

Article Microstructures of Three In-Situ Reinforcements and the Effect on the Tensile Strengths of an Al-Si-Cu-Mg-Ni Alloy

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Abstract: In the present paper, the microstructures of three kinds of in-situ reinforcements Al-Ti-C, Al-Ti-B, and Al-Ti-B-C-Ce were deeply investigated using a combination of scanning electron microscopy, X-ray diffraction spectroscopy, and transmission electron microscopy. The effect of in-situ reinforcements on the room temperature and elevated temperature (350 °C) tensile strengths of Al-13Si-4Cu-1Mg-2Ni alloy were analyzed. It is found that doping with trace amounts of B and Ce, the size of the Al₃Ti phase in the in-situ reinforced alloy changed from 80 µm (un-reinforced) to about 10 µm, with the simultaneous formation of the AlTiCe phase. The Al-Ti-B-C-Ce reinforcement which is rapid solidified, was more effective and superior to enhance the tensile strengths of the Al-13Si-4Cu-1Mg-2Ni alloy, both at room and high temperatures than those of addition other reinforcements. The room temperature (RT) strength increased by 19.0%, and the 350 °C-strength increased by 18.4%.

Keywords: Al-Ti-C; Al-Ti-B; Al-Ti-B-C-Ce; in-situ reinforcement; Al-Si-Cu-Mg-Ni alloy; microstructure; tensile strength

1. Introduction

In last two decades, in situ metal matrix composites, as a branch of discontinuous reinforced metal matrix composites, have been attracting many researchers interest and have made notable achievements [1]. The word "in situ composite" comes from "in situ crystallization". The concept of in-situ composite was proposed by Soviet scientist Merzhanov et al., where they synthesized TiB₂ reinforced Cu based functional gradient materials by Self-Propagating High-temperature Synthesis in 1987 [2–4]. High quality in situ aluminum-matrix and titanium-matrix composites have been developed for various applications in vehicles, aerospace, and the machinery industries [5,6]. However, the research on in situ metal matrix composites and its current research investment, are far from meeting the urgent needs of the high-tech development of modern industry and the military [7,8]. Therefore, it is of great importance to conduct more in-depth research on in situ metal matrix composites, for applications in leading-edge manufacturing and innovation areas, such as alloy material design theory, amorphous nano-crystalline matrix inoculation and refinement mechanism, and ceramic nano-particulate reinforcement. The goal is to make major breakthroughs rapidly in nano-fabrication technology and basic theoretical research in new types of metal matrix composite materials, so as to contribute to the transformation and upgrade of the traditional metal material industry [9–11].



The advantages of aluminum-based composite materials include high specific strength, excellent corrosion resistance, and outstanding electrical conductivity [12]. The primary purpose of adding reinforcement to the aluminum matrix, is to compensate for the low strength, inferior high-temperature performance, and poor wear resistance of aluminum. For aluminum matrix composites, the most effective particulate reinforcements are mostly ceramic particles. These particles can be divided into two types, one is directly formed in the matrix and the other is added after artificial synthesis. In addition to the high specific strength and specific modulus, these reinforcements have superior high-temperature performance; they are therefore widely used in the production of composite materials [13,14].

Table 1 shows the property parameter of the compound, which can be used as a particle enhancer. In recent decades, studies on TiC, TiB₂, ZrB₂, AlN or its biphasic particle composite reinforced aluminum matrix composites have been increasing. TiC particles, as the reinforced phase of in-situ aluminum matrix composites, show many excellent properties: high hardness, high melting point, high elastic modulus, low thermal conductivity, and good wettability and thermodynamic stability in molten aluminum [15]. TiB₂ has been intensively investigated in modern engineering materials, due to its high melting point, superior hardness, and excellent corrosion resistance, as well as good thermal and electrical conductivity. At present, TiB₂ is widely applied in the field of high-temperature electrodes, armor, cutting tools, and other structural materials [16].

Particle	Density/(g·cm ^{−3})	Melting Point/°C	Coefficient of Thermal Expansion/ $(10^{-6} \circ C^{-1})$	Thermal Conductivity	Elasticity Modulus/(GPa)
TiC	4.93	3160	7.74	24.28	450
TiB ₂	4.25	2980	4.6-8.01	24.4-26	530
TiB	4.5	2473	8.6	-	550
SiC	3.19	2970	4.3	-	430
VC	5.36	2810	4.2	24.7	430
WC	15.55	2720	3.84	29.31	810
Al_2O_3	3.9	2050	8.6	28.89	420
Al ₃ Ti	3.3	1623	-	-	220

Table 1. Properties of particle—enhancing compounds [17–19].

TiC and TiB₂ are usually synthesized in situ by Al-Ti-C and Al-Ti-B systems. At present, the most commonly used reinforcements in the industry are Al-Ti-C and Al-Ti-B reinforcements [20,21]. Table 2 shows the characteristics of various reinforcements [22–26]. Researches have been fully developed and widely used in industrial production. However, Al-Ti-C as well Al-Ti-B, have some disadvantages in the application process, where Al-Ti-B contains TiB₂ which tends to accumulate in molten aluminum, decreasing the refining effect. In addition, Al₃Ti particulates contained in Al-Ti-C and Al-Ti-B refinements have low refinement efficiency and degrade the matrix properties because of its needle-like appearance. New Al-Ti-B-C-Ce reinforcement, enhance and inherited the merits of the traditional reinforced body, have the effect of refining grain size, and improved its shortcoming to further improve the refining effect, and thus have a great advantage in improving the materials mechanical performance [27].

Table 3 shows the tensile properties of different alloys in the reference literature, at room temperature.

Al-13Si-4Cu-1Mg-2Ni alloy, is a widely used piston aluminum alloy through the enhanced in-situ method which further improves its mechanical properties. This is of great significance in meeting the research and development needs of high performance engines, such as high-power density diesel engines. In this paper, the strengthening effect of these three kinds of enhancers, and the addition to the piston alloy by in-situ generation, is studied to provide guidance for the development of a new piston alloy.

Reinforcement Types	Advantages	Disadvantages	
Al-Ti-B	 High refinement efficiency that is 12 times better than that of Al-Ti TiAl₃ and TiB₂ are heterogeneous crystal cores of α(Al) 	 Accumulation of TiB₂ can impair the quality "Poisoning" by Zr, Cr, and Mn can lead to failure 	
Al-Ti-C	 Non-contaminating addition of a refinement ager "Immune" to Zr, Cr, and Mn The grain size of TiC even smaller than that of TiE 	 Poor attenuation Refinement effect worse than that of Al-Ti-B 	
Al-Ti-B-C-Ce	 They have all the above mentioned advantages Particle size is refined by adding rare earth to prevent aggregation and precipitation of TiAl₃ an TiB₂ 	1. Research not yet well developed	

 Table 2. Characteristics of reinforcements.

Table 3. The tensile properties of different in-situ reinforced aluminum matrix composites at room temperature.

Materials	Enhanced Phase Content/vol. %	Tensile Strength/MPa	Elongationδ/%	Reference
TiC/Al	15	610	4.9	[28]
TiC/Al-4.5Cu	20	540	18	[29]
TiB ₂ /Al	16	349	3.8	[30]
TiB ₂ /Al	5	124	9.2	[31]
TiB ₂ /A356	2.5	290	10	[32]
TiB ₂ /A356	5	302	9	[32]
TiB ₂ /A356	7.5	317	8	[32]
TiB ₂ /A356	10	328	6	[32]
TiB ₂ /ZL109	-	258.7	7.5	[33]

2. Experimental

2.1. Intermediate Alloy Preparation

The powders needed to prepare the intermediate alloy were Ti, C, KBF₄, K₂TiF₆, and B₄C powder. The Al-13Si-5Cu-1Mg-2Ni matrix alloy was prepared using highly pure Al (99.95 wt. %), pure Mg (99.9 wt. %), pure Si (99.9 wt. %), Al-50 wt. % Cu, and Al-10 wt. % Ni master alloys. The matrix alloy preparation process also used Al-20 wt. % Ce, Al-P alterative, mischmetal rich in La and Ce, and Hexachloroethane. Table 4 are the powders used to prepare intermediate alloys.

Table 4. Raw materials for chemical reagents in the experiment.

Powders	Particle Size	Purity	Manufacturer
Al	200 mesh	≥99.0%	Shanghai shanpu chemical Co., Ltd. (Shanghai, China)
Ti	200–300 mesh	$\geq 99.0\%$	Sinopharm chemical reagent Co., Ltd. (Shanghai, China)
С	2000 mesh	$\geq 99.9\%$	Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China)
K ₂ TiF ₆	/	$\geq 99.0\%$	Shanghai SSS Reagent Co., Ltd. (Shanghai, China)
KBF ₄	/	$\geq 99.0\%$	Shanghai SSS Reagent Co., Ltd. (Shanghai, China)
B_4C	100–300 mesh	$\geq 99.0\%$	Nangong ruiteng alloy material Co., Ltd. (Nangong, China)

For Al-Ti-C intermediate alloy, Ti powder and C powder in a Ti:C = 4:1 mass ratio and 10 wt. % were used. Al were measured according to the reaction formula:

$$Al + Ti \rightarrow Al_3Ti$$
 (2)

$$Al + C \to Al_4C_3 \tag{3}$$

These powders were mixed uniformly in a mortar and poured into a stainless-steel briquette mold (Φ 35 mm × 10 mm). The powder was pressed to form a powder briquette. The briquette was dried and placed in molten pure aluminum liquid at 1000 °C, for an in-situ reaction to produce Al-3Ti-0.25C intermediate alloy.

For Al-Ti-B intermediate alloy, KBF_4 and K_2TiF_6 were blended according to the reaction formula and stirred directly into 850 °C pure molten aluminum. The in-situ reaction then occurred in molten aluminum to produce the Al-Ti-B intermediate alloy.

$$K_2 \text{TiF}_6 + 2\text{KBF}_4 \rightarrow \text{TiB}_2 + 4\text{KF} + 5\text{F}_2 \tag{4}$$

$$2K_2TiF_6 + 2KBF_4 + 5Al \rightarrow TiAl_3 + TiB_2 + 6KF + 2AlF_3 + 4F_2$$
(5)

Al-Ti intermediate alloy was prepared by melting in a Model WK-II non-consumable vacuum electric arc furnace, according to a specific composition. B_4C powder wrapped in aluminum foil at 800 °C, was placed in a melting crucible to prepare Al-Ti-B-C intermediate alloy. Al-Ti-B-C-Ce was then prepared by melting Al-Ti-B-C intermediate alloy and Al-20Ce alloy, in the WK-II non-consumable vacuum arc furnace. The prepared block of Al-Ti-B-C-Ce reinforcement was then placed in a Model LZK-12A vacuum quenching furnace, for rapid solidification.

2.2. Experimental Process

2.2.1. The Process of Matrix Alloy

In the experimental study, an alloy model of Al-13Si-4Cu-1Mg-2Ni (wt. %) was prepared in an intermediate frequency induction melting furnace. Firstly, pure aluminum ingot blocks were added into the graphite crucible and were melted, then the pieces of pure silicon Al-10 wt. %Ni and Al-50 wt. %Cu intermediate alloys were added into the melt, respectively. Furthermore, mischmetal, rich in elements La and Ce, together with Al-P alloy as the modifier agents, were added into the molten alloy. Hexachloroethane as the degassing agent was added at 720–740 °C, and held for 15 min. Then Mg block was added under the melt completely, to keep it from contacting oxygen and burning. The crucible was removed with a crucible clamp and the slags were removed with a stainless-steel spoon. After skimming off slag, it was poured into a metal mold to obtain Φ 20 mm × 100 mm cast rods.

2.2.2. The Process of Composite Alloys

When the matrix alloy was melted, three different reinforcements Al-Ti-C, Al-Ti-B, and Al-Ti-B-C-Ce (5 wt. %) briquette were added in an aluminum foil to the molten aluminum. Figure 1 shows the preparation technology of the composite alloy. After skimming off slag, it was poured into a metal mold to obtain Φ 20 mm × 100 mm cast rods.



Figure 1. The preparation technology of composite alloy.

2.2.3. The Microstructure Analysis

The composite materials alloy when solidified, was analyzed using a Quanta 400 F (FEI, Hillsboro, OR, USA) thermal field emission scanning electron microscope equipped with an INCA energy dispersive spectrometer and JEM-2010 transmission electron microscope (JEOL, Tokyo, Japan) in detail. The phase compositions contained in the alloy prepared were examined using an XRD-6000 X-ray diffract meter (Shimadzu, Kyoto, Japan).

2.2.4. The Mechanical Tensile Tests

The tensile strengths of the cast Al-13Si-4Cu-1Mg-2Ni alloy at 25 °C and 350 °C, were tested with the Instron 1195 mechanical testing machine (Instron, Shanghai, China).

3. Results and Discussion

3.1. Metallurgical Analysis of Al-3Ti-0.25C Intermediate Alloy

3.1.1. X-ray Diffraction Analysis

Figure 2 shows the X-ray diffraction of the Al-Ti-C intermediate alloy. The XRD results show that there were Al, Al₃Ti, and TiC phases present in the Al-Ti-C intermediate alloy, prepared by the in-situ reaction.



Figure 2. XRD analysis of Al-Ti-C intermediate alloy.

3.1.2. SEM Analysis

Figure 3 demonstrates a scan of the Al-Ti-C intermediate alloy, and energy spectral analysis of the different phases. The micrograph showed that the dimension of the long stripe phase was about 20–50 μ m, and the maximum dimension of the small particle phase was approximately 1 μ m. Figure 3a shows the energy spectrum of the long rod phase. The atomic ratio of Al:Ti was 3:1, and the long rod phase is Al₃Ti. Figure 3b shows the energy spectrum of the small particle phase. Herein, the grayish white near spherical nano-phase is TiC (Ti:C = 1:1). At 1200 $^{\circ}$ C, Ti and graphite react violently in the alloy melt, and a large amount of TiC crystals are formed in the early phase of the reaction. The spherical clusters mainly comprise Ti and C, with Ti:C = 49.08:50.92, which is close to the Ti:Cratio in the TiC compound. From the XRD results, it is believed that the spherical clusters are TiC phases. The reasons for the clustering may be that, in small particles, the large specific surface area leads to a high specific surface energy and they cluster to reduce the specific surface area and energy. In the meantime, calculations made using Image Pro showed that the volume fraction of Ti phase in the alloy was about 10.5%. Figure 3c shows the SEM image of the extracted Al-Ti-C intermediate alloy. Since the matrix had been dissolved and the other large phases were also removed by sieving, only TiC remained. The figure shows that TiC was mostly irregularly granular. Since the specimen was adsorbed on the copper mesh after extraction, the energy spectrum showed a strong uncalibrated Cu peak.



Figure 3. SEM micrograph and energy spectrum: (**a**) rod-like Al₃Ti phase; (**b**) grain-like TiC phase; (**c**) extracted TiC.

3.1.3. TEM Analysis

TiC is a face-centered cubic crystal; its close packed plane and close packed direction are {111} and [110], respectively. Since the (111) plane is a regular hexagonal base plane, the growth of a complete hexagonal TiC crystal is along the [111] direction, i.e., a coarse hexagonal TiC crystal grain is

formed by hexagonal monolayers in a layered growth pattern along the [111] crystallographic direction. The formation of such a thick hexagonal TiC crystal is shown schematically in Figure 4.



Figure 4. Schematic of the growth process of the hexagonal TiC crystal layers.

Figure 5 shows that the nano phases are distributed mainly on the grain boundaries. The size of the irregular hexagonal phase TiC was about 200 nm. At the same time, the diffraction pattern showed that the irregular hexagons mainly grew in the [011] and [21-1] directions.



Figure 5. Nano-phase distribution and identification of diffraction spots. (**a**) TEM images of the nano phase; (**b**) diffraction spots of nano phase; (**c**) TEM images of the nano phase; (**d**) diffraction spots of nano phase.

3.2. Al-5Ti-B Intermediate Alloy Phase Analysis

3.2.1. X-ray Diffraction Analysis

Figure 6 shows the XRD results of Al-Ti-B master alloy. The XRD results showed that there were Al, Al_3Ti , and TiB_2 phases in the Al-Ti-B intermediate alloy, produced by the in-situ reaction.



Figure 6. XRD spectrum of Al-Ti-B intermediate alloy.

3.2.2. SEM Analysis

Figure 7 shows the scan image of the Al-Ti-B intermediate alloy. It can be seen that there were two phases that were different in morphology and size, one of which was in the shape of a rod and the other was in the form of a grain. Figure 8 shows the scan image and energy spectrum of different phases. The energy spectrum showed that the atomic ratio of Al to Ti in the rod-shaped phase was 3:1. Further analysis showed that the long rod phase was Al₃Ti and the small grain was TiB₂. Furthermore, the extracted photos suggested that the granular TiB₂ was an irregular polygon with a constant thickness. The volume fraction of the Ti phase in the Al-Ti-B alloy was about 16.5%. Moreover, the Al₃Ti particles in Al-Ti-B alloy were smaller than the Al₃Ti particles in Al-Ti-C.



Figure 7. SEM image of the Al-Ti-B alloy. (a) Low magnification SEM; (b) High magnification SEM.



Figure 8. SEM image and energy spectrum of different phases: (**a**) rod-shaped Al₃Ti; (**b**) grain-shaped TiB₂; (**c**) extracted TiB₂.

3.2.3. TEM Analysis

Figure 9 shows the TEM and diffraction patterns of Al-Ti-B intermediate alloy. It showed that the nano-phase resides at the grain boundary and that the size of TiB_2 was about 200 nm. Moreover, there was a certain phase relationship between the Al (111) direction and the TiB_2 (100) direction.



Figure 9. The TEM and diffraction patterns of Al-Ti-B intermediate alloy. (**a**) Low magnification SEM, (**b**) High magnification SEM.

3.3. Al-5Ti-B-C-Ce Phase Analysis

3.3.1. XRD Analysis

Figure 10 exhibits the X-ray diffraction pattern of Al-5Ti-B-C-Ce alloy. It indicated that the Al-Ti-B-C-Ce alloy included Al, Al₃Ti, TiB₂, and TiC phases. No Ce-containing phase was detected in the X-ray diffraction of Al-5Ti-B-C-Ce, due to the relatively low content of element Ce, which was only confirmed by energy spectrum analysis.



Figure 10. XRD spectrum of Al-Ti-B-C-Ce intermediate alloy.

3.3.2. SEM Analysis

Figure 11 shows the SEM image of the Al-5Ti-BC-Ce alloy specimen and EDX analysis. Figure 11a,b suggests that the nano-reinforcing particulates are distributed in the form of clusters. The particulates are small but numerous. The solidification process of the aluminum melt can provide more nucleation particles, which can be used as an effective intra-crystalline reinforcement to improve the performance of the alloy. The dark regions of the image are the aluminum substrates, and the bright colors refer to the ceramic particles. In Figure 11c1, the larger particles are found to be Al₃Ti from energy spectrum analysis. Figure 11c2 shows that trace amounts of rare earth element Ce can inhibit the rod-shaped Al₃Ti phase (80 μ m is reduced to about 10 μ m) and generate the Ti₂Al₂₀Ce phase. The energy spectrum of Figure 11d1, demonstrates that elements B and Ti are high in weight percentage, indicating that the larger particles in Figure 11d are TiB₂. Figure 11d2 shows that the weight percentage of elements C and Ti are high, indicating that the gray spot particles in Figure 11d

are TiC. Figure 11e is the photomicrographs of the same extraction, showing a hexagonal prismatic phase, with numerous fine granular compounds attached around the hexagonal prism. The energy spectral analysis showed that it is composed of elements Ti, B, Al, and Cu, and has a high content of elements B, Al, and Cu in the spectrum, which are generated by the matrix and the net; therefore, the hexagonal prism is TiB₂. The energy spectrum analysis of the particles attached to the surface of the hexagonal prism, showed that it is composed of elements Ti, C, and B. The generation of B was mainly due to the small phase generated by the hexagonal prism. Therefore, the attached particles were TiC compounds. The energy spectrum analysis of the particles near the hexagonal prism, revealed that the particles were composed of elements C, Ti, and B, and the C content was high; so these fine particles were TiC phases. The results of scanning electron micrographs and energy spectra provided initial confirmation that TiB₂, TiC, and Al₃Ti particles were contained in the Al-5Ti-B-C-Ce alloy. The scan images also revealed the morphology of TiB₂ and TiC. Compared to Al-5Ti-C alone, the Al-5Ti-B and Al-5Ti-B-C-Ce phases were smaller and more uniform.



Figure 11. SEM images and EDX analysis of Al-5Ti-B-C-Ce alloy specimens SEM images and EDX analysis of Al-5Ti-B-C-Ce alloy specimens. (a) Low magnification SEM; (b) High magnification SEM; (c) nano phases; (c1) EDS of $AlTi_xCe_y$; (c2) EDS of Al_3Ti ; (d) nano phases; (d1) EDS of TiB_{2} ; (d2) EDS of TiC; (e) nano phases; (e1) EDS of TiC; (e2) EDS of TiB_2 .

In the early formation stage of the TiC phase, in the high-temperature in situ reaction in the molten alloy, the TiC structure itself contains many C vacancies [34]. This caused instability in the TiC phase structure and poor reinforcement efficiency. According to reports, TiC can degrade rapidly in 30 min. Element B is adjacent to C in the periodic table and has similar properties. In a melt, element B may diffuse and blend into the TiC lattice. This provides a prerequisite for doping with small- sized B atoms, and a way to control the structure and performance of the TiC reinforcement phase. The size of TiC is about 200 nm and the size of TiB₂ ranges from 200–900 nm.

3.4. Effects of Three Different Reinforcements on the Tensile Properties of the Al Alloy

Figure 12 is a bar graph showing the tensile strength of the Al-13Si-4Cu-1Mg-2Ni aluminum alloy cast piston, with three different reinforcements. The RT tensile strength increased by 13.8%, 8.6%, and 19.0%, respectively. The 350 °C tensile strength increased by 3.4%, 2.3%, and 18.4%, respectively. It revealed that all three reinforcements were effective, and that the addition of Al-5Ti-B-C-Ce reinforcement was more effective than the other two reinforcements, in increasing the room temperature and high-temperature tensile strength.



Figure 12. Tensile strengths of Al-13Si-4Cu-1Mg-2Ni alloy, with and without in situ reinforcements.

3.5. Strengthening Mechanism

In the process of solidification of the aluminum alloy, the dissolution and formation of intermetallic compounds will be formed, and the formed or added heteromorphic nuclear particles can be uniformly dispersed in the matrix alloy to promote the nucleation. By increasing the nucleation core of the non-uniform nucleation, it is precisely the principle of adding reinforcement to the matrix to refine the grain.

These lumpy Al₃Ti particles are block phase, which can cause cleavage phenomenon in the grain boundary and seriously affect the properties of the aluminum alloy [35]. To improve the performance of single Al-Ti-C and Al-Ti-B, the Al-Ti-B-C-Ce hybrid enhancement was prepared, which made TiC and TiB₂ play a double enhancement role. Simultaneously, the rare earths surface active elements can increase the wetting angle, improve the wettability of boride aluminum liquid, are easy to gather on the phase interface and grain interface adsorption, can fill in the surface of the grain defect, whilst making the grain continue to grow unhampered leading to the refinement of grain. Rare earth Ce, also has the effect of degassing (deoxygenation) [36,37]. In this way, TiC and TiB₂ are improved in the aluminum solution and the strength of the alloy is improved.

4. Conclusions

In this paper, three different kinds of reinforcements Al-Ti-C, Al-Ti-B, and Al-Ti-B-C-Ce were added to the alloy Al-13Si-4Cu-1Mg-2Ni, to compare its strengthening effect. The three reinforcements were also analyzed by SEM and TEM. The results are summarized as follows:

- 1. After doping with trace amounts of elements B and Ce, the size of reinforcement Al_3Ti phase changed from 80 μ m (un-reinforced) to about 10 μ m, with the simultaneous formation of $Ti_2Al_{20}Ce$ phase.
- 2. Since doping with element B destroys the equilibrium growth conditions for TiC phase, small nano phases of TiC attached to the surface and vicinity of hexagonal TiB₂. Compared with alloy without element B doping, the hexagonal TiB₂ phase turns out to be a growth carrier for TiC nano-phase, and the distribution of TiC nano-phase is more uniform.
- 3. All three in situ reinforcements were effective to the Al-13Si-4Cu-2Ni-1Mg alloy, and the addition of Al-5Ti-B-C-Ce reinforcement was more effective than the other two reinforcements in increasing the room temperature and high-temperature tensile strength. The RT strength increased by 19.0%, and the 350 °C-strength increased by 18.4%.

Author Contributions: L.T. wrote the main part of the manuscript and took part in the planning and execution of the experiments. Y.G. conceived and designed the study. J.L. participated in the coordination of the study and reviewed the manuscript. F.X. carried provided experimental alloys and analytical samples. M.L. analyzed part of experimental results. Transmission experiments were carried by H.D., P.W. and J.W. performed performance tests and made a final examination of the article.

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