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Enhanced grain refinement of in situ CeB₆/Al composite inoculant on pure aluminum by

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Shuiqing Liu, Xin Wang, Chunxiang Cui^{*}, LiChen Zhao, Nuo Li, Zhe Zhang, Jinhua Ding,

Denghao Sha

Key Lab. for New Type of Functional Materials in Hebei Province, School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, P. R. China

*To whom all correspondence should be addressed: Tel: +86-022-26564125, Fax: +86-022-60204125;

Email: hutcui@hebut.edu.cn

Abstract

In situ CeB₆/Al composite has been proven to be an effective refiner for commercial pure aluminum, however, it remains unclear as to the mechanisms of synthesis and grain refinement. We use low-temperature alloying and high-speed melt spinning to optimize the microstructure of CeB₆. It is found that *in situ* CeB₆/Al composite shows controllable microstructure and its refining effect is obviously dependent on the size of CeB₆ particle/cluster. As nano-CeB₆ particles self-assemble into submicron clusters, the inoculant shows significantly enhanced refining effect, reducing the grain size of pure aluminum to ~110 μ m. The refining mechanism is attributed to the combining effect of the cluster structure in submicron scale and the excellent crystallography matching relationship of CeB₆ and Al. Mechanical properties of pure aluminum are also improved by addition of *in situ* CeB₆/Al composite inoculant due to collaboration effect of dispersion strengthening and grain refining strengthening.

Keywords: Aluminum alloys; Cerium hexaboride; Rapid solidification; Grain refinement; Mechanical properties; Inoculation mechanism;

1. Introduction

Inoculation is a common industrial technology in the field of metallurgy, which has been widely applied in aluminum alloys for almost 100 years [1-3]. By minute quantities of refiner (~0.5%) that added to the melt prior to solidification, inoculation can significantly reduce the grain size of metals, and in turn improve the mechanical properties. In the past decades, there has been increased interest in the development of new inoculants for aluminum alloys [4, 5]. From the first modern refiner Al-Ti alloy [6], Al-Ti-B intermediate alloys were successfully developed and applied in many cast alloys [7]. However, with the development of aluminum alloys, Al-Ti-B refiner shows limitations for Al-Si based alloys with high Si content or under certain conditions (i.e. poisoning) [8, 9]. Further studies on alloying of Al-Ti alloys were carried on, resulting in the discovery of some new refiners such as Al-Ti-C [10], Al-Ti-C-B [8] and Al-Ti-B-Re [11]. In addition, other binary alloys free of titanium were also developed for refining aluminum alloys, which includes Al-Sc [12], Al-Zr [13], Al-Sr [14], Al-Y [15], Al-Ce/La [16] and so on. Recently, some borides except TiB₂ such as NbB₂ [17, 18], LaB₆[19] and CeB₆ [20], were also found to be potential refiners for aluminum alloys. However, it remains unclear as to the physical and chemical behavior of the borides in aluminum melt, and the corresponding grain refinement mechanism should be clarified.

Refiner particle provides the nucleant substrate for heterogeneous nucleation of aluminum and plays an important role for grain refinement of aluminum alloys. In general, the refining efficiency of a refiner is strongly affected by the distribution, size, surface status of the particle and degree of super cooling. Greer et al indicated that the refining effect of Al-Ti-B inoculant is increased with the decreased size of TiB₂ particle, and the optimum size is ~2 μ m [21]. If the size of TiB₂ particles were very small (< 1 μ m), heterogeneous nucleation just occur under a large/deep degree of super cooling

[21]. Later in 2004, Quested and Greer developed their theory based on TiC and TiB₂ particles and indicated that the best particle size range is 300-500 nm [22]. Meanwhile, we also found that AlN particle possesses the best refining effect with a size of ~400 nm in an earlier work [23]. The optimum size of AlN particle accords with Greer' model and is in sub-micron scale. It is suggested that the crystal growing behavior at sub-micron is very important for aluminum alloys.

Aimed at improving the inoculation efficiency, many technologies have been used, including chemical modification [24], rapid solidification [25-29], ultrasonic processing [30, 31] and so on. Melt spinning is a typical rapid solidification method and has been used in preparation of inoculant due to many benefits such as chemical homogeneity and large solid solubility [32]. In particular, the secondary phases in aluminum alloys could be significantly refined under large degree of super cooling caused by high cooling rate [33-36]. For example, when the cooling rate of Al-Si alloy exceeded ~10⁶ K/s, the size of primary silicon could be reduced to nano-scale [37, 38]. Under this strategy, we used melt-spinning to prepare an in situ CeB₆/Al inoculant and the size of CeB₆ particle was controlled to >1 μ m [20]. However, the rotating speed of melt spinning in the previous work [20] was limited (3000 rpm) and the corresponding cooling rate was relatively low. It is necessary to investigate the effect of higher rotating speed on microstructure control of CeB₆/Al inoculant. Moreover, it remains unknown that whether the inoculant is effective as the CeB₆ particle size is reduced to submicron-scale or nano-scale.

In the present work, the CeB_6/Al composite inoculant was treated by melt spinning with different cooling rates for reducing the size of CeB_6 particle. A melt-spinning equipment with a high rotating speed up to 10000 rpm was used. The microstructure evolution of the refiner in the process of synthesis, controlling and inoculation was investigated in turn. The grain refinement mechanism was also discussed based on a cluster-swallowing model.

2. Materials and methods

2.1. Low-temperature preparation

Al-Ce alloy and Al-B alloy were used as raw materials to fabricate the refiner. According to the binary phase diagram as shown in Fig. 1 [39], Al-3B (all compositions quoted in this work are in wt.% unless otherwise stated) and Al-20Ce are both in liquid status at a temperature ~1200 K. It indicates that they are easy to melt and this is beneficial for the fabrication of master alloy. Therefore, commercial Al-20Ce and Al-3B alloys were used to prepare the Al-Ce-B master alloy with a nominal composition of Al-4.8Ce-2.3B (Al₉₃Ce₁B₆ in at %, denoted as C0 alloy). For low-temperature melting, induction melting (High frequency power,10 KW) was used under real-time monitoring by a double color infrared laser thermometer, and the reaction temperature was controlled to be about 1300 K. Then the master alloy was re-melted by induction melting (Middle frequency power, 40 KW) and the obtained melt was blew to the surface of a copper roller with a diameter of 22 cm to prepare the CeB₆/Al ribbons. The rotating speed of the copper roller was set as 2000 rpm, 4000 rpm and 8000 rpm, respectively (the obtained ribbons are denoted as C1, C2 and C3, respectively).

Scanning electron microscopy (SEM, S4800) was used to examine the three-dimensional (3D) morphologies of the refiner particles that were extracted from the ribbons by dilute hydrochloric acid, following the program detailed in reference [40]. The phase structure was confirmed by X-ray diffraction (XRD, Bruker D8 Discover) with Cu K α radiation. The phase composition was examined by energy dispersive spectrometer (EDS). The thermal stability of melt-spun sample was analyzed by differential scanning calorimetric (DSC, SDT/Q600).

2.2. Grain refining effect estimation

The CeB₆/Al ribbons prepared with different rotating speed were used as inoculants and added

into aluminum melt at 993 K (720 °C). The addition amount of inoculants was about 0.4% of the total weight of aluminum melt. We have proven that CeB₆/Al ribbon has the best refining effect with this amount of addition in previous work [20]. The melt was stirred for 10 s and then poured into a steel mold with a cavity of 20 mm in diameter and 120 mm in height. The specimens for metallographic examination were cut from the middle part of the as-cast rod and carefully grinded by sandpaper. After mechanical polishing, the specimens were etched in 0.5% HF solution for macroscopic observation. Next, re-polished Poulton's the specimens were and etched with reagent (60%HCl+30%HNO₃+5%HF+5%H₂O) for microscopic observation by optical microscopy (OM, Olympus). The grain size of each sample was examined by intercept method according to ASTM standard E112 [41]. Tensile mechanical test was performed on a WDW-100 KN material test machine following ASTM B557M-02 standard [42]. The microstructure of refiner particles was examined by High-Resolution Transmission Electron Microscopy (HRTEM, JEOL 2000FX).

3. Results

3.1. Low-temperature synthesis

Fig. 2 shows the typical XRD spectrum of Al-Ce-B master alloy (C0). It is clear that the spectrum has two groups of sharp diffraction peaks corresponding to α -Al and CeB₆, respectively. It is suggested that the CeB₆ phase has been fabricated in the melt at a temperature much lower than its melting point. In addition, some weak peaks of Al₁₁Ce₃ are also detected as shown in the inset of Fig.2. It indicates that the actual ratio of Ce:B is a little higher than 1:6 and the volatilizing of Ce is not obvious. In general, the melting of aluminum alloys with Ce-rich is accompanied by volatilizing of Ce. As the melting temperature is increased, the amount of volatilization is increased. The synthesis temperature in this case (1300 K) is much lower than the boiling point of Ce (3699 K [43]), which is beneficial for

reducing the volatilization of rare-earth elements.

Fig. 3 shows the SEM image and chemical composition of alloy C0. As shown in Fig. 3a, there are many white particles with different sizes on the α -Al matrix. The particles are aggregated in the melt due to interfacial tension, resulting in the heterogeneous distribution of particles in the matrix. In high-magnification SEM image as displayed in Fig. 3b, some of the white phases show small plane characteristics (Marked by B) and some particles show short rod-like morphology (Marked by A). According to the EDS results shown in Fig.3c and 3d, particle B can be speculated as cerium boride phase owing to a high Ce-B content; particle A might be some Al-Ce intermetallic. In combining consideration of the phase-diagram (see Fig. 1), EDS data (Fig. 3) and XRD results (see Fig. 2), the cerium boride (A) and Al-Ce intermetallic (B) can be confirmed as CeB₆ and Al₁₁Ce₃, respectively.

Fig. 3e shows the 3D morphologies of the CeB₆ particles in C0 alloy. In general, CeB₆ particles show cubic shape and smaller particles are incline to combine bigger clusters with many zigzag steps. In particular, the small CeB₆ cubes in a cluster have similar orientation. It is strongly suggested that big clusters are actually assembled by small particles (so called self-assembled). This phenomenon is in accordance with that of sub-micron CeB₆ particles synthesized by sintering of CeO and B₂O₃ [44]. In our opinion, the growth of CeB₆ particles in Al melt is similar with that of sintering method. During self-assembling, nano-CeB₆ particles with similar crystalline orientation would connect together and combine into a bigger particle/cluster. The self-assembled particle/cluster can self-assemble again and grows into big cluster step-by-step. As a result, CeB₆ can grow into some very big particles/clusters with a size of ~100 μ m. For example, Fig. 3f shows a hexagonal particle composited of many small particles.

3.2. Microstructure control

Fig. 4 shows the optical pictures of the cross-section surface of the melt-spun CeB₆/Al ribbons with different rotating speeds. The thickness of C1, C2 and C3 alloy is about 132 μ m, 42 μ m and 12 μ m, respectively. As well known, the thickness of melt-spun ribbon is related to the cooling rate of the melt during solidification. According to the method proposed in references [37,38], the average cooling rates of ribbon C1, C2 and C3 can be calculated as 4.59×10^5 K/s, 1.14×10^7 K/s and 1.58×10^8 K/s, respectively.

Fig. 5 shows the XRD spectra of the ribbon samples. All the XRD spectra have typical peaks of α -Al_s Al₁₁Ce₃ and CeB₆ phase. It is demonstrated that the phase composition of the alloy is not obviously changed by melt spinning. However, it should be noted that the major peak of Al₁₁Ce₃ phase is weakening with the increased cooling rate. It is suggested that the formation of Al₁₁Ce₃ phase is inhibited to some extent due to fast solidification.

Fig. 6 shows the SEM images of the CeB₆/Al ribbons with different cooling rates. For alloy C1, the size of the particles is in a range of 0.5-13.5 μ m and the particles are inclined to agglomerate to big clusters as shown in Fig. 7a. As the cooling rate is increased to ~10⁷ K/s (alloy C2), the size of the CeB₆ particles is reduced to 0.5-7 μ m as shown in Fig. 7b. Furthermore, when the cooling rate is increased to ~10⁸ K/s (alloy C3), the size of CeB₆ particles is reduced to ~80 nm as shown in Fig. 7c. It is demonstrated that the size of CeB₆ particles is strongly dependent on the cooling rate. As well known, the degree of supper cooling is increased with cooling rate, which in turn causes improved nucleation rate or refining effect [21]. For similar reason, CeB₆ particles in C3 homogeneously distributes on the matrix. This also is attributed to the applied high cooling rate, which suppresses the settlement and aggregation of nano particles [45]. It should be noted that the nano-CeB₆ particles are not separately

distributed; in fact, they are also organized into small clusters with a size of \sim 300 nm as shown in the inset of Fig. 6c. To sum up, it indicates that melt-spinning is an effective method to control the microstructure of *in situ* CeB₆/Al alloy.

It is also worth noting that Fig. 6 shows the two-dimensional (2D) morphology of the CeB_6 particles on the surface of ribbons. All the particles are wrapped by Al matrix, thus the 3D morphology/size of CeB_6 particles cannot be clearly observed. In order to know the actual size of the particles rather than some sections of them, we extracted the ribbons and obtained the 3D morphology as shown in Fig. 8. It can be found that the actual 3D sizes of the CeB_6 particles are comparable to that of the 2D image. It is also in accordance with the result shown in Fig. 7.

3.3 Grain refining effect examination

Fig. 9 shows the macro/micro metallographic images of the Al samples refined by alloy C1, C2 and C3, respectively. The macro metallographic images indicate that all the samples are free of columnar grain as shown in Fig. 9a-d. Meanwhile, the grain size of the sample is significantly decreased with the increased cooling rate of ribbon, as shown in Fig. 9e-h. By adding C1 and C2 alloy, the grain of pure Al with size of ~ 820 μ m is obviously refined into small grain with ~ 260 μ m and ~ 195 μ m, respectively. In particular, the grain size of pure Al is reduced to ~110 μ m after refinement with alloy C3. This refined grain size is smaller by 30% than that of previous work [20]. Therefore, it is demonstrated that the grain refining efficiency of CeB₆/Al ribbon is greatly improved by the high-speed melt-spinning treatment.

Fig.10 shows the mechanical properties of the samples after inoculation. The mechanical properties of Al samples have been enhanced by grain refinement. After refining by alloy C3, the tensile strength and yield strength of the Al samples are 115.7 MPa and 71.8 MPa, respectively. In

comparison with pure aluminum without inoculation, the strength values are increased by 1.75 times and 1.47 times. Moreover, the elongation of the sample inoculated by alloy C3 is still good.

The enhancement of strengthening effect is mainly resulted from the following two aspects. The first, according to the Hall-Petch theory, grain refinement could improve the toughness and strength of metallic matrix [46]. If the grain size were finer, the amount of grain boundaries turns more, resulting in an enhanced grain boundary strengthening [47]. The second, according to the dispersion strengthening theory, the homogeneously distributed ceramic particles can pin the motion of dislocations, leading to the increased deforming resistance [48, 49]. Under the combining effect of above two aspects, the strength and elongation of the Al samples are obviously improved by the inoculation treatment.

3.4 Identification of nucleant particles

Fig. 11 shows the TEM image of a typical cluster in alloy C3, which indicates that the size of the cluster is about 128 nm. The cluster is composed of several particles less than 100 nm as shown in Fig. 11a. Meanwhile, no obvious grain boundary can be found, which indicates that the cluster is an intracrystalline one. Fig. 11b shows the electron diffraction pattern of this cluster. Interestingly, some of the electron diffraction spots (marked by dotted rectangles in Fig. 11b) are actually composed of two or three spots next to each other. It is demonstrated that the cluster is assembled by several particles with similar crystallographic orientation. For a clearer observation, the inverting image of Fig. 11b is shown in Fig. 11c and the diffraction spots are connected by lines. Based on the diffraction result, the cluster can be confirmed as CeB_{6} , which is in accordance with the XRD results shown in Fig. 5.

Fig. 12 shows the TEM image of the as-cast aluminum alloy after inoculation by alloy C3. It is found that the size of the dispersion particles is about 5 nm which is much smaller than that in

inoculant ribbons (~100 nm). Fig. 12b shows the HRTEM image of the particle marked by A in Fig. 12a. The interplanar crystal spacing d can be measured from Fig. 12b as following: d(111) = 0.2391 nm and d(200) = 0.2070 nm, which is equal to the corresponding values of CeB₆ (X-ray crystallology card number 38-1455, 0.23900 nm and 0.20698 nm, respectively). Meanwhile, the angle between the (111) plane and the (200) plane is measured to be about 54°76′, which is very closed to the theoretical value of CeB₆ (54°73′, based on crystallography calculation [43]). Therefore, this precipitate phase could be confirmed as CeB₆. In addition, the crystal orientation of these nano CeB₆ particles is almost the same, which implies that they are divided from (or belong to) one bigger particle/cluster.

4. Discussion

Size-effect of refiner particle, which was presented by Greer et al, is the basis for microstructure control/optimization of inoculants in present work. Greer indicated that the most favorable size range of particles is about 0.3-0.5 μ m [22]. In this work, the size of CeB₆ particle in alloy C3 is only 50-100 nm (see Fig. 6c and Fig. 11a) and the refining effect is also significant. It is worthy of noticing that, several nano CeB₆ particles generally unites to clusters in a range of 50-200 nm as shown in Fig. 7c (Measured from 2D image). In consideration of 3D space, the actual size of clusters must be a little large, which is in a sub-micron scale and closed to the ideal size range 0.3-0.5 μ m. Moreover, alloy C3 almost contains no big cluster over 1 μ m, which rules out the negative effect of larger particles on nucleation events. As it was known, larger particles motivate the nucleation first due to the small undercooling needed [22]. Then, the temperature of the melt around big particles will be increased by the recalescence of the first nucleation events, resulting in that smaller particles become inactive due to the decreased undercooling. This reduces the number efficiency of inoculants and efficiency of the master alloy. In the present work, C1 has the widest size range of particles and C3 got minimum.

Therefore, the improved efficiency of *in situ* CeB₆/Al composite inoculants can be attributed to the reduced size spreading of the particles in C3 ribbons.

After adding in Al melt during the inoculation treatment, the sub-micron CeB_6 clusters in C3 are reduced to smaller particles (~10 nm) and have a tendency to dispersion (Fig. 12a). In particular, the dispersed nano-particles almost have the same crystallographic orientations as shown in Fig. 12b. It is suggested that sub-micron CeB_6 clusters continue to be reduced during the inoculation treatment. In other words, CeB_6 clusters might is instable or soluble in pure Al melt, although CeB_6 has a high melting point. To know the thermal stability of CeB_6/Al inoculant, Fig. 13 shows the DSC examination result of C3 alloy. It is clearly that no other thermic event is observed except two endothermic peaks. The higher peak (934.2 K) is associated with the melting of α -Al matrix, and the lower one (912.7 K) is associated with the melting temperature of eutectic (α -Al+ Al₁₁Ce₃) according to Fig. 1. It can be confirmed that no chemically decomposition of CeB_6 occurs at the inoculation temperature range. We think that the reduced particles might relate to the pre-melting of low-melting-point eutectic phase (α -Al+Al₁₁Ce₃) around the CeB₆ clusters.

Fig. 14 shows a schematic image explaining the refinement of sub-micron CeB_6 cluster. According to Fig. 3b, we assume that big CeB_6 clusters are composited of smaller clusters that are connected by eutectic. During the addition of inoculant into Al melt, eutectic phase melts first leading to the formation of thin liquid bands (Ce-rich liquid) among the CeB_6 particles in the cluster (Fig. 14 t_1 - t_2). These liquid bands can act as cracks in the cluster, leading to the subsequent crack of big cluster with the role of heat stress. Next, Ce atoms in Ce-rich liquid must diffuse to the Al liquid without Ce content (Fig. 14 t_3). Affected by the crack and diffusion of Ce atoms, big clusters tend to divide into smaller clusters, which not only increase the amount of potential nucleated surface but also narrowing

the distribution of cluster size to an ideal range. The melting of eutectic phase and diffusion of Ce atoms also generate a diluted Al-Ce liquid layer around the cluster. It was known that solute atoms can restrain the growth of the nucleated Al crystal [22]. Therefore, the growth of Al crystal will mainly along the zigzag surface of the cluster while not toward the free liquid region as shown in Fig. 14 t_5 - t_8 . In fact, it is a process of Al crystal swallowing the cluster, which causes nano particles to exist intracrystaline whilst not on the grain boundary (see Fig. 12).

In previous work [20], we presented that $\{200\}CeB_6$ can match $\{111\}Al$ to stimulate the nucleation of Al crystal. The zigzag surface of nano-CeB₆ cluster promotes the probability of $\{200\}CeB_6$ matching $\{111\}Al$, such that the α -Al nucleus can be fast formed among the small particles. In addition, it is important that nano particles in a cluster have almost the same crystallographic orientation. This guarantees that aluminum crystals nucleated on the zigzag surface grows on a same space orientation so that the grown crystal is a single one. If the orientation of the particles in one cluster were very different, the cluster might stimulate multiple crystalline nuclei, resulting in the cluster to stay between the nuclei. It also makes the cluster distribute on the grain boundary and decreases the effect of dispersion strengthening.

5. Conclusions

- 1) In the present work, a preparation route of low-temperature synthesis and high-speed melt spinning treatment of CeB_6/Al inoculant is developed and the *in situ* inoculant shows highly controllable microstructure. The size of CeB_6 particles strongly dependes on the cooling rate in preparation.
- 2) The grain refining effect of CeB_6/Al inoculant is dependent on the size of CeB_6 particle and cluster. As the size of CeB_6 clusters is reduced to ~300 nm, the inoculant shows enhanced

grain refining effect, and the average grain size of pure aluminum can be reduced to 110 ± 25 $\mu m.$

- 3) The sub-micron CeB₆ clusters are de-agglomerated to smaller ones composed of nano particles with sizes of ~10 nm. The nano-CeB₆ particles are highly in dispersion, resulting in strong strengthening effect.
- 4) A cluster-swallowing model is proposed to explain the inoculation mechanism of CeB_6 clusters. Nano-sized CeB_6 particles are inclined to organize into sub-micron clusters in which the crystallographic orientation of nano particles are matching. The naked zigzag step plays an important role for the growth of the α -Al nuclei.

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Figures caption

Fig. 1. Binary alloy phase diagrams of (a) Al-B system and (b) Al-Ce system [39].

Fig. 2. XRD spectrum of the C0 inoculant alloy.

Fig. 3. SEM images and EDS patterns of alloy C0. (a) Typical SEM image, (b) Al-Ce eutectic in local region of alloy C0, (c)-(d) EDS spectrum of point A and B in (b) and (e)-(f) SEM image showing the morphology of the particles extracted from C0 alloy.

Fig. 4. (a) Temperature-time plots of different CeB_6/Al ribbons during solidification and (b)-(d) Optical micrographs of the ribbons with different cooling rates showing the corresponding thickness.

Fig. 5. XRD spectra of the inoculant alloys with different cooling rates. (a) C1 alloy, (b) C2 alloy and (c) C3 alloy.

Fig. 6. SEM image of (a) C1 alloy, (b) C2 alloy, (c) C3 alloy and (d) EDS spectrum of (c).

Fig. 7. Distribution diagram of the size of the CeB₆ particles in (a) C1 alloy, (b) C2 alloy and (c) C3 alloy.

Fig. 8. SEM images of the particles extracted from (a) C1 alloy, (b) C2 alloy and (c) C3 alloy, respectively.

Fig. 9. Optical images of as-cast aluminum samples: (a),(e) pure Al without inoculation, (b),(f) (c),(g) and (d),(h) are inoculation with C1, C2 andC3 alloy, respectively.

Fig. 10. Mechanical properties of different as-cast aluminum samples after inoculation.

Fig. 11. (a) Typical TEM image of C3 alloy, (b) Electron diffraction pattern of the cluster in (a) and (c) Inverting image of (b) showing the marked diffraction information.

Fig. 12. TEM characterization of the as-cast aluminum inculanted by CeB_6/Al ribbon C3. (a) TEM micrograph showing nano-sized CeB_6 particles cluster and (b) HRTEM image of the particle marked in

Fig. 12(a).

Fig. 13. DSC curve showing the melting behavior of C3 alloy.

Fig. 14. Schematic image showing the nucleation and growth process of an aluminum grain upon a sub-micron cluster composed of nano-sized CeB_6 particles.

Figures

Figure 1











AS CRIP

























Highlights

- CeB_6 was *in situ* fabricated in Al melt at a low temperature by induction melting.
- CeB_6/Al inoculant can be refined to nano-scale by melt spinning and shows controllable feature.
- Grain refining effect of CeB_6/Al inoculant is obviously enhanced by microstructure control.
- An inoculation model based on nano-particle clusters was proposed.

CER ANA