

The effect of Nb, Ti introduction sequence on the adsorption of Nb on TiB₂ surface and grain refinement performance of Al-4Ti-1Nb-1B

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Abstract: In recent years, Al-Ti-Nb-B grain refiners have attracted increasing attention due to their grain refinement performance and anti Si-poisoning ability. This study investigates the influence of the introduction sequence of Ti and Nb during the synthesis of Al-4Ti-1Nb-1B refiners on their refinement performance and Si poisoning resistance. It is found that Al-4Ti-1Nb-1B prepared by introducing Ti prior to Nb exhibits the best grain refinement and anti-Si poisoning properties, refining Al-7Si to $150.12 \pm 27.5 \mu\text{m}$. This superior performance is attributed to the fact that the variation in ground-state energy ΔE for the Ti prior to Nb sequence is lower than that of other sequences, thereby facilitating Nb adsorption on the TiB₂ surface. TEM observations corroborate these findings, showing that TiB₂ prepared by this sequence has the highest average Nb content of 3.80 at.%. First-principles calculations reveal that this unique Nb adsorption enhances the TiB₂/Al interfacial adhesion energy W_{ad} and suppresses the segregation tendency of Si atoms at the interface, $\kappa_{Si}(c_{Si})$. The higher the Nb adsorption at the TiB₂/Al interface, the stronger the resistance to Si poisoning. These findings underscore the pivotal role of Nb-modified TiB₂ in improving grain refinement and offer a novel strategy for advancing grain refiner technologies in Al-Si alloys.

Keywords: Introduction sequence, grain refinement, Nb adsorption, nucleation mechanism.

1 Introduction

Cast Al-Si alloys are widely used in modern industries, such as aerospace, aviation, construction, and transportation, due to their excellent castability, lightweight nature, and corrosion resistance [1-4]. During the casting of Al-Si alloys, grain refinement is a critical process, as it effectively refines primary α -Al grains, thereby improving both the castability and mechanical properties of the alloys [5, 6]. Currently, the most common grain refinement strategy involves the addition of grain refiners into the Al-Si melt [7, 8]. Among which the Al-5Ti-1B grain refiner is the most extensively used. However, during practical applications, the presence of Si in the Al-Si melt can lead to the formation of silicides, such as TiSi₂ and Ti₅Si₃ on the surface of TiB₂ particles in Al-5Ti-1B [9, 10]. These silicides inhibit the heterogeneous nucleation of α -Al, resulting in a significant deterioration of grain refinement performance in Al-Si alloys [11, 12], especially Al-Si alloys with Si content exceeding 5 wt.%, which is commonly known as the Si-poisoning effect.

In recent years, novel grain refiners have been developed to overcome the issue of Si-poisoning in Al-Si

alloys. Nb has attracted attention due to its ability to form NbAl₃ and NbB₂ phases, which are analogous to TiAl₃ and TiB₂ in Al-5Ti-1B. Consequently, Al-Nb-B grain refiners were developed and have demonstrated better grain refinement performance in Al-Si alloys compared to conventional Al-5Ti-1B refiners [13-15]. This improvement is primarily attributed to the higher thermodynamic stability of NbAl₃ compared to TiAl₃, which makes it less reactive with Si to form Nb-based silicides such as NbSi₂, Nb₃Si, and Nb₅Si₃ [16-18]. However, the limited anti-fading performance of Al-Nb-B restricts its widespread industrial application [19, 20]. To address this limitation, researchers have attempted to integrate the advantages of both Ti and Nb, leading to the development of Al-Ti-Nb-B grain refiners. Xu et al. [21] developed an Al-1.67Ti-3.33Nb-0.5B refiner and reported that (Nb, Ti)B₂ particles acted as highly effective heterogeneous nucleation sites for α -Al in Al-Si alloys. Li et al. [22, 23] introduced Ti into the Al-Nb-B melt, forming (Nb, Ti)B₂ core-shell structure with TiB₂ as the core and NbB₂ as the shell, which also exhibited excellent resistance to Si poisoning. Wu et al. [24]

synthesized an Al-3.5Nb-1Ti-1B refiner containing (Ti, Nb) B_2 particles with a distinctive sandwich-like Nb-Ti-Nb structure, achieving notable refinement performance in Al-Si alloys. Additionally, Li et al. [25-27] developed the TCB refiner based on the Al-Ti-B-C system, and Xue et al. [28] proposed an Al-4.2V-1.8B refiner. Both refiners also demonstrated excellent refinement efficiency in Al-Si alloys and provide valuable insights into overcoming Si poisoning.

Among these recently developed grain refiners, Al-Ti-Nb-B has emerged as a promising and significant candidate. Our previous study [29] observed a nanoscale Nb adsorption layer on the (01 $\bar{1}$ 0) plane of TiB_2 , which can activate TiB_2 as an effective heterogeneous nucleus for α -Al. The composition design and processing parameters significantly influence the morphology and structure of the resulting borides. Ti and Nb are the two most critical refining elements in the Al-Ti-Nb-B system, and the sequence in which they are introduced plays a crucial role in achieving Nb adsorption on the TiB_2 surface, thereby affecting both the grain refinement efficiency and Si-poisoning resistance.

In this study, Al-4Ti-1Nb-1B grain refiners were prepared via different sequences for introducing Ti and Nb to investigate their influence on Nb adsorption at the TiB_2 surface and refinement performance. The grain refinement performance of the prepared refiners were evaluated on CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si alloys. The Nb adsorption behavior on the TiB_2 surface was quantitatively characterized and compared via TEM

and EDS line-scanning techniques. First-principles calculations were further applied to elucidate the mechanisms underlying Nb atom adsorption and its impact on grain refinement performance and Si-poisoning resistance. These findings provide valuable guidance for the innovative design of Al-Ti-Nb-B grain refiners and contribute to the development of more efficient grain refinement strategies for Al-Si alloys.

2 Experiment method

2.1 Preparation process of Al-4Ti-1Nb-1B master alloys

A series of Al-Ti-Nb-B alloys were synthesized via different Nb and Ti introduction sequences. Al-10Ti and Al-8B master alloys were first put into a SiC crucible at a stoichiometric Ti/B ratio of 2.2 and melted at 800 °C. The melt was stirred and held for 30 min to ensure the complete formation of TiB_2 . Subsequently, as illustrated in Fig. 1, Al-10Nb and Al-10Ti were introduced into the melt in three different sequences, followed by an increase in temperature to 900 °C. Fig. 1(a) shows the process in which Nb was added prior to Ti; the resulting refiner is labeled as A-Al-4Ti-1Nb-1B (hereafter referred to as Sample A). In contrast, Fig. 1(b) depicts the process where Ti was added before Nb, producing a refiner designated as B-Al-4Ti-1Nb-1B (Sample B). Fig. 1(c) illustrates the simultaneous addition of Ti and Nb, resulting in C-Al-4Ti-1Nb-1B (Sample C). During the holding time, all melts were stirred using a graphite rod at a constant rotation speed. Finally, the melt was poured into a plate-shaped mold preheated to 200 °C.

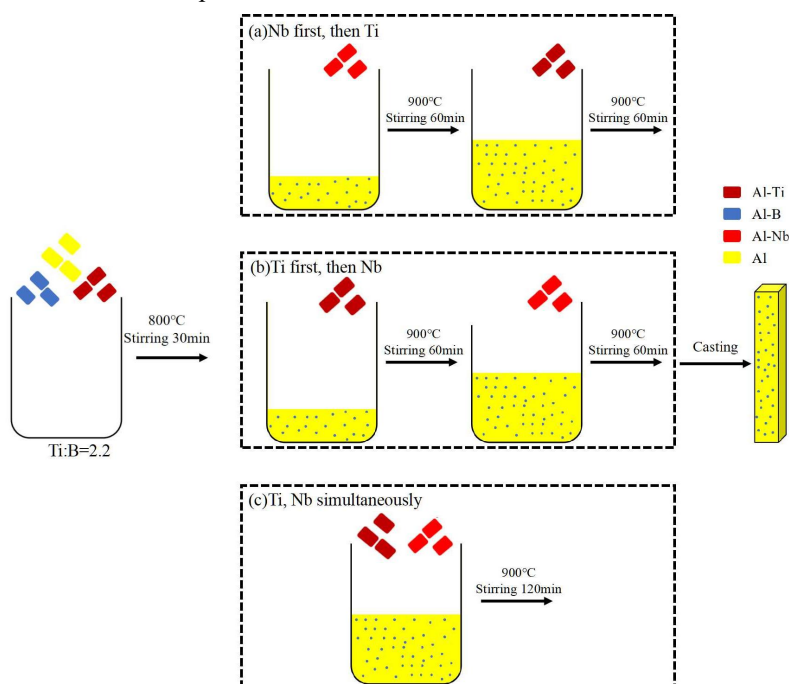


Fig. 1 Schematic diagram of the processing route for introducing Nb and Ti

2.2 Grain refinement experiments of Al-4Ti-1Nb-1B master alloys

To comprehensively evaluate the grain refinement performance of Al-4Ti-1Nb-1B prepared with different Nb and Ti introduction sequences, a series of Al-Si alloys (CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si) were fabricated by melting CP-Al ($\geq 99.9\%$) with Al-20Si alloys. To modify the eutectic Si phase, 0.2 wt.% Al-10Sr was added, followed by the addition of 0.5 wt.% Al-4Ti-1Nb-1B grain refiners at 720 °C. The melt was immediately stirred with a graphite rod for 1 min to promote complete melting and uniform dispersion of the grain refiners, and held for 2 min. Then the melt was cast into a KBI cylindrical steel mold (Φ 75 mm $\times$ 25 mm) [30], which was placed on a refractory brick preheated to 200 °C, as illustrated in Fig. 2. The cooling rate under

this solidification condition was approximately 0.4 °C/s. For comparison, a commercial Al-5Ti-1B refiner (provided by AMG) was also conducted under same casting conditions to refine the Al-Si alloys. The detailed parameters for the grain refinement experiments are summarized in Table 1.

To accurately determine the grain size of the refined α -Al phase, the surfaces of the aluminum ingots in contact with the refractory brick were ground and polished. An electrolytic corrosion test was conducted using a WY-06 model apparatus, applying an anode coating with a 1 wt.% fluoboric acid solution. The α -Al grain size was observed using a polarized optical metallographic microscope (SG-51) and measured by the mean linear intercept method in accordance with ASTM E112-10.

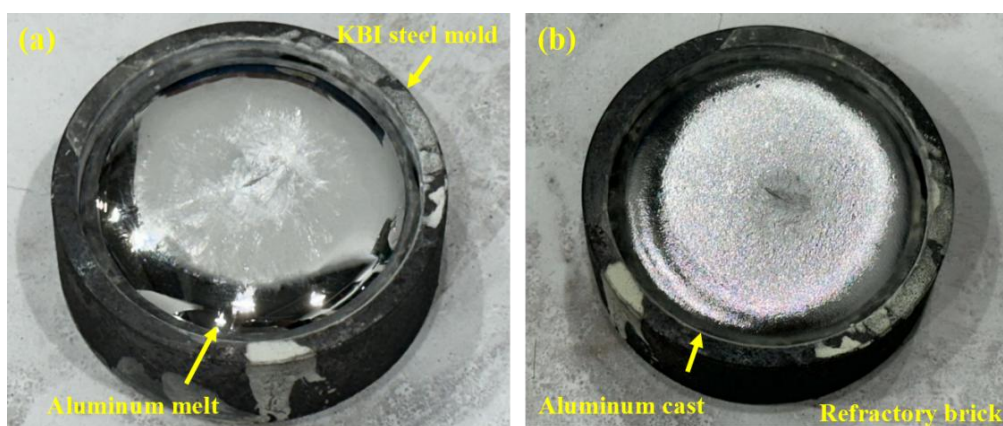


Fig 2 KBI standard solidification experiment: (a) Aluminum melt poured into KBI ring mold; (b) Solidified aluminum casting.

Table 1 Experimental parameters of grain refinement.

Grain refiner	Addition level/wt.%	Aluminum
Sample A	0.5	CP-Al
		Al-3.5Si
		Al-7Si
		Al-10.5Si
Sample B	0.5	CP-Al
		Al-3.5Si
		Al-7Si
		Al-10.5Si
Sample C	0.5	CP-Al
		Al-3.5Si
		Al-7Si
		Al-10.5Si
Al-5Ti-1B	0.5	CP-Al
		Al-3.5Si
		Al-7Si
		Al-10.5Si

2.3 Characterization of Al-4Ti-1Nb-1B master alloys

Samples were sectioned from Al-4Ti-1Nb-1B. After ground and polished, the microstructure of the Al-4Ti-1Nb-1B was observed using a field emission scanning electron microscope (Phenom-XL G2), and elemental distribution was analyzed via the integrated energy-dispersive X-ray spectroscopy (EDS). To precisely investigate Nb adsorption on the surface of TiB_2 particles, site-specific slices containing representative TiB_2 particles were prepared by focused ion beam (FIB) milling using a Helios G4 CX system. The particle structure and elemental adsorption at nucleation sites were further examined by transmission electron microscopy (Talos F200X).

2.4 First-principle calculations

First-principles calculations based on the density functional theory (DFT) were performed using the Vienna Ab-initio Simulation Package (VASP) in this study [31-35]. Perdew-Burke-Ernzerhof (GGA-PBE) exchange correlation functional was used to calculate the electronic correlation function, and conjugate gradient algorithm was applied to optimize the geometry. The plane-wave cutoff energy of diboride/Al interface system was set to be 450 eV, and the self-consistency convergence criteria for energy tolerance was 10^{-6} eV/atom. Relevant interface models were constructed by

Materials Studio. To ensure adequate space for all atoms and full relaxation of cells, a vacuum layer of 15 Å was reserved for the surface supercell.

3 Results

3.1 Microstructure of Al-Ti-Nb-B alloys

Fig. 3 presents the microstructures of Al-4Ti-1Nb-1B alloys prepared with different Ti and Nb introduction sequences. The alloys primarily contain two secondary phases: MAI_3 (where $M = \text{Ti}$ or Nb) and TiB_2 . The composition and morphology of the MAI_3 phase have been analyzed and discussed in our previous study [36]. Therefore, this work focuses on the characterization and analysis of TiB_2 in the different Al-4Ti-1Nb-1B samples. All three preparation methods yield fine, particulate TiB_2 phases with particle sizes ranging from approximately 0.5 to 3 μm . There is no significant difference in the size or distribution of TiB_2 particles among the different processing routes. The TiB_2 particles exhibit polyhedral morphology, with some degree of agglomeration observed. EDS mappings confirm the overlapping distribution of Ti and B, indicating the formation of TiB_2 . Furthermore, both SEM and EDS analyses reveal that TiB_2 particles in all three Al-4Ti-1Nb-1B samples exhibit negligible Nb signals. At this magnification, no evidence of Nb adsorption was observed.

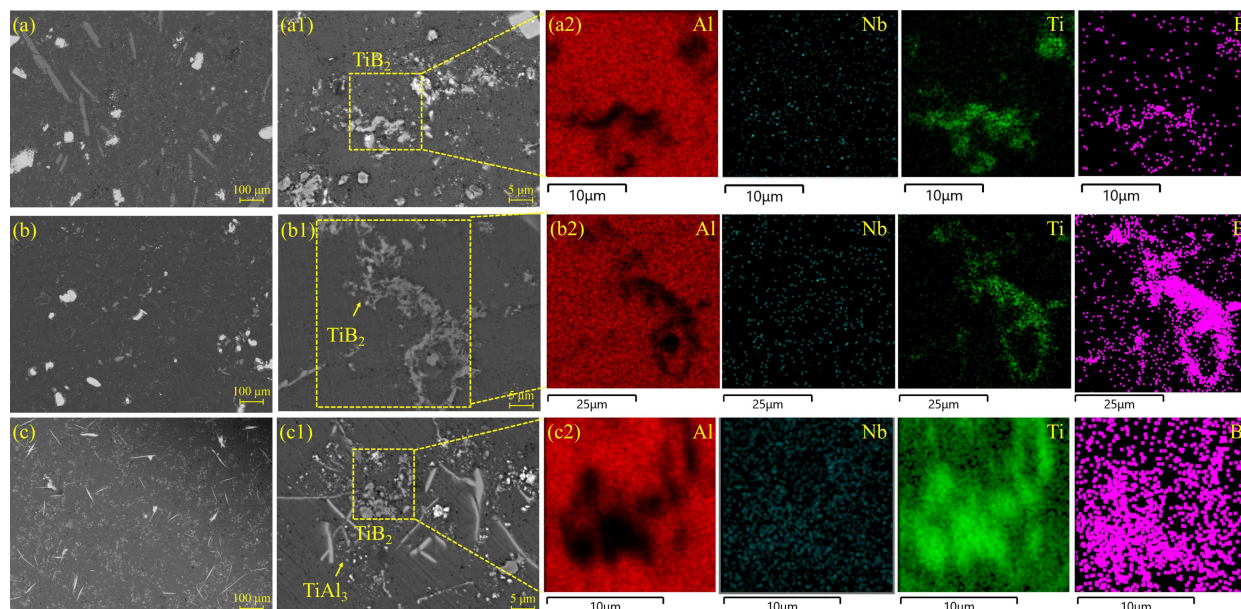


Fig. 3 SEM morphology and EDS mappings of TiB_2 phase in Sample (a-a2) A; (b-b2) B; (c-c2) C.

3.2 Grain refinement effect of Al-Ti-Nb-B alloys



Fig. 4 Polarized morphologies of α -Al in Al alloys.

Table 2 Average grain sizes (μm) of the Al-7Si alloys with different grain refiners

	CP-Al	Al-3.5Si	Al-7Si	Al-10.5Si
Sample A	176.6 $\pm$ 7.1	174.8 $\pm$ 6.6	207.8 $\pm$ 27.1	472.6 $\pm$ 8.2
Sample B	132.3 $\pm$ 14.2	148.5 $\pm$ 7.7	150.12 $\pm$ 27.5	311.1 $\pm$ 52.2
Sample C	147.5 $\pm$ 20.9	152.7 $\pm$ 8.2	180.9 $\pm$ 13.6	375.6 $\pm$ 65.2
Al-5Ti-1B	175.5 $\pm$ 28.1	268.7 $\pm$ 45.2	541.1 $\pm$ 26.3	559.2 $\pm$ 46.6
unrefined	>1500	>1500	>1500	>1500

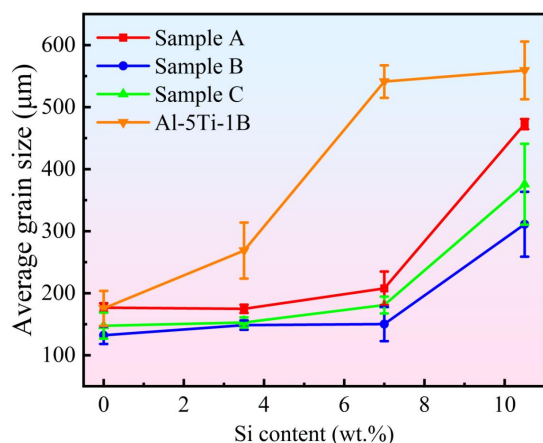


Fig. 5 (a) Grain refinement of Al-Ti-Nb-B with different Nb content.

(b) Grain refinement of Al-4Ti-1Nb-1B with different holding times.

Fig.4 presents the grain refinement results of CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si alloys inoculated with Sample A, B, C, and commercial Al-5Ti-1B. Table 2 summarizes the α -Al grain size after treatment with various refiners, while Fig. 5 also illustrates the grain refinement size. As shown in Fig. 4, the unrefined alloys (CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si) exhibit coarse dendritic α -Al grains with average grain size exceeding 1500 μm . Among the refiners tested, Sample B acquires the finest grain sizes: $132.3 \pm 14.2 \mu\text{m}$ for CP-Al, $148.5 \pm 7.7 \mu\text{m}$ for Al-3.5Si, $150.1 \pm 27.5 \mu\text{m}$ for Al-7Si, and $311.1 \pm 52.2 \mu\text{m}$ for Al-10.5Si. Sample A exhibits slightly inferior refinement compared to Sample B, with grain sizes of $176.6 \pm 7.1 \mu\text{m}$, $174.8 \pm 6.6 \mu\text{m}$, $207.8 \pm 27.1 \mu\text{m}$, and $472.6 \pm 8.2 \mu\text{m}$ for CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si, respectively. Refinement performance of Sample C is intermediate between Samples A and B. Overall, Samples A, B, and C demonstrated superior grain refinement compared to the commercial Al-5Ti-1B refiner.

Notably, for CP-Al and Al-3.5Si alloys, Samples A, B, and C showed comparable and excellent refinement performance. Even commercial Al-5Ti-1B exhibits effective refinement for CP-Al. However, as the Si content increased to 7 wt.%, notable differences in refinement performance among Samples A, B, and C emerges. Sample B significantly outperform Sample C, which in turn was superior to Sample A. At 10.5 wt.% Si, the differences become more pronounced. These results

indicate that at low Si concentrations (0 or 3.5 wt.%), Samples A, B, and C exhibit similarly excellent grain refinement. At higher Si concentrations (7 or 10.5 wt.%), Sample B maintains the strongest resistance to Si poisoning and sustained refinement performance. Sample A shows weaker resistance, and Sample C performs intermediate to A and B.

3.3 Nucleation substrates in the Al-Ti-Nb-B alloys

To further investigate the factors contributing to the grain refinement performance among Samples A, B, and C, TiB_2 particles from each sample were extracted and thinned using focused ion beam (FIB) techniques. Subsequently, STEM combined with EDS was applied to observe the TiB_2 particles in Samples A, B, and C. Fig. 6 summarizes the observations of these particles. Fig. 6(a) shows a block-shaped TiB_2 particle from Sample A. The yellow boxed area in Fig. 6(a1) corresponds to the TiB_2/Al interface, where EDS mappings confirm a distinct Nb-enriched layer, indicating Nb adsorption. Analysis of the SAED pattern in Fig. 6(b) and the HRTEM image and EDS line scan in Fig. 6(c) reveal that Nb atoms segregate along the (01 $\bar{1}$ 0) plane on the TiB_2 surface at the TiB_2/Al interface. Fig. 6(d) presents a stacked, elongated TiB_2 particle from Sample B. A pronounced Nb-enriched layer is evident on the TiB_2 surface, as shown in Fig. 6(d5). SAED pattern in Fig. 6(e), HRTEM image and EDS line scan in Fig. 6(f) confirm that Nb atoms adsorb along the (0001) plane toward the TiB_2/Al interface. Moreover, Fig. 6(g) depicts a cubic TiB_2 particle from Sample C, with Fig. 6(g1–g5) illustrating Nb adsorption on its surface. The Nb distribution at the TiB_2/Al interface in Sample C is further detailed in Fig. 6(g) and (h).

In summary, all TiB_2 particles from Samples A, B, and C exhibit evident Nb adsorption on the TiB_2/Al interface. Comparative EDS line scans of Nb along the TiB_2/Al interfaces in Fig. 6(c), (f), and (i) indicate that Sample B exhibits the most pronounced Nb adsorption with the highest Nb concentration, followed by Sample C and then Sample A. Correspondingly, Sample B demonstrates superior grain refinement performance across CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si alloys, especially at higher Si contents (Al-7Si and Al-10.5Si), compared to Samples A and C. Therefore, subsequent analyses focus on the influence of Nb adsorption on the TiB_2 surface on its grain refinement performance.

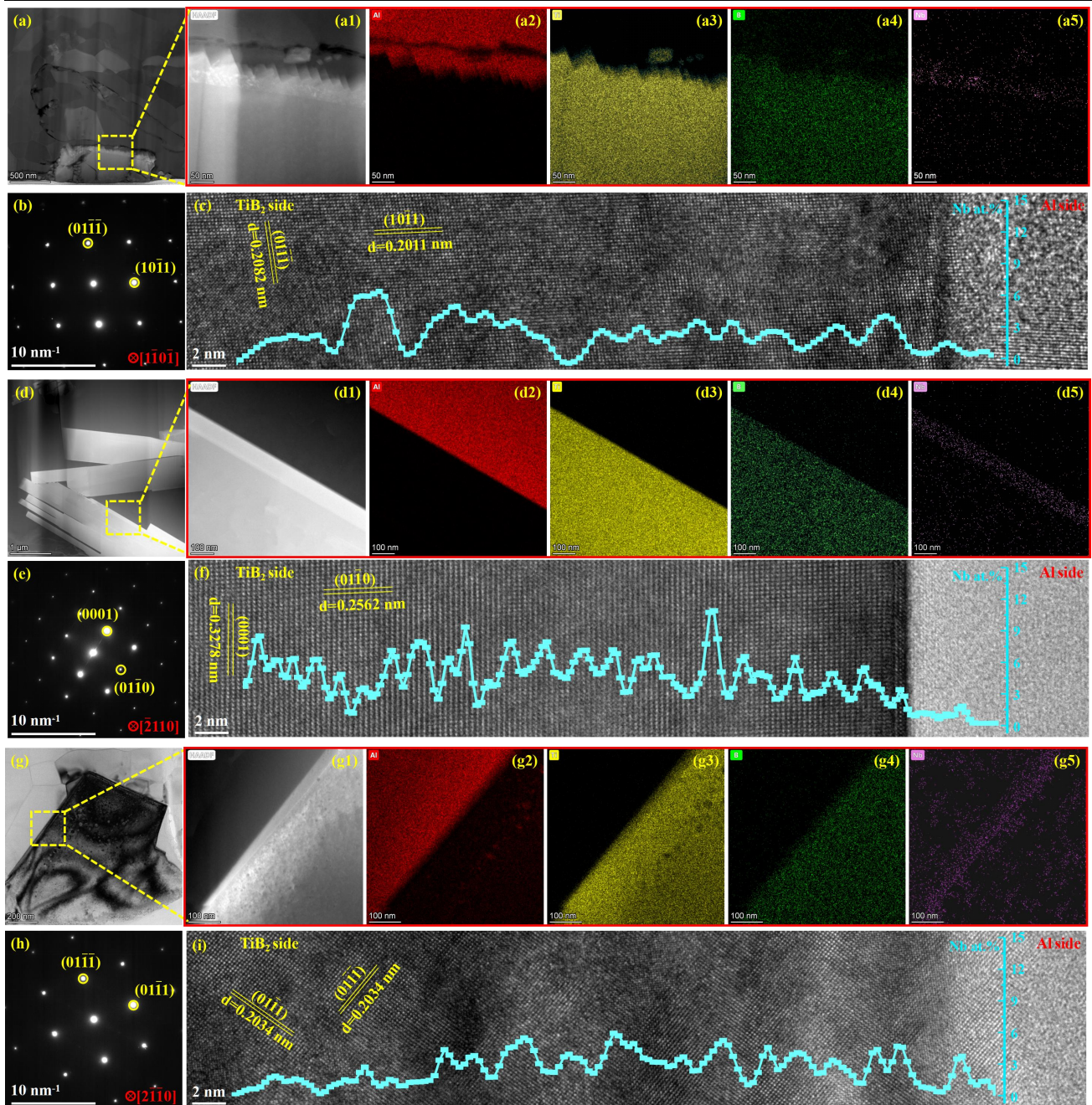


Fig 6 (a-a5) TiB_2 particle in Sample A and corresponding EDS mappings; (b) SAED pattern of the yellow box in (a); (c) HRTEM image of the surface of TiB_2 in Sample A and the EDS line-scanning pattern of Nb. (d-d5) TiB_2 particle in Sample B and corresponding EDS mappings; (e) SAED pattern of the yellow box in (d); (f) HRTEM image of the surface of TiB_2 in Sample B and the EDS line-scanning pattern of Nb. (g-g5) TiB_2 particle in Sample C and corresponding EDS mappings; (h) SAED pattern of the yellow box in (g); (i) HRTEM image of the surface of TiB_2 in Sample C and the EDS line-scanning pattern of Nb.

4 Discussion

4.1 Effect of the Ti and Nb introduction sequence on Nb adsorption at the TiB_2 surface

In the above experimental investigations, the TiB_2 particles in Sample B, prepared by introducing Ti prior to Nb, exhibited the most pronounced Nb surface adsorption. This is considered a major factor contributing to the superior grain refinement performance of Sample

B in CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si alloys. To elucidate the mechanism behind this observation, TiB_2/Al interface models with different Ti and Nb addition sequences are constructed to investigate their influence on Nb adsorption behavior at the TiB_2 surface.

According to the process shown in Fig. 1(b), during the 60 min holding period at 900 °C after the addition of the Al-Ti alloy, the melt environment contains insoluble TiB_2 particles and excess Ti and Al. This condition

resembles that used in the preparation of Al-Ti-B grain refiners. Based on the work by Fan et al. [37, 38], such an environment facilitates the formation of a two-dimensional TiAl_3 compound (TiAl_3 2DC) on the (0001) surface of TiB_2 . Following this, Nb is introduced. Driven by the tendency of the TiB_2/Al interface to evolve toward a thermodynamically stable state, Nb atoms may diffuse through the TiAl_3 2DC layer and subsequently enter the TiB_2 particles, resulting in interface reconstruction. Our previous study confirmed that in the presence of excess Nb in the melt, a NbAl_3 2DC layer can form at the TiB_2 surface [29]. Fig. 7(a1-a3) illustrates this evolution process. TiB_2 initially coated with a TiAl_3 2DC layer undergoes Nb diffusion into the 2DC, forming NbAl_3 2DC, followed by further Nb diffusion into the TiB_2 particles, ultimately producing Nb surface adsorption.

In contrast, when TiB_2 is synthesized in situ prior to Ti and Nb addition, as shown in Fig. 1(a), the Ti:B ratio is controlled at 2.2, and the reaction is maintained for 30

min. No excess Ti remains in the melt to form a TiAl_3 2DC layer. When Nb is introduced first under these conditions, Nb atoms gradually diffuse directly to the TiB_2 surface and progressively incorporate into it, resulting in Nb adsorption. Therefore, Fig. 7(b1-b3) illustrates the interface evolution under the Nb-first route. The ground-state energies for both addition sequences are calculated using the *ab initio* method and are summarized in Fig. 7(c). It is evident that the Ti-first followed by Nb introduction sequence results in a smaller ground-state energy change (ΔE), along with lower intermediate energy levels and a stronger driving force. This indicates that Nb adsorption on the TiB_2 surface under this sequence is more thermodynamically favorable. Consequently, Sample B exhibits the most pronounced Nb adsorption on the TiB_2 surface, followed by Sample C, while Sample A shows the weakest adsorption.

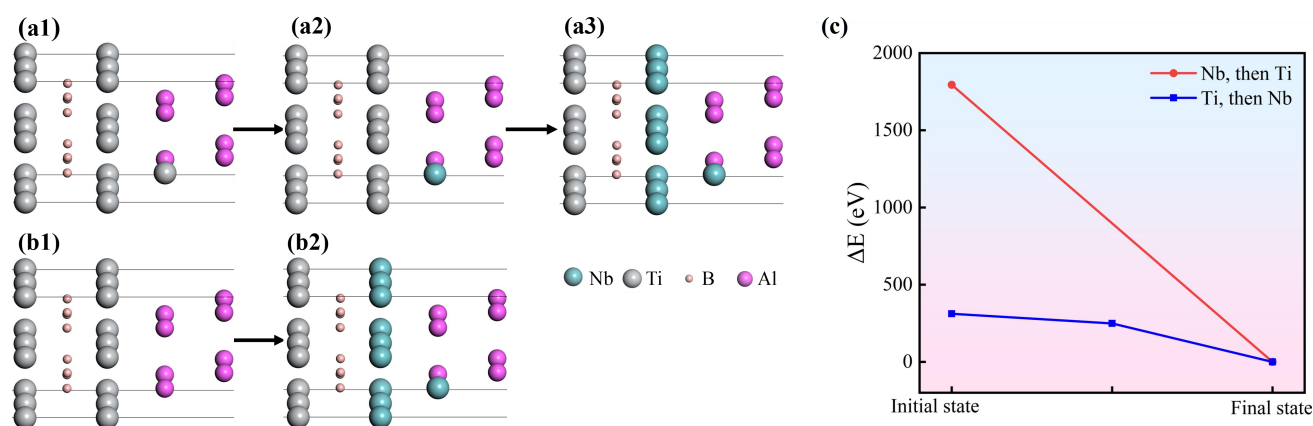


Fig. 7 (a1-a3) Reconstruction of the TiB_2/Al interface under the introduction sequence of Ti followed by Nb. (b1-b2) Reconstruction of the TiB_2/Al interface under the introduction sequence of Nb followed by Ti. (c) Energy variation, ΔE , induced by the introduction sequence of Ti and Nb.

4.2 Effect of Nb adsorption amount on grain refinement performance and Si-poisoning resistance

The grain refinement results shown in Fig. 4 demonstrate that Sample B exhibits superior refinement efficiency for CP-Al, Al-3.5Si, Al-7Si, and Al-10.5Si compared to Samples A and C. The Nb elemental line scans presented in Fig. 6(c), (f), and (i) reveal significant differences in Nb adsorption at the TiB_2 surfaces among the three samples. The corresponding Nb line scan profiles for Samples A, B, and C are compared in Fig. 8, with their average and maximum Nb concentrations summarized in Table 3. Sample B shows the highest Nb surface adsorption on TiB_2 , with an average Nb content of 3.80

at.%, which significantly exceeds the critical threshold of 1.92 at.% previously reported to activate TiB_2 as an effective nucleation site [36]. Sample C exhibits a moderate Nb adsorption level of 2.38 at.%, while Sample A presents the lowest, at only 2.03 at.%. Although all three samples outperform the commercial Al-5Ti-1B refiner in refining CP-Al and various Al-Si alloys, the grain refinement performance of Sample B is clearly superior to that of Sample C, and markedly better than that of Sample A. Therefore, the influence of Nb adsorption content at the TiB_2 surface on grain refinement and Si-poisoning resistance is investigated in detail.

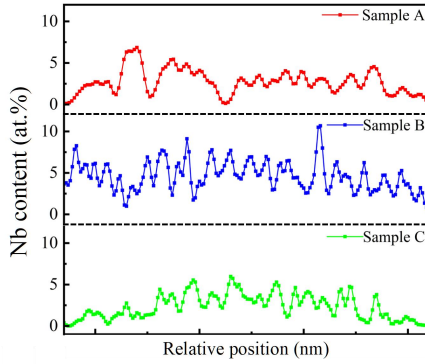


Fig. 8 The EDS line-scanning patterns showing the composition profiles of Nb on the surface of TiB₂

Table 3 Nb content on the surface of TiB₂ in Al-Ti-Nb-B

Grain refiner	Average Nb content (at.%)	Maximum Nb content (at.%)
Sample A	2.03	6.85
Sample B	3.80	10.68
Sample C	2.38	5.98

To quantify the nucleation tendency of α -Al on the TiB₂ surface, the adhesion energy W_{ad} , which represents the work required to separate one interface into two free surfaces, is calculated using the following equations^[39,40]:

$$W_{ad} = \frac{1}{A} (E_{slab}^{Al} + E_{slab}^{TiB_2} - E_{interface}) \quad (9)$$

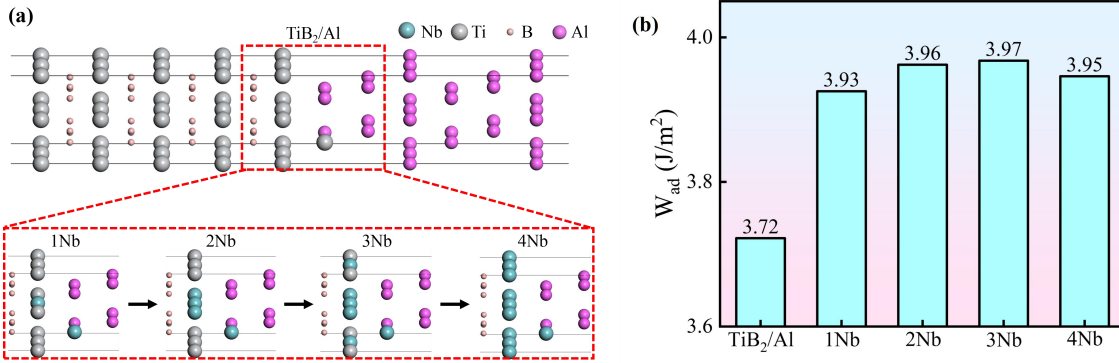


Fig. 9 Effect of Nb adsorption at TiB₂/Al interface on the adhesion energy W_{ad} . (a) TiB₂/Al interface models with various Nb atoms. (b) Variation of the adhesion energy W_{ad} of corresponding structures.

In addition, the superior resistance to Si poisoning of Sample B is a critical distinguishing feature, compared to Samples A and C. It is important to investigate the influence of Nb adsorption on Si atoms at the TiB₂ surface. To quantitatively compare the Si adsorption propensity at TiB₂/Al and TiB₂(Nb)/Al interfaces, the Si adsorption factor $\kappa_{Si}(c_{Si})$ is defined^[25]

$$\kappa_{Si}(c_{Si}) = \frac{W_{ad}(c_{Si})}{W_{ad}(0)} \quad (10)$$

where $E_{interface}$, E_{slab}^{Al} and $E_{slab}^{TiB_2}$ are calculated by the *ab initio* method, denoting the ground state energies of the interface model, the Al, and the substrate slab, respectively. W_{ad} denotes the adhesion energy of the TiB₂/Al and interface. A denotes the interfacial area of the TiB₂/Al interface. Various TiB₂/Al interfaces incorporating different numbers of Nb atoms are constructed, as shown in Fig. 9. For comparison, the TiB₂/Al interface from commercial Al-5Ti-1B was also modeled, based on previous studies^[37, 41, 42]. The adhesion energies, W_{ad} , of the corresponding interface models are calculated and presented in Fig. 9(b). The adhesion energy of the TiB₂/Al interface without Nb atoms is 3.72 J/m², which is in good agreement with the result reported by Li et al. (3.77 J/m²)^[25]. For comparison, the W_{ad} of the TiB₂/Al interface with one Nb atom increases to 3.93 J/m². With the adsorption of two Nb atoms, W_{ad} increases to 3.96 J/m². The adhesion energies of TiB₂/Al interfaces with three and four Nb atoms are 3.97 and 3.95 J/m², respectively. These results clearly demonstrate that the presence of Nb atoms at the TiB₂/Al interface significantly enhances the adhesion energy, indicating a strong tendency to form a more stable interface. Thus, the Nb adsorption at the TiB₂ surface is the key factor contributing to the superior grain refinement performance of Samples A, B, and C.

where $W_{ad}(c_{Si})$ and $W_{ad}(0)$ denote the adhesion energies when the Si concentration at the interface is c_{Si} and 0, respectively. The TiB₂/Al interfaces with adsorbed Si atoms and their corresponding segregation tendency, denoted as $\kappa_{Si}(c_{Si})$, are presented in Fig. 10. As the interfacial Si concentration, c_{Si} , increases, $\kappa_{Si}(c_{Si})$ of TiB₂/Al, TiB₂/Al with 1 Nb atom, and TiB₂/Al with 2 Nb atoms rises, indicating a higher tendency for Si segregation at higher concentrations. However, $\kappa_{Si}(c_{Si})$ is lower for TiB₂/Al interfaces with 2 Nb atoms than with 1

Nb, and both are lower than the Nb-free interface, suggesting that greater Nb segregation reduces Si accumulation. For TiB_2/Al interfaces with 3 or 4 Nb atoms, $\kappa_{\text{Si}}(c_{\text{Si}})$ reaches a maximum at $c_{\text{Si}} = 0.75$ and then decreases as c_{Si} increases to 1, indicating that further Si enrichment becomes increasingly difficult at higher Nb concentrations. Furthermore, $\kappa_{\text{Si}}(c_{\text{Si}})$ consistently decreases with increasing

Nb content from 1 to 4 Nb atoms under the same c_{Si} , reinforcing the conclusion that higher Nb adsorption at the TiB_2/Al interface suppresses Si segregation. These findings explain why Sample B, which exhibits the highest Nb adsorption content at the TiB_2 surface, achieves superior refinement performance in Al-7Si and Al-10.5Si alloys compared to Samples A and C.

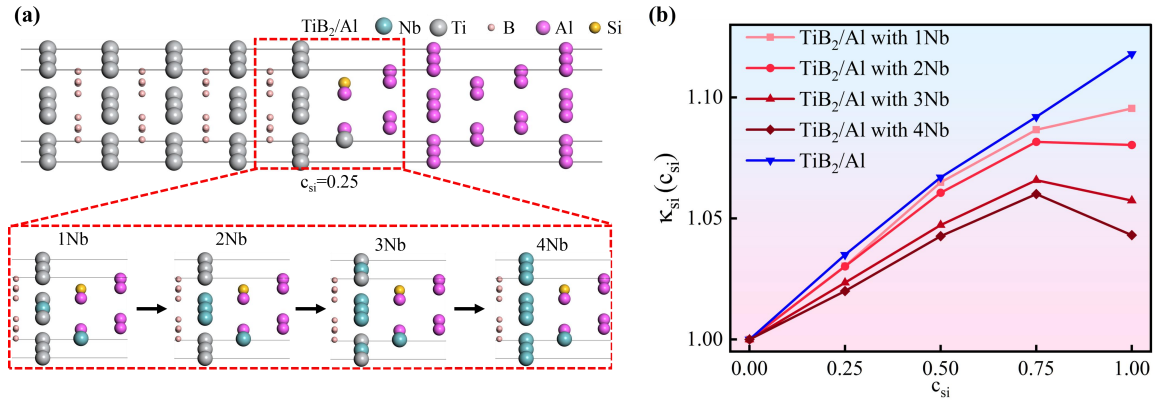


Fig. 10 Effect of Nb adsorption at TiB_2/Al interface on Si segregation propensity, $\kappa_{\text{Si}}(c_{\text{Si}})$. (a) TiB_2/Al interfaces with various Nb atoms and Si segregation. (b) Variation of $\kappa_{\text{Si}}(c_{\text{Si}})$ for corresponding interfaces.

In summary, the enhanced grain refinement and Si-poisoning resistance in Sample B can be attributed to the higher Nb adsorption at the TiB_2 surface. As shown in Fig. 11, Ti is first introduced to form a Ti-rich Al-Ti-B melt. Nb is then added, and through substitution of Ti in the TiAl_3 2DC layer and subsequent diffusion, Nb atoms are incorporated into the TiB_2 surface, leading to a significant content of Nb adsorption. This unique Nb

adsorption increases the interfacial adhesion energy W_{ad} and reduces the Si segregation tendency $\kappa_{\text{Si}}(c_{\text{Si}})$ at the TiB_2/Al interface. The higher the Nb content at the interface, the stronger the resistance to Si poisoning. The superior performance of Sample B is thus attributed to an average Nb content of 3.80 at.%, which optimizes both grain refinement and resistance to Si poisoning.

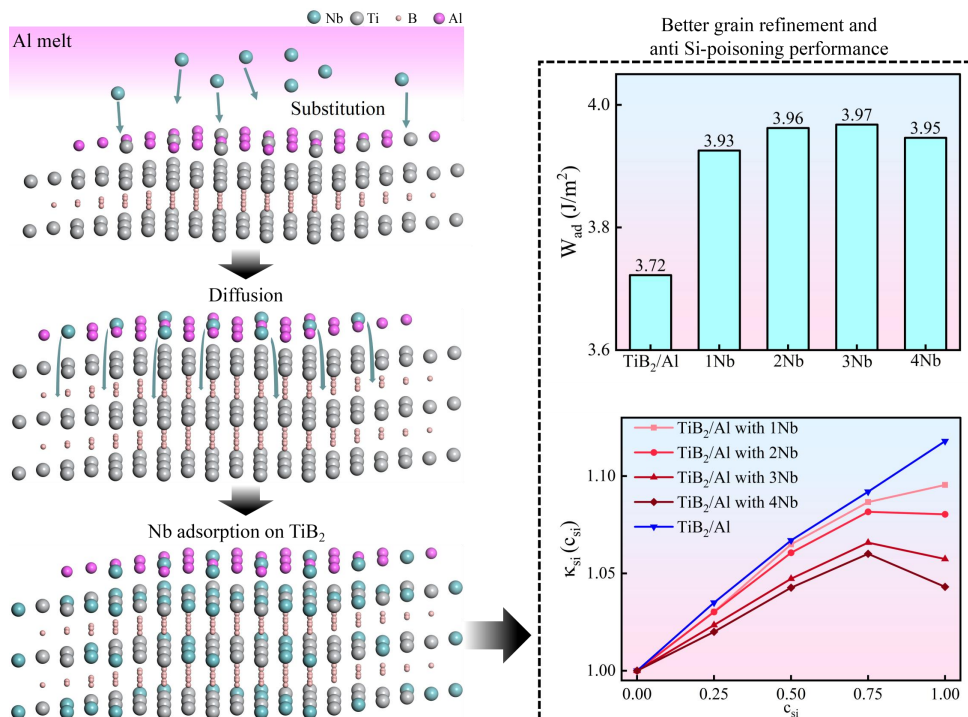


Fig. 11 A schematic illustration of the Nb adsorption mechanisms on TiB_2

5 Conclusions

In this study, a series of Al-4Ti-1Nb-1B grain refiners were prepared via different sequences for introducing Ti and Nb. It was found that the sequence of Ti and Nb addition significantly influences the adsorption behavior of Nb at the TiB₂ surface, thereby affecting both the grain refinement efficiency and resistance to Si poisoning. The following conclusions can be drawn:

(1) All Al-4Ti-1Nb-1B refiners, regardless of the Ti and Nb addition sequence, exhibited excellent grain refinement performance in low-Si aluminum alloys such as CP-Al and Al-3.5Si. For high-Si alloys such as Al-7Si and Al-10.5Si, the refiner synthesized by first adding Ti followed by Nb demonstrates the best refinement performance, refining the α -Al grain size of Al-7Si to $150.12 \pm 27.5 \mu\text{m}$.

(2) Introducing Ti prior to Nb lead to the most pronounced Nb adsorption at the TiB₂ surface. Initially, Ti promotes the formation of a TiAl₃ 2DC on the in-situ formed TiB₂. Subsequently, due to thermodynamic driving forces favoring lower ground-state energy, Nb atoms replace Ti in the surface TiAl₃ 2DC and gradually diffuse into the TiB₂, forming a stable Nb-enriched layer. The ground-state energy change ΔE for the Ti prior to Nb process is lower than that of the reverse sequence, making Nb adsorption more favorable in this route.

(3) Varying degrees of Nb adsorption are observed at the TiB₂ surface. The highest concentration, 3.80 at.%, is obtained in the sample introducing Ti prior to Nb. First-principles calculations revealed that higher Nb content enhance the TiB₂/Al interfacial adhesion energy W_{ad} and suppress the segregation tendency of Si atoms, represented by $\kappa_{\text{Si}}(c_{\text{Si}})$. The Nb adsorption at the TiB₂ surface is thus the key factor contributing to the superior performance of the Al-4Ti-1Nb-1B refiners. A higher level of Nb adsorption at the TiB₂ surface leads to improved refinement performance and stronger Si-poisoning resistance, particularly in high-Si alloys such as Al-7Si and Al-10.5Si.

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