the alloy. In summary, Hf addition to Nb-16Si binary alloys significantly modifies the microstructural morphology, refines the structure with increasing Hf content, and increases fracture toughness.

2.1 Effects on Microstructure

BSE images of Nb-20Ti-3Cr-3Al-18Si (alloy A), Nb-20Ti-3Cr-3Al-18Si-1.5Sn (alloy B), and Nb-20Ti-3Cr-3Al-18Si-1.5Sn-4Hf (alloy C) are shown in [Figure 4: see original paper][1]. XRD and EPMA analysis results indicate that the microstructure consists of gray-white (Nb, Ti)ss and (Nb, Ti)₅Si₃ phases. In alloys without Sn (alloy A) and with Sn only (alloy B), the (Nb, Ti)₅Si₃ phase belongs to the tetragonal β phase (gray), while in the alloy with both Sn and Hf (alloy C), the (Nb, Ti)₅Si₃ belongs to either the β phase or the Hf-rich hexagonal γ phase (white). The typical microstructure comprises primary (Nb, Ti)₅Si₃ and (Nb, Ti)ss+(Nb, Ti)₅Si₃ eutectic. As shown in Fig. 4, Sn addition alone does not significantly alter the microstructure (Figs. 4a and 4b). However, simultaneous addition of Sn and Hf causes obvious changes: the eutectic structure coarsens significantly, and Hf-rich phases precipitate along phase boundaries. Selected area electron diffraction analysis (Fig. 5 [Figure 5: see original paper][1]) reveals that the Hf-rich phase is β -(Nb,Ti)₅Si₃. EPMA analysis (Table 2 [1]) shows that in alloy B, Sn preferentially dissolves in (Nb, Ti)ss rather than (Nb, Ti)₅Si₃, while simultaneously reducing the Cr content in (Nb, Ti)ss, indicating that Sn decreases the solubility of Cr in (Nb, Ti)ss. However, Ti, Al, and Si contents are unaffected by Sn. In the Hf-containing alloy (alloy C), the Hf content in the Hf-rich γ -(Nb, Ti)₅Si₃ phase is three times higher than in β -

(Nb, Ti)₅Si₃, and the Ti content is also higher, demonstrating that Hf addition promotes Ti segregation in the Hf-rich phase. This reduces the Ti content in β -(Nb, Ti)₅Si₃, thereby decreasing its growth rate and contributing to eutectic coarsening. Other elements in (Nb, Ti)_{ss} and β -(Nb, Ti)₅Si₃ phases show no significant changes.

2.2 Effects on Room-Temperature Mechanical Properties

The Vickers hardness of the (Nb, Ti)_{ss} phase decreases with Sn addition but increases with Hf addition. The Vickers hardness of β -(Nb, Ti)₅Si₃ is insensitive to Sn addition but sensitive to Hf addition, showing a significant increase (Table 3 [1]). Therefore, Sn addition weakens the (Nb, Ti)_{ss} phase, while Hf addition strengthens both (Nb, Ti)_{ss} and β -(Nb, Ti)₅Si₃. The hardness of the γ -(Nb, Ti)₅Si₃ phase could not be measured due to its small size.

As shown in Table 3, the base alloy (alloy A) fractures before yielding with zero compressive plasticity. Alloy B, with 1.5% Sn addition, exhibits improved compressive plasticity of 2.1% but a reduced fracture strength of 126 MPa. Hf addition increases both yield strength and fracture strength: compared with alloy B, yield strength increases by 73 MPa and fracture strength by 166 MPa, while compressive plasticity rises to 6.3%. The lower room-temperature fracture strength of alloy B is primarily attributed to reduced Cr content in the (Nb, Ti)_{ss} phase, which weakens solid solution strengthening and increases plasticity. The strength enhancement in the Hf-containing alloy (alloy C) mainly results from significant solid solution strengthening of (Nb, Ti)_{ss} due to the large atomic size difference between Nb and Hf. The improved compressive plasticity is attributed to eutectic coarsening and compositional changes. The former increases (Nb, Ti)_{ss} thickness from 3.9 μ m in alloy A and 3.5 μ m in alloy B to 7.2 μ m in alloy C (Fig. 4). Thicker (Nb, Ti)_{ss} can effectively hinder crack propagation. The latter involves Hf addition reducing the Peierls-Nabarro energy barrier, thereby increasing the fracture toughness and plasticity of (Nb, Ti)_{ss}.

3.1 Effects on Microstructure

The as-cast microstructures of Nb-22Ti-16Si-7Cr-3Al alloys with different Ta contents (0, 2%, 5%, 10%) are shown in [Figure 6: see original paper][13]. When Ta content exceeds 5%, the microstructure consists of (Nb, Ti)_{ss}, β -(Nb, Ti)₅Si₃, and α -(Nb, Ti)₅Si₃ phases. With increasing Ta content, the α -(Nb, Ti)₅Si₃ phase increases while the β -(Nb, Ti)₅Si₃ phase decreases. This indicates that Ta addition promotes the transformation from β -(Nb, Ti)₅Si₃ to α -(Nb, Ti)₅Si₃, as Ta dissolved in the silicide stabilizes the α -(Nb, Ti)₅Si₃ phase, and the $\beta \rightarrow \alpha$ allotropic transformation readily occurs during solidification. The transformation becomes more complete with higher Ta content, yielding more α -(Nb, Ti)₅Si₃ phase.

Increasing Ta content also affects the composition of constituent phases. Energy dispersive spectroscopy analysis (Table 4 [13]) reveals that Ta can dissolve in

both (Nb, Ti)_{ss} and (Nb, Ti)₅Si₃ phases, with much greater solubility in (Nb, Ti)_{ss}. As Ta content increases, Si content in (Nb, Ti)_{ss} gradually rises from 1.81% in the Ta-free alloy to 8.87% in the 10% Ta alloy. According to the Nb-Si and Ta-Si binary phase diagrams, Si solubility in Ta is greater than in Nb at the same temperature; therefore, Ta addition promotes Si solubility in (Nb, Ti)_{ss}.

3.2 Effects on Compressive Properties

[Figure 7: see original paper][13] shows the room-temperature compressive yield strength and fracture strain of Nb-22Ti-16Si-7Cr-3Al alloys with different Ta contents. With increasing Ta addition, the room-temperature compressive yield strength continuously increases, attributed to solid solution strengthening by Ta. However, Ta content has no significant effect on room-temperature plasticity, as indicated by the fracture strain.

[Figure 8: see original paper][13] presents the compressive yield strength at 1000 °C for Nb-22Ti-16Si-7Cr-3Al alloys with different Ta contents. As Ta content increases from 0 to 5%, the compressive yield strength rises from 640 MPa to 790 MPa. At 10% Ta, the strength is 780 MPa, essentially the same as the 5% Ta alloy, indicating that Ta can further improve high-temperature strength. This is because Ta, as a high-melting-point element, reduces the alloy's diffusion coefficient and hinders high-temperature deformation, thereby increasing strength.

4 Effects of Alloying Element Zr

4.1 Effects of Zr Content on Microstructure

BSE images of as-cast Nb-22Ti-16Si alloys with different Zr contents (0, 2%, 3%, 4%) are shown in [Figure 9: see original paper][11]. XRD and EDS analysis (Table 5 [12]) identify the white phase as (Nb, Ti)_{ss} dendrites, the dark gray phase as (Nb, Ti)₃Si, and the black phase as γ -(Nb, Ti)₅Si₃. The (Nb, Ti)₃Si phase forms the matrix, with (Nb, Ti)_{ss} dendrites embedded in it, primarily distributed at the (Nb, Ti)_{ss}/(Nb, Ti)₃Si phase boundaries. Zr addition causes obvious microstructural coarsening, particularly increasing the size of the (Nb, Ti)_{ss} phase, likely by affecting the nucleation and growth kinetics of primary (Nb, Ti)_{ss} during solidification and increasing its average size. Zr also promotes the formation of eutectic structures composed of lamellar (Nb, Ti)_{ss} and black Ti- and Zr-rich γ -(Nb, Ti)₅Si₃ phases, as shown in [Figure 10: see original paper][11]. Table 5 shows that Zr content is highest in the γ -(Nb, Ti)₅Si₃ phase and lowest in the (Nb, Ti)₃Si phase, indicating that Zr preferentially dissolves in the (Nb, Ti)₅Si₃ phase, with its content in each phase increasing to varying degrees as overall Zr content increases.

High-resolution TEM (HRTEM) observations reveal that the (Nb, Ti)_{ss}/ γ -(Nb, Ti)₅Si₃ interface lacks a consistent orientation relationship, contrary to literature reports. In a 73.5Nb-25Si-1.5Zr alloy, a definite orientation relationship of

$\langle 001 \rangle \text{Nb}_5\text{Si}_3 // \langle 111 \rangle \text{Nb}$ and $\{110\}\text{Nb}_5\text{Si}_3 // \{011\}\text{Nb}$ was reported. [Figure 11: see original paper][11] shows that the $(\text{Nb}, \text{Ti})_{\text{ss}}/\gamma\text{-(Nb, Ti)}_5\text{Si}_3$ interface is smooth and planar without any interfacial intermediate phase, which is beneficial for alloy strength.

4.2 Effects of Zr Content on Compressive Properties

[Figure 12: see original paper][11] shows the room-temperature compressive properties of alloys with different Zr contents. With increasing Zr content, the room-temperature compressive yield strength increases, mainly due to solid solution strengthening by Zr. Lattice distortion caused by Zr dissolution increases deformation resistance, significantly enhancing room-temperature compressive yield strength. Microhardness measurements (Table 6 [11]) indicate that when Zr content is less than 1%, the solid solution strengthening effect on $(\text{Nb}, \text{Ti})_{\text{ss}}$ is weak while that on $(\text{Nb}, \text{Ti})_3\text{Si}$ is strong, so the increase in room-temperature yield strength is primarily caused by solid solution strengthening of $(\text{Nb}, \text{Ti})_3\text{Si}$. When Zr content exceeds 1%, both $(\text{Nb}, \text{Ti})_{\text{ss}}$ and $(\text{Nb}, \text{Ti})_3\text{Si}$ are solid-solution strengthened, increasing alloy strength. Additionally, the appearance of $(\text{Nb}, \text{Ti})_{\text{ss}}/(\text{Nb}, \text{Ti})_5\text{Si}_3$ eutectic structures creates more phase interfaces that effectively hinder dislocation glide, further increasing yield strength. The plasticity improvement may be related to appropriate coarsening of the ductile $(\text{Nb}, \text{Ti})_{\text{ss}}$ phase caused by Zr addition. When the $(\text{Nb}, \text{Ti})_{\text{ss}}$ phase is relatively fine, the brittle $(\text{Nb}, \text{Ti})_3\text{Si}$ phase constrains it strongly, making plastic deformation difficult. Larger $(\text{Nb}, \text{Ti})_{\text{ss}}$ particles experience less constraint from brittle phases, facilitating plastic deformation and interfacial debonding between ductile and brittle phases, thus increasing plasticity. The reduced plasticity in the alloy with 4% Zr may be due to further increased Zr content in the $(\text{Nb}, \text{Ti})_{\text{ss}}$ phase, enhancing solid solution strengthening and restricting plastic deformation.

[Figure 13: see original paper][12] presents the room-temperature compressive fracture morphologies of Nb-22Ti-16Si alloys with different Zr contents. The Zr-free alloy exhibits completely transgranular cleavage fracture (Fig. 13a), while Zr-containing alloys show mixed fracture characteristics of transgranular cleavage and interfacial debonding (Figs. 13b and 13c), accompanied by tearing ridges in the $(\text{Nb}, \text{Ti})_{\text{ss}}$ phase. Without Zr, the small $(\text{Nb}, \text{Ti})_{\text{ss}}$ particles lose their plastic deformation capability under constraint from brittle phases and fracture by cleavage. With Zr addition, the increased $(\text{Nb}, \text{Ti})_{\text{ss}}$ particle size promotes interfacial debonding, which reduces constraint on $(\text{Nb}, \text{Ti})_{\text{ss}}$ and creates free surfaces, enabling some plasticity and resulting in mixed fracture characteristics. At 3% Zr content, the alloy achieves a good combination of room-temperature strength and plasticity.

5.1 Effects on Microstructure

The as-cast microstructure of the Nb-23Ti-10Ta-2Cr-18Si alloy is shown in [Figure 14: see original paper][13]. XRD and selected area electron diffraction identify three phases: gray-white $(\text{Nb}, \text{Ti})_{\text{ss}}$, dark gray $\alpha\text{-(Nb, Ti)}_5\text{Si}_3$, and

black γ -(Nb, Ti) $_5$ Si $_3$. Adding 0.1% Dy significantly refines the microstructure, particularly reducing the size of the (Nb, Ti) $_5$ Si $_3$ phase and forming a small amount of bright white phase. EDS analysis shows its main chemical composition is 39.40% Dy and 59.79% O (Table 7 [13]), with a stoichiometric ratio of approximately Dy:O = 2:3, suggesting the bright white phase is Dy $_2$ O $_3$. Adding Ho to the Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf alloy produces even more pronounced refinement of grain size and (Nb, Ti) $_5$ Si $_3$ phase, with bright white phases forming at the (Nb, Ti) $_{ss}$ /(Nb, Ti) $_5$ Si $_3$ interfaces. Selected area electron diffraction identifies these as cubic Ho $_2$ Hf $_2$ O $_7$ oxide particles, 0.3–1.5 μ m in size, with an fcc structure and lattice parameter $a = 5.206$ nm, as shown in [Figure 15: see original paper][11]. The chemical compositions of (Nb, Ti) $_{ss}$, α -(Nb, Ti) $_5$ Si $_3$, γ -(Ti, Nb) $_5$ Si $_3$, and Dy $_2$ O $_3$ phases are listed in Table 7 [13]. The (Nb, Ti) $_{ss}$ phase contains Nb, Ti, and certain amounts of Ta, Cr, and Si. The α -(Nb, Ti) $_5$ Si $_3$ and γ -(Ti, Nb) $_5$ Si $_3$ phases also contain some Ta and Cr, with the former having higher Nb and lower Ti content than the latter. Adding 0.1% Dy has little effect on the chemical compositions of these three phases. The two silicide phases have different structures: α -(Nb, Ti) $_5$ Si $_3$ has a D 8_1 structure, while γ -(Ti, Nb) $_5$ Si $_3$ has a tI 32 structure.

The as-cast eutectic structure of the Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf alloy consists of α -(Nb, Ti) $_5$ Si $_3$ and (Nb, Ti) $_{ss}$ lamellae with an orientation relationship of $(002)_\alpha // (002)_{Nb}$ and $[310]_\alpha // [110]_{Nb}$, as shown in [Figure 16: see original paper][20]. The atomic structure at the α -(Nb, Ti) $_5$ Si $_3$ /(Nb, Ti) $_{ss}$ interface involves Nb atomic layers from the α -(Nb, Ti) $_5$ Si $_3$ phase bonding with the (Nb, Ti) $_{ss}$ phase, rather than pure Si layers or (Nb+Si) mixed layers. Edge dislocations are periodically arranged at the interface with a line direction of $[110]_{Nb}$, Burgers vector of $[110]_{Nb}$, and spacing of 2.1 nm to accommodate a 10.9% misfit strain. The interface is smooth without any amorphous phase, which is beneficial for mechanical properties. EDS line scanning shows that Dy exhibits a distinct peak at the (Nb, Ti) $_{ss}$ /(Nb, Ti) $_5$ Si $_3$ phase interface (Fig. 17 [Figure 13: see original paper]), indicating significant segregation of Dy to the interface, with minor solid solution in (Nb, Ti) $_{ss}$ and (Nb, Ti) $_5$ Si $_3$. The segregation ratio of Dy at the phase interface versus within the phases is approximately 2.5. This segregation occurs because Dy has a larger atomic radius (0.177 nm) than Nb and Si (0.148 nm and 0.117 nm, respectively), making the distortion energy from Dy solid solution higher than that from segregation at phase boundaries. To minimize distortion energy, Dy diffuses and segregates to phase and grain boundaries. This behavior is characteristic of rare earth elements with high surface activity, which can reduce surface tension and nucleation energy in the liquid state, increasing nucleation rate. Additionally, rare earth elements like Dy readily react with O and S in the melt to form oxides and sulfides that act as nucleation sites, accelerating solidification and refining grains and (Nb, Ti) $_5$ Si $_3$ phases. Ho exhibits similar effects to Dy.

5.2 Effects on Compressive Properties

Appropriate amounts of Dy and Ho can significantly improve the yield strength and fracture plasticity of (Nb, Ti)₅Si₃ eutectic alloys, as shown in Table 8 [14] and [Figure 18: see original paper][15]. Table 8 demonstrates that adding 0.1% Dy to the Nb-23Ti-10Ta-2Cr-18Si eutectic alloy significantly improves yield strength from room temperature up to 1200 °C and enhances room-temperature compressive plasticity. The yield strength increase is attributed to: (1) solid solution strengthening by Dy atoms, where lattice distortion from the larger Dy atoms increases deformation resistance; (2) interface strengthening, where Dy atoms segregated at interfaces fill vacancies, reducing interface sliding and propagation rates, while the surface-active element Dy reacts with O and S to form oxides and sulfides that purify interfaces and increase interfacial strength; and (3) fine-grain strengthening, as microstructural refinement generally benefits room- and intermediate-temperature strength and plasticity.

Similarly, adding 0.1% Ho to the Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf alloy improves yield strength from room temperature to high temperatures and significantly enhances room-temperature plasticity (Fig. 18). However, at 0.2% Ho content, mechanical properties deteriorate due to excessive precipitation of cubic Ho₂Hf₂O₇.

5.3 Effects of Directional Solidification

To further improve the mechanical properties of (Nb, Ti)₅Si₃ eutectic alloys, directionally solidified alloys were prepared using optical floating zone melting. The alloy composition was the same as the 0.1% Ho-containing alloy described above. The microstructural morphology is shown in [Figure 19: see original paper][14]. The longitudinal microstructure shows lamellar silicides growing parallel to the growth direction with a strong orientation relationship: the [110] direction of (Nb, Ti)_{ss} and the [310] direction of (Nb, Ti)₅Si₃ are parallel to the growth direction. HRTEM results indicate no definite crystallographic orientation relationship between (Nb, Ti)₅Si₃ and (Nb, Ti)_{ss} or between (Ti, Nb)₅Si₃ and (Nb, Ti)_{ss}, though the interfaces are clean without any interfacial phases, and the (Nb, Ti)₅Si₃ and (Ti, Nb)₅Si₃ phases bond well with the (Nb, Ti)_{ss} matrix, which is clearly beneficial for mechanical property improvement.

[Figure 20: see original paper][19] shows the true stress-true strain curves at 1623 K. After peak stress, the stress gradually decreases but remains at a high level. The directionally solidified alloy exhibits significantly higher true stress-true strain curves than the conventionally cast alloy, demonstrating superior high-temperature compressive yield strength.

Conclusions

1. The binary Nb-16Si alloy consists of primary Nb_{ss} and fine Nb_{ss}/Nb₃Si eutectic. Adding 1–7% Hf significantly refines the microstructure, increases

primary Nbss particles, decreases eutectic cell size, and produces small amounts of HfO₂ at phase boundaries. The ternary Nb-16Si-22Ti alloy consists of (Nb, Ti)_{ss} and (Nb, Ti)₃Si phases. Adding 2–4% Zr coarsens the microstructure, enlarges (Nb, Ti)_{ss}, and promotes formation of (Nb, Ti)_{ss} + γ -(Nb, Ti)₅Si₃ eutectic.

2. The multi-component Nb-20Ti-3Cr-3Al-18Si alloy consists of primary (Nb, Ti)₅Si₃ and (Nb, Ti)_{ss}+(Nb, Ti)₅Si₃ eutectic. Adding 1.5% Sn has no obvious effect on microstructure. Adding 1.5% Sn + 4% Hf significantly coarsens the eutectic structure and precipitates Hf-rich γ -(Nb, Ti)₅Si₃ phases along phase boundaries. The multi-component Nb-22Ti-16Si-7Cr-3Al alloy consists of (Nb, Ti)_{ss} and β -(Nb, Ti)₅Si₃ phases. When Ta content exceeds 5%, the microstructure contains (Nb, Ti)_{ss}, β -(Nb, Ti)₅Si₃, and α -(Nb, Ti)₅Si₃ phases, with the α phase increasing and β phase decreasing as Ta content rises.
3. The multi-component Nb-22Ti-10Ta-2Cr-18Si and Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf alloys consist of (Nb, Ti)_{ss}, α -(Nb, Ti)₅Si₃, and γ -(Ti, Nb)₅Si₃ phases. Adding 0.1% Dy to the former alloy significantly refines the microstructure, reduces (Nb, Ti)₅Si₃ phase size, and forms bright white Dy₂O₃ phases at phase boundaries. Adding 0.1% Ho to the latter alloy produces even more pronounced refinement of grain size and (Nb, Ti)₅Si₃, with Ho₂Hf₂O₇ oxide particles forming at phase boundaries. After directional solidification, the (Nb, Ti)₅Si₃ phases grow parallel to the growth direction.
4. The as-cast eutectic structure of Nb-22Ti-16Si-7Cr-3Al-3Ta-2Hf alloy consists of α -(Nb, Ti)₅Si₃ and (Nb, Ti)_{ss} lamellae with orientation relationship $(002)\alpha // (002)\text{Nb}$, $[310]\alpha // [110]\text{Nb}$. The interfacial atomic structure consists of Nb atomic layers from the α -(Nb, Ti)₅Si₃ phase bonding with (Nb, Ti)_{ss}, rather than Si layers or (Nb+Si) mixed layers. The interface is smooth without amorphous phases. In contrast, the (Nb, Ti)_{ss}/ γ -(Nb, Ti)₅Si₃ interface in Nb-22Ti-16Si alloy has no consistent orientation relationship but is smooth and planar without intermediate phases, which is beneficial for mechanical properties.
5. Adding alloying elements Hf, Zr, Sn+Hf, Ta, Dy, and Ho to Nb-Si binary or multi-component alloys significantly improves room- and high-temperature compressive yield strength, plasticity, and fracture toughness. The strength enhancement is related to solid solution strengthening by the alloying elements, while the plasticity and toughness improvement is associated with microstructural refinement and increased numbers of (Nb, Ti)_{ss} particles exceeding the critical size.

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