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Research on microstructure and solidification mechanism of Al-Ti-C-Ce mother alloy prepared by titanium hydride-petroleum coke

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Abstract. Microstructure of Al-Ti-C-Ce mother alloy which was prepared by titanium hydride-graphite-aluminum cerium alloy and aluminum liquid was studied by modern detection analysis methods, such as X-ray diffraction (XRD), scanning electron microscope (SEM), and energy disperse spectroscopy (EDS). Results demonstrated that the prepared Al-Ti-C-Ce mother alloy is composed of $\alpha$(Al), (TiC) and (Ti$_2$Al$_2$0Ce). Particle boundary of casting samples used the continuous eutectic structure. There are extensive distributions of coarse second-phase structures in crystals. Eutectics in the crystal boundary and the second-phase in crystals all contain Ti$_2$Al$_2$0Ce phase. The second-phase structure of most large particles is composite structures. There are $\alpha$(Al)+Ti$_2$Al$_2$0Ce+ Al$_4$C$_3$+(TiC) peritectic structures with deep colors in composite particles. According to the linear analysis results, distribution of the element C is relatively uniform in the second-phase particles. C and Al contents in particles are relatively low, while Ti and Ce contents are relatively higher. Ce content in the second-phase particles is significantly higher than that in the external regions of particles. In particle regions which are covered by the second phase of composite structure, Ti and C contents are extremely higher, while Al and Ce contents are relatively lower. During the solidification process of alloy, particles containing Ti and C are precipitated firstly as crystal nucleus. The Ti$_2$Al$_2$0Ce-containing phase realizes nucleation through particles containing Ti and C particles. $\alpha$(Al) realizes nucleation through the composite particles composed of Ti phase, C phase and Ce phase. The composite particles containing Ti, C and Ce precipitated firstly as the primary phase. Al-Ti-C-Ce mother alloy crystal particles are refined.

1. Introduction

With characteristics of low density, high specific strength and excellent conductivity of heat and electricity, aluminum (Al) is widely used in various fields, such as traffic transportation, submarine and ships, aerospace, machinery manufacturing, etc. [1-3] Particle refiner can refine particle sizes and improve the quality of the cast ingot. It is the key essential material in casting of aluminium alloy 4-7. Since the discovery of TiB$_2$ particle segregation in Al-Ti-B [8-9], Banerji and Reif[10-11] et al. from the Technical University of Berlin developed the Al-Ti-C intermediate alloy. This Al-Ti-C intermediate alloy has no poison and particle segregation problems. Al-Ti-C is one great breakthrough in particle refiner technology of Al alloys [12-13]. At present, Al-Ti-C alloy still has some problems that restrict its industrial applications. Firstly, C is an element which is difficult to be dissolved in Al alloy [14-15]. The production conditions to prepare the Al-Ti-C intermediate alloy based on powder metallurgy and
detonation method [16] are very strict. Besides, the production cost is high. To dissolve carbon in the Al alloy, C-containing Al alloy was manufactured in industry by using high-temperature (1200-1300°C) technology. However, this will bring some problems, such as very serious oxidization and inspiration of alloys, poor quality of the prepared Al-Ti-C intermediate alloy, and influences on the refining effect. Environmental and equipment pollution caused by metal volatilization and oxidization may affect the normal operation of equipments and threat physical health of operators. Secondly, there’s a problem of titanium source selection. However, the refining effect of the Al-Ti-C intermediate alloy which is prepared by using Al-Ti as the titanium source is not stable, which is caused by difference C contents in products and physical state of carbides. With a high melting point, the sponge titanium requires high temperature and long time for reaction. When K₂TiF₆ was used as the titanium source, there’s fluorine dust contamination and the reaction byproducts have to be treated by special equipments. Thirdly, C content in the Al-Ti-C alloy which is prepared by the direct melt reaction method is generally about 0.15%-0.25%. Due to the low TiC-phase content, the refining effect is restricted. Therefore, exploring an environmental-friendly preparation method of the Al-Ti-C intermediate alloy with stable quality is an important task in the industry. The decomposition temperature of titanium hydride is about 400°C. The high temperature of 740~760°C is adequate for decomposition of titanium hydride and Al-Ti-C synthesis. The preparation of the intermediate alloy does not experience high temperature and reduces the probability for intermediate alloy to produce coarse equilibrium phase. Moreover, no harmful fluorine dust is generated, which relieves the environmental pollution pressure. To solve the problem that aluminum melt is difficult to wet graphite, researchers in the world have developed various methods for preparation of Al-Ti-C alloy. In this study, rare earth Ce is added into the preparation process of Al-Ti-C alloy. It attempted to improve carbon wettability by Al by taking advantages of surface activity of rare earth elements, aiming to acquire the Al-Ti-C-Ce alloy with higher C content, higher volume fraction of TiC and better refining effect. The relevant low-temperature preparation technique was developed.

2. Experiment
In this experiment, 99.85% commercial-purity aluminum, titanium hydride and graphite were used as the raw materials. The intermediate alloy of Al-30% Ce was used as the surfactant. Under the temperature of 760-930°C, a group of Al-Ti-C-Ce mother alloy was prepared using the crucible resistance smelting furnace and water-cooling copper mold casting. The chemical composition of the Al-Ti-C-Ce mother alloy was analyzed by the LEEMANSPEC-E inductive coupling plasma atomic emission spectrometer. The chemical composition of the Al-Ti-C-Ce mother alloy is shown in Table 1. Microstructure and solidification mechanism of the Al-Ti-C-Ce mother alloy prepared by reactions of titanium hydride, graphite, and Al-Ce alloy and Al liquid were studied by XRD, SEM and EDS.

![Figure 1. XRD analysis of phase composition of Al-Ti-C-Ce mother alloy](image)

| Table 1. Chemical composition of Al-Ti-C-Ce mother alloy (Mass fraction, %) |
|---|---|---|---|---|---|
| alloy | Al  | Ti  | C   | Ce  | Other impurities |
| 1#    | 88.35 | 4.79 | 0.63 | 5.6  | Bal. |
3. Results and Analysis

3.1. XRD Analysis of the Al-Ti-C-Ce Mother Alloy
The Al-Ti-C-Ce mother alloy was prepared by using the commercial-pure Al as the raw material, titanium hydride and graphite as the titanium source and carbon source, Al-30%Ce as the active additive, and hexachloroethane-cryolite as the refining agent under 760-930°C. The XRD analysis results of the prepared Al-Ti-C-Ce mother alloy are shown in Fig.1. The alloy matrix is composed of α (Al), (TiC) and Ti2Al20Ce phases.

3.2. SEM Analysis of the Al-Ti-C-Ce Mother Alloy
The SEM metallographic structure of the Al-Ti-C-Ce mother alloy casting sample is shown in Fig.2. Fig.2 (a) is the structure of the sample under 800 magnifications. Fig.2 (b) is the structure of the second phase of typical large particles under 2000 magnifications. It can be seen from Fig.2 (a) and Fig.2 (b) that the crystal boundary of the mother alloy casting sample is a continuous eutectic structure. There’s extensive distribution of coarse second-phase structures in the crystals. The second phase structures of some large particles are composite structural particles. Deep ash black structures are existed in the second-phase particles.

EDS of the second-phase particles in the Al-Ti-C-Ce mother alloy casting samples is shown in Fig.3. The second-phase regional distributions in the matrix, crystals and crystal boundary of the prepared Al-Ti-C-Ce mother alloy are shown in Fig.3 (a). EDS curves of chemical composition of the second-phase regions in the matrix, crystals and crystal boundary of the prepared Al-Ti-C-Ce mother alloy are shown in Fig.3 (b) and Fig.3(c). EDS analysis results in regions a-1, a-2 and a-3 are listed in Table 2. By combining EDS analysis results in Table 2 and the corresponding aluminum alloy phase diagram, a-1 is the eutectic structure composed of α (Al)+ (Al4Ce)+Ti2Al20Ce. a-2 is the eutectic structure composed of α (Al)+ (Al4Ce). a-3 is the eutectic structure composed of α (Al)+Ti2Al20Ce. a-4 is the eutectic structure composed of α (Al)+Ti2Al20Ce+(Al4C3). a-5 is the eutectic structure composed of α(Al)+ Ti2Al20Ce+(Al4C3). a-6 is the eutectic structure composed of α(Al)+ Ti2Al20Ce+(TiC)+ (Al3C4). Based on above analysis, eutectics at crystal boundary and the second phase in crystals contain the Ti2Al20Ce phase.
Figure 3. EDS analysis of the second-phase particles of the Al-Ti-C-Ce mother alloy casting samples

Table 2. EDS results of chemical composition of the second-phase particles (Atom number, %)

| area | Al   | Ti   | C    | Ce   | the phases                                      |
|------|------|------|------|------|-------------------------------------------------|
| a-1  | 96.70| 2.05 | -    | 1.25 | α(Al)+(Al$_4$Ce)+Ti$_2$Al$_{20}$Ce               |
| a-2  | 97.48| 0.09 | -    | 2.43 | α(Al)+(Al$_4$Ce)                                |
| a-3  | 99.47| 0.30 | -    | 0.23 | α(Al)+Ti$_2$Al$_{20}$Ce                         |
| a-4  | 91.94| 0.18 | 7.65 | 0.24 | α(Al)+Ti$_2$Al$_{20}$Ce+(Al$_4$C$_3$)            |
| a-5  | 94.16| 4.22 | -    | 1.62 | α(Al)+Ti$_2$Al$_{20}$Ce+(AlTi)                  |
| a-6  | 99.51| 0.11 | -    | 0.38 | α(Al)+Ti$_2$Al$_{20}$Ce                         |
| a-7  | 93.71| 0.23 | 5.78 | 0.28 | α(Al)+Ti$_2$Al$_{20}$Ce+(Al$_4$C$_3$)            |
| a-8  | 99.81| 0.10 | -    | 0.09 | α(Al)                                           |
| a-9  | 89.80| 2.12 | 7.60 | 1.48 | α(Al)+Ti$_2$Al$_{20}$Ce+(TiC)+(Al$_3$C$_4$)      |

Figure 4. Site distribution in EDS analysis of the Al-Ti-C-Ce mother alloy and EDS analysis results

The EDS results of the second-phase particles in the Al-Ti-C-Ce mother alloy are shown in Fig.4. Fig.4 (a) is distribution of the second phase in matrix, crystals and crystal particles of the Al-Ti-C-Ce mother alloy. Fig.4 (b) and Fig.4(c) are EDS curves of chemical composition of the second phase in matrix, crystals and crystal boundary of the alloy. EDS analysis results of regions b-1, b-2, b-3 and b-4 are shown in Table 3. By combining EDS analysis results in Table 3 and the corresponding aluminum alloy phase diagram, b-1 and b-2 are eutectic structures composed of α (Al)+Ti$_2$Al$_{20}$Ce+(Al$_4$Ce). b-3 is the eutectic structure composed of α (Al)+Ti$_2$Al$_{20}$Ce+Al$_4$C$_3$+(TiC). b-4 is the eutectic structure composed of Ti$_2$Al$_{20}$Ce+Al$_3$Ti+(TiC)+α(Al). It can determine from Fig.4 (a) preliminary that b-3 and b-4 form the particle A, where b-3 is the nucleus of the particle A.
Table 3. EDS analysis of the second-phase particles of the alloy (Atom number, %)

| area | Al    | Ti    | C     | Ce   | the phases                                      |
|------|-------|-------|-------|------|------------------------------------------------|
| b-1  | 98.45 | 0.43  | -     | 1.12 | α(Al)+Ti2Al20Ce+(Al5Ce)                         |
| b-2  | 97.11 | 0.21  | -     | 2.68 | α(Al)+Ti2Al20Ce+(Al5Ce)                         |
| b-3  | 80.79 | 3.96  | 13.74 | 1.51 | α(Al)+Ti2Al20Ce+Al4C3+(TiC)                    |
| b-4  | 87.18 | 8.69  | 1.13  | 4.13 | Ti2Al20Ce+Al4Ti+(TiC)+α(Al)                     |

SEM linear scanning images of Al, Ti, C and Ce distribution in the second-phase structure of the alloy are shown in Fig.5. Fig.5 (a) is positions of regions for element linear distribution analysis in particle A in the second-phase region. All selected region have one second-phase particle B with irregular shapes. The linear scanning element distribution line A runs through particle A and particle B. Fig.5 (b) shows positions of sites for element linear distribution analysis in particle C in the second-phase region. The linear scanning element distribution line B runs through particle c. Fig.5(c) is the linear scanning analysis results of Al, Ti, C and Ce in particle A and particle B along the line A. It can be seen from Fig.5(c) that distribution of C is relatively uniform in particle A in the second-phase of mother alloy. Moreover, C and Al contents in particles are relatively low, while Ti and Ce contents are relatively high. In particular, Ce content in the second-phase of mother alloy is significantly higher than that in external region of particles. In particle B, C content is extremely, but Ti and Ce contents are relatively low. This conforms to the analysis results of Fig.4. Particle B shall be the nucleus of nucleation of particle A. The linear scanning analysis results of Al, Ti, C and Ce distributions in particle C along line A are shown in Fig.5(d). Clearly, distribution of C in particle C is relatively uniform. C accumulation only occurs in the local region. Al content in particles is lower than that in surrounding matrix regions. Ti and Ce contents in particles are significantly higher than those in the alloy matrix. In C accumulation region in particle C, Al content increases and Ce content decreases.

Figure 5. SEM linear scanning images of Al, Ti, C and Ce in the second-phase of the alloy

3.3. Analysis on Solidification Process of the Al-Ti-C-Ce Mother Alloy

Major phases of the test alloy mainly include α (Al), (TiC) and (Ti2Al20Ce). According to different adding sequence of titanium hydride, graphite and Al-Ce intermediate alloy, alloy may produce different phases, such as TiAl3, Al2(Ce3, Al4(Ce2, Ti3AlC2, Ti5AlC and Ti5C5. In the solidification process of Al alloy, the key of nucleation is to gain the nucleation “base” with very small wetting angle of crystal nucleus. This “base” refers to the atomic cluster which has similar atomic structure and bond type with crystal nucleus. One refining mechanism of Al alloy crystals by Titanium in the Al-Ti-B alloy is widely accepted. In this mechanism, Ti Al5 precipitated on the TiB2 surface, forming a
thin shell and α (Al) forms nucleus through this shell [12-13]. In the Al-Ti-C-Ce alloy, there are simple cubic TiC phases whose melting point is 3140°C. It is a kind of aluminide with high melting point and stable performance in high-temperature aluminum melt. The lattice constant is 0.4329 nm, which is close to that of α (Al). According to analysis in Fig.4, composite particles containing TiC and TiAl3 exist in particle A. Fig.5 shows that Ti, C and Ce contents in particle A and particle C in the second phase are significantly higher than those in the alloy matrix. Abnormal accumulations of Ti and C at particle B are observed. During alloy solidification, the TiC indissovable phase which coherent with α (Al) not only can be used as the heterogeneous nucleus for α (Al) solidification, but also can inhibit dissolution of Ti Al3 and (Ti2Al20Ce) phases in aluminum liquid. The remained Ti Al3 and (Ti2Al20Ce) phases are precipitated on the TiC phase surface. TiC phase is the “base” of nucleation of Ti Al3 and (Ti2Al20Ce) phases and the heterogeneous nucleus of α(Al). The Ti Al3 and (Ti2Al20Ce) shells which are precipitated on the TiC phase surface are the heterogeneous nucleus of α(Al) solidification. Hence, the solidification mechanism of the alloy can be depicted as follows. In the solidification process of alloy, particles containing Ti and C are precipitated firstly as nucleus, while particles containing Ce phase (Ti2Al20Ce) nucleate through particles containing Ti and C. α (Al) nucleates through the composite particles containing Ti, C and Ce. Composite particles containing Ti, C and Ce are precipitated firstly as the leading phase. Particles of the Al-Ti-C-Ce mother alloy are refined.

4. Conclusions
The Al-Ti-C-Ce mother alloy is prepared using titanium hydride, graphite and electrolytic liquid-Al as raw materials and Al-Ce alloy as the surfactant under high temperatures (760-930°C). It has excellent structures and compositions. Microstructure and solidification process of the alloy have following characteristics:

1. The prepared Al-Ti-C-Ce mother alloy is composed of α (Al), (TiC) and (Ti2Al20Ce) phases.

2. Crystal boundary of the prepared Al-Ti-C-Ce mother alloy is a continuous eutectic structure. There’s an extensive distribution of coarse second-phase structures in crystals. Ti2Al20Ce phase exists in eutectics in the crystal boundary and the second phase in crystals. The second-phase structures of some large particles are composite structural particles. α (Al)+Ti2Al20Ce+Al4C3+(TiC) peritectic structures with deep colors are observed in the second-phase particles.

3. C distributes uniformly in the second-phase particles. C and Al contents in particles are relatively low, while Ti and Ce contents are relatively high. In particular, Ce content in the second-phase particles is significantly higher than that in external regions. Ti and C contents in particle regions in the composite second phase are extremely high, but Al and Ce contents are low.

4. In the solidification process of the prepared alloy, particles containing Ti and C are precipitated firstly as nucleus. Particles containing (Ti2Al20Ce) phase nucleate through particle containing Ti and C. α(Al) nucleates through the composite particles composed of Ti, C and Ce phases. Composite particles containing Ti, C and Ce are precipitated firstly as the leading phases, thus refining crystals of the Al-Ti-C-Ce mother alloy.

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