Effect of the addition of cerium on the microstructure evolution and thermal expansion properties of cast Al-Cu-Fe alloy

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Abstract

The evolution of the microstructure and the variation in the thermal expansion properties of the Al_{63}Cu_{25}Fe_{12} alloy by the addition of different amounts of cerium (Ce) are investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). Herein, a new series of quasicrystal alloys containing Ce are prepared. Results revealed that the Al_{63}Cu_{25}Fe_{12} alloy contains icosahedral quasicrystal phase (I-phase), \( \lambda - Al_{13}Fe_4 \) phase, \( \beta - Al_{0.5}Fe_{0.5} \) phase and \( Al_2Cu \) phase. The addition of Ce is confirmed to lead to grain refinement, formation of the \( Al_{13}Ce_2Cu_{13} \) phase, disappearance of the \( \lambda - Al_{13}Fe_4 \) phase. Furthermore, the area fraction of the I-phase in the alloy is confirmed to reach the maximum value, and the linear expansion coefficient of the alloy is the lowest due to the addition of Ce of up to 1 at%. The addition of Ce can reduce the linear expansion coefficient of the Al_{63}Cu_{25}Fe_{12} alloy by \( \sim 20\% \). The contribution of Ce will render better prospects for the application of Al-Cu-Fe-Ce materials.

1. Introduction

Aluminum alloys have been widely used in modern industrial production due to their good mechanical performance. Extensive applications of aluminum alloys are restricted due to their high linear expansion coefficient, especially at elevated temperatures. Hence, it is crucial to develop a novel aluminum alloy that exhibits a low linear expansion coefficient at elevated temperature [1–3]. Some researchers have utilized one type of ceramic particles (such as oxides, carbides, and nitrides) as the strengthening phase to develop aluminum matrix composites [4–7]. Unfortunately, the lack of bonding at the interface between the aluminum matrix and ceramic particulates leads to the incoherency between the matrix and strengthening phase. Meanwhile, this incoherency serves as a point of stress concentration for the generation and propagation of cracks [8]. In addition, aluminum alloys reinforced by the quasicrystal phase has received attention recently due to their excellent mechanical properties and thermal stability [9–14].

Shechtman et al first discovered an icosahedral quasicrystal structure [15–17], which opened a whole new research field. The I-phase has been described as a construction with disallowed symmetries (e.g., twofold, tenfold, eightfold, and fivefold rotation axis) and a long-range orientational order [18–20]. Clearly, the emergence of I-phase alloys and their potential for utilization have attracted considerable research interest in recent years, and quasicrystal materials demonstrate high potential for applications [21, 22].

The Al-Cu-Fe system is one of the first metallic systems in which the formation of a stable I-phase has been reported [20, 23, 24], and Al-Cu-Fe quasicrystal (QC) alloys have been reported to exhibit a high intrinsic brittle characteristic [25, 26].

However, the category and content of the alloying elements predominantly affect the properties of the Al-Cu-Fe alloy. Some studies have revealed that as additive agents, boron (B), silicon (Si), magnesium (Mg), stannum (Sn), cobalt (Co), and chromium (Cr) [27–32] can modify the fragility and fortify the I-phase alloys [26, 33]. Some researchers have also investigated the effect of Cr and Ni on the structure and mechanical
properties of Al-Cu-Fe alloy. The results show that alloying by chromium (Cr) ensures the highest thermal stability, while nickel (Ni) addition refines the microstructure of the consolidated alloy [34].

Cerium (Ce) is well known to provide superior grain refinement to aluminum alloys and to effectively increase the mechanical properties and thermal stability of materials [35]. For example, the addition of Ce into an Al-Mn alloy increases the hardness and the wear resistance of alloys [36–38]. Ce additions increase strength and elongation of Al alloys, and Ce additions were the most effective in improving the fatigue resistance of AlLiCuMgZr alloys [39]. In alloys with high stress concentration sensitivity, Ce additions reduce this detrimental behavior [40].

Nonetheless, the effect of Ce addition on the properties and morphology of the Al-Cu-Fe alloy has rarely been examined. In this study, the effect of Ce addition on the thermal expansion and morphological properties of Alₓ₆₃Cu₂₅Fe₁₂ is investigated with the aim to obtain a novel aluminum alloy with perfect strength and a low linear expansion coefficient by the addition of Ce.

2. Materials and methods

Conventionally cast alloys with nominal compositions of the (Alₓ₆₃Cu₂₅Fe₁₂)₁₀₀−xCex (x = 0, 0.1, 0.5, 1 and 2 at%) alloys were prepared with high purity 99.99% Al, Cu, 99.98% Al–60Fe and 99.5% Al–30Ce master alloys in a vacuum-arc furnace. The raw materials with mass of ~80 g were put into a copper crucible in an argon-filled vacuum chamber to avoid oxidation. Then, they were melted by arc with a DC current for 60 s. After turning off the DC current, the melted material was rapidly cooled to room temperature in 5 min by the flowing cooling water around the walls of the copper crucible. In order to improve the uniformity, the solidified sample was flipped and re-melted. This process was repeated for 4 times in order to ensure uniformity.

X-ray diffraction (XRD–6000) patterns of (Alₓ₆₃Cu₂₅Fe₁₂)₁₀₀−xCex (x = 0, 0.1, 0.5, 1, and 2 at%) alloys were recorded using Cu Kα radiation (λ = 0.1542 nm) at a scanning angle from 20° to 90° and a scanning speed of 4°/min. A high-temperature differential scanning calorimetry (TGA/SDSC1) system was utilized for thermal analysis at a heating rate of 20°C/min under Ar.

Scanning electron microscopy (TESCAN, VEGA II-XMU) equipped with an energy-dispersive x-ray spectroscopy (EDS) system and high-resolution transmission electron microscopy (HRTEM, JM–2010) was employed to analyze microstructures. For SEM observations, a diluted Kellers reagent (95 ml water + 2.5 ml HNO3 + 1.5 ml HCl + 1.0 ml HF) was used as an etchant for the polished samples.

X-ray elemental mapping and EDS point analysis were performed for both alloys to understand different phases and element distribution in the materials with different amounts of added Ce. EDS measurement of the whole region was carried out on each face of each sample, and then the average value was taken to ensure the accuracy of experimental data. Furthermore, TEM (JM–2010) was employed to examine the Al-Cu-Fe-Ce alloy. TEM studies were conducted using powder samples that were prepared from sections of a fractured Al-Cu-Fe-Ce billet by carefully crushing in a mortar.

Quantitative analysis of the SEM images was conducted by using Image-Pro Plus 6.0 software. The (Alₓ₆₃Cu₂₅Fe₁₂)₁₀₀−xCex alloy was machined to Ø5 mm × 5 mm to investigate the thermal expansion properties by using a thermal mechanical analyzer (TMA/SDTA–840). During the test, the specimen was heated from 30°C to 500°C at a rate of 10°C/min under argon. Test data were recorded by a computer, and data were analyzed using a Mettler Toledo thermal analysis system.

3. Results

3.1. Microstructure and thermal properties of (Alₓ₆₃Cu₂₅Fe₁₂)₁₀₀−xCex (x = 0, 0.1, 0.5, 1 and 2 at%) alloys

In this study, the phase diagram calculation method is first employed to analyze the precipitated phases during the solidification of Al-Cu-Fe-Ce alloy. The figure 1 shows a partial (Alₓ₆₃Cu₂₅Fe₁₂)₁₀₀−xCex pseudo-binary phase diagram with the composition axis varying cerium. For the figure 1, the equilibrium crystallization process of (Alₓ₆₃Cu₂₅Fe₁₂)₁₀₀−xCex alloy is simulated by using Thermo-Calc software. It can be seen from the figure 1 that the equilibrium crystallization process is: the high-temperature liquid phase first precipitates the AlFe phase, and as the temperature decreases, it enters the three-phase zone of α − Al₁₇Fe₁₃ + AlFe + Liquid, and when the temperature continues to decrease, then enters the four-phase zone of the α − Al₁₅Fe₁₃, Al₁₇Fe, FCC − Al phase. The final phase obtained is: α − Al₁₅Fe₁₃ + Al₁₇Fe + Al₁₂Ce₂ + FCC − Al. This is the phase formed during equilibrium crystallization. However, the cooling rate of conventional solidification is higher than that of equilibrium solidification. It is difficult to realize the equilibrium crystallization process, and the main crystallization process is non-equilibrium crystallization.

Therefore, XRD, DSC, and microstructure analysis are performed on the conventional solidification Al − Cu − Fe − Ce alloy to determine the existing phase. Figure 2 shows the XRD patterns of the conventional
The Al-Cu-Fe alloy is mainly composed of four phases: a monoclinic \( \lambda-\text{Al}_{13}\text{Fe}_{4} \) phase (\( \lambda \)-phase), a \( \beta-\text{Al}_{0.3}\text{Fe}_{0.5} \) phase (\( \beta \)-phase), an \( \text{Al}_{2}\text{Cu} \) phase, and an I-\( \text{Al}_{60.3}\text{Cu}_{30}\text{Fe}_{9.7} \) phase (I-phase). Without the addition of Ce, the monoclinic \( \lambda-\text{Al}_{13}\text{Fe}_{4} \) phase (\( \lambda \)-phase) crystallizes in the C2/m space group, and its lattice parameters are \( a = 1.549 \text{ nm}, b = 0.808 \text{ nm}, c = 1.248 \text{ nm}, \) and \( \beta = 107.7^\circ \). With a cubic crystal system, the \( \beta-\text{Al}_{0.3}\text{Fe}_{0.5} \) phase (\( \beta \)-phase) crystallizes in the Pm-3m space.
group, and its lattice parameter is a = 0.291 nm. With a hexagonal crystal system, the $\text{Al}_2\text{Cu}_3$ phase crystallizes in the P63/mmc space group, and its lattice parameters are $a = 0.829$ nm, $b = 0.829$ nm and $c = 0.497$ nm, respectively. The fourth type of phase is the $\text{I-Al}_{63}\text{Ce}_{25}\text{Fe}_{12}$ phase (I-phase) with an icosahedral construction. Similar results also have been reported previously [41–44]. With the addition of Ce, the diffraction peaks of $\lambda$-phase disappear because the addition of Ce changes the cooling rate of the alloy during solidification. The diffraction peaks of the $\text{Al}_{13}\text{Ce}_2\text{Cu}_{13}$ phase (Bravais lattice: cubic, space group: Fm-3m, and $a = 1.189$ nm, $\alpha = 90^\circ$) are observed with the increase in the Ce addition amount; meanwhile, the intensities of the diffraction peaks corresponding to the $\text{Al}_{13}\text{Ce}_2\text{Cu}_{13}$ phase and I-phase increase, suggesting that the area fractions of the $\text{Al}_{13}\text{Ce}_2\text{Cu}_{13}$ phase and I-phase increase with the increase in the addition amount of Ce.

Figure 3 shows the thermal characteristics of conventional solidiﬁed ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100-x}\text{Ce}_x$ samples, which are examined by DSC analysis with a heating process. In the DSC curve of the investigated $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy, the following phases are observed: The $\text{Al}_2\text{Cu}_3$ phase (the melting temperature of which is $\sim 584^\circ$C), I-phase ($873^\circ$C), $\beta$-phase ($\sim 988.6^\circ$C), and $\beta$-Al$_4$Cu$_4$ phase (1039°C). In addition, one weak endothermic peak is observed at 686.7°C, corresponding to an unstable $\tau$-phase in thermodynamics that is converted to the $\beta$-phase after the cooling process, as reported previously [44].

In the DSC curves of the ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100-x}\text{Ce}_x$ alloy, four phases are observed with the increase in the Ce addition amount: The $\text{Al}_2\text{Cu}_3$ phase, $\text{Al}_{13}\text{Ce}_2\text{Cu}_{13}$ phase, I-phase, and $\beta$-phase. Meanwhile, the $\lambda$-phase disappears. These results are in good agreement with those obtained by XRD. Clearly, the melting temperature of the investigated ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100-x}\text{Ce}_x$ alloy is markedly reduced with the increase in the Ce addition amount. Clearly, the melting temperature of the ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100-x}\text{Ce}_x$ alloy is 5060°C less than that of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ sample, and the contribution of Ce may affect the compositional undercooling of the alloy. Compositional undercooling is probably related to the fact that the nucleation of the $\beta$-phase and I-phase is considerably more easy than the precipitation of the $\lambda$-phase.

### 3.2. Microstructural characterization of ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100-x}\text{Ce}_x$

Figure 4 and figure 5 show the SEM micrographs of ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100-x}\text{Ce}_x$ alloys ($x = 0, 0.1, 1, and 2$ at%) alloys. When $x = 0$, the microstructure of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy is composed of four areas: dark(A), dark gray(B), light gray(C) and off-white(D). To identify the nature of these areas, EDS was conducted in the representative areas, and the energy spectrum analysis is shown in table 1. Meanwhile, combined with the previous XRD analysis results, we know that these four regions represent four different phases, a $\lambda$ – $\text{Al}_{13}\text{Fe}_{4}$, a $\beta$-phase, an I-phase and an $\text{Al}_2\text{Cu}_3$ phase. Similar results have been previously reported [43]. The chemical composition of each phase in $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy is summarized in table 1. The dark area(A) of SEM image with a small amount of copper (6.83 at.% in EDS) and thus corresponds to the $\lambda$ – $\text{Al}_{13}\text{Fe}_{4}$ phase. The light gray area(C) represents the I-phase. The off-white area(D) represents the $\text{Al}_2\text{Cu}_3$ phase with a small amount of iron (0.67 at.% in EDS). The remaining dark gray area(B) matches with the $\beta$-phase [43].

After the addition of Ce into $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$, the grain refinement of the Al-Cu-Fe-Ce alloy microstructure is observed. Figure 4(b-d) and figure 5(b-d) show the SEM low-magnification and high-magnification morphologies respectively, when the cerium content is 0.1 at%, 1 at% and 2 at%, respectively. With the increase of cerium content, the morphology of different phase is similar. Take an alloy with a cerium content of 1 at% as an example to confirm its composition phase. According to figure 4(c) and 5c, it can be seen that the microstructure of the ($\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$)$_{100}\text{Ce}_1$ alloy is composed of four areas: dark(A), dark gray(B), light gray(C),...
According to the results of x-ray diffraction and energy spectrum analysis in table 2, we know that these four areas represent a $\beta$-phase, an $I$-phase, an $Al_{13}Ce_2Cu_{13}$ phase and an $Al_{2}Cu_{3}$ phase, respectively. The addition of cerium leads to the formation of $Al_{13}Ce_2Cu_{13}$ phase, and the disappearance of the $\lambda - Al_{13}Fe_4$ phase.

Figure 5(b-d) shows the different morphologies of the microstructure with the addition of different amounts of Ce. With the increase in the Ce addition amount from 0.1 to 2 at%, the morphology of the $\beta$-phase changes from a long-strip structure into a dendritic structure, and the $I$-phase is gradually refined, accompanied by the increase in the amount of the $Al_{13}Ce_2Cu_{13}$ phase; meanwhile, the morphology of the $I$-phase changes from a dendritic to an ellipsoid structure. In addition, the $I$-phase is continuously dispersed along the $\beta$-phase boundary, indicative of the nucleation of the $I$-phase on the $\beta$-phase by a peritectic reaction.

To quantitatively estimate the microstructure evolution of ($Al_{63}Cu_{25}Fe_{12}$)$_{100-x}Ce_x$ alloys, the area fractions of the $I$-phase and average grain sizes of the $I$-phase in the alloys are measured (figure 6). By the addition of Ce, the area fraction of the $I$-phase significantly increases, and the area fraction of the $I$-phase in the alloy reaches the maximum (66.7%). At a Ce addition amount of 1 at%, the area fraction of the $I$-phase increases by 1.5 times in comparison with that in the $Al_{63}Cu_{25}Fe_{12}$ alloy. On the contrary, the average grain size of the $I$-phase gradually reduces with the increase in the amount of added Ce.

In order to further determine the existence of the quasicrystalline phase and the cerium-containing phase in the Al-Cu-Fe-Ce alloy, as well as the distribution of each element in the two phases, the alloys with different cerium contents were analyzed by elemental distribution maps and electron diffraction patterns. The results show that all alloys contain these two phases, so the alloys with cerium content of 0.5 at% and 1 at% are taken as examples for illustration, when the content of cerium is increased from 0.1 at% to 2 at%.

High-magnification SEM analysis and x-ray elemental mapping were conducted to ascertain the distribution of elements in the $I$-phase and the amount of Ce elements in the ($Al_{63}Cu_{25}Fe_{12}$)$_{99.5}Ce_{0.5}$ and ($Al_{63}Cu_{25}Fe_{12}$)$_{99}Ce_{1}$ alloys. Moreover, EDS point analysis was conducted to estimate the local composition of the $I$-phase and $Al_{13}Ce_2Cu_{13}$ phase.

Figure 7 shows the high-magnification SEM images and associated EDS maps of the phase containing Ce elements in the ($Al_{63}Cu_{25}Fe_{12}$)$_{99.5}Ce_{0.5}$ alloy. The elemental maps and EDS results revealed that the phase containing Ce is composed of 43.68 at% Al, 48.26 at% Cu, 1.44 at% Fe, and 6.62 at% Ce; besides, Al, Ce, and Cu are enriched in the white areas (figure 7a), indicative of the presence of the $Al_{13}Ce_2Cu_{13}$ phase. In order to characterize the microstructure in more detail, the ($Al_{63}Cu_{25}Fe_{12}$)$_{99.5}Ce_{0.5}$ alloy was analyzed by TEM to further...
confirm the existence of Al-Ce-Cu phase. From the SAED analysis of the white area in figure 7d, the Al-Ce-Cu phase exhibits a cubic crystal structure. Owing to the content of Al atoms and Cu atoms in the area, the chemical formula of the Al-Ce-Cu phase is identified as $\text{Al}_{13}\text{Ce}_{2}\text{Cu}_{13}$.

Figure 8 shows the SEM images and EDS maps of the $I$-phase in the $(\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12})_{99}\text{Ce}_1$ alloy. In the backscattered image of figure 8a, combined with the previous analysis, we can know that the dark gray area corresponds to the quasicrystal phase. The dark gray area is composed of Al, Cu, and Fe, and elemental maps and EDS results revealed that the dark gray area is composed of 64.17 at% Al, 23.67 at% Cu, and 12.16 at% Fe.
indicating that the areas belong to the I-phase. Figure 8 (d-f) shows the electron diffraction patterns of the I-phase, according to which, five-fold axis, three-fold axis and two-fold axis are present, respectively.

3.3. Analysis of thermal expansion properties

Linear expansion coefficient can be used to estimate the thermal expansion properties of materials, which characterizes the thermal stability of materials, and the linear expansion coefficient is expressed by the formula shown in (1).

$$\alpha = \frac{1}{L_0} \frac{dL}{dT}$$

(1)

Here, $L_0$ is the original size of the sample, $dL$ is the change in the line size of the sample corresponding to temperature changes, and $\alpha$ is the linear expansion coefficient.

Figures 9 (a) and (b) shows the linear expansion coefficients of the (Al$_{63}$Cu$_{25}$Fe$_{12}$)$_{100-x}$Ce$_x$ alloys. Figure 9 (a) shows the relationship between $\alpha$ and the sample temperature with different Ce addition amounts. Figure 9 (b) shows the relationship between $\alpha$ and Ce at 30100°C and 30500°C. Results revealed that the $\alpha$ of (Al$_{63}$Cu$_{25}$Fe$_{12}$)$_{100-x}$Ce$_x$ continually increases with the increase in temperature, and $\alpha$ reaches the maximum value at 30–500°C. Meanwhile, $\alpha$ slightly decreases first, and then it increases gradually with increase in the addition amount of Ce in the same range of temperatures, and the $\alpha$ of the alloy reaches the minimum at a Ce addition amount of 1 at%.
At 30 °C–100 °C, the $\alpha$ of Al$_{63}$Cu$_{25}$Fe$_{12}$ is 14.766 × 10$^6$/°C, and the $\alpha$ of Al$_{63}$Cu$_{25}$Fe$_{12}$Ce$_9$ is 11.899 × 10$^6$/°C. Clearly, with the increase in the Ce addition amount from 0 to 1 at%, the $\alpha$ of the alloy decreases by ∼20%. Meanwhile, $\alpha$ exhibits the same behavior with the increase in the Ce addition amount at different temperature ranges.

The $I$-phase of alloys [5, 45] is known to play critical roles in decreasing the $\alpha$ of the alloys; notably, the area ratio of the $I$-phase continually increases with the increase in the Ce addition amount from 0 to 1 at%. This relationship between the area ratio of the $I$-phase and $\alpha$ suggested that the $I$-phase considerably affects the $\alpha$ of Al-Cu-Fe-Ce alloys.

At the same time, Ce has a larger atomic radius and is easier to segregate in the grain boundary, which limits the straightening of the grain boundary. Therefore, adding an appropriate amount of rare earth cerium can inhibit the growth of grains and play a role in grain refinement. Accompanied by the refinement of grains, the areal density of grain boundaries is obviously increased, thus effectively retarding the movement of atoms, strengthening the bonding force between the atoms, and weakening the thermal motion of the atoms. Therefore, the higher the energy required for the atom to leave the equilibrium position, the smaller the coefficient of thermal expansion.
4. Discussion

The results explained in the previous sections demonstrated that the rare-earth element Ce clearly affects the morphology and thermal expansion properties of the Al-Cu-Fe alloy. Ce exhibits crucial effects on the formation process of the I-phase in the Al-Cu-Fe alloy (with Ce or without). Therefore, the solidification sequence of various phases in the Al-Cu-Fe alloy (with or without Ce) is discussed. The solidification sequence of various phases in the Al-Cu-Fe alloy without the addition of Ce is as follows:

\[ L \rightarrow \lambda \]  
\[ L + \lambda \rightarrow \beta \]  
\[ L + \lambda + \beta \rightarrow 1 - \text{phase} \]  
\[ L \rightarrow Al_2Cu_3 \]  

First, the formation of the primary \( \lambda - Al_3Fe_4 \) phase in the molten alloy starts at the liquidus temperature, further affording the \( \beta \)-phase by a peritectic reaction, and the I-phase is formed by a second peritectic reaction with the decrease in the temperature. Finally, the \( Al_2Cu_3 \)-phase is formed by the remaining liquid, as reported previously in several studies [46]. Compared with the alloy without cerium, the solidification process of the alloy is slightly different, when a small amount of rare earth cerium is added to the alloy.

Figure 10 shows the solidification process of various phases in the Al-Cu-Fe-Ce system. It can be seen from morphology in figure 4 and figure 5 that the morphologies of the phases in the alloy are slightly different, each phase is smaller, but the types of phases are same with the increase of cerium content. So take the alloy with 1 at% cerium as an example for analysis. In figure 10, the abscissa represents the solidification time, the ordinate represents the reaction temperature, \( T_1 \) represents the temperature at which the \( \beta \)-phase begins to precipitate from the liquid phase, \( T_2 \) is the initial precipitation temperature of the quasicrystalline I-phase, and \( T_3 \) is the beginning temperature of the formation of the cerium-containing phase. Combined with the DSC curve in figure 3 shows that \( T_1 \) is 983.7°C, \( T_2 \) is 882.1°C, \( T_3 \) is about 692.4°C. Analysis of the solidification process in figure 10 shows:

The solidification of the primary \( \beta \)-phase in the molten alloy starts at the liquidus temperature (\( T_1 \)), affording an I-phase by a peritectic reaction \( (L + \beta \rightarrow 1 - \text{phase}) \) along the \( \beta \)-phase boundaries at the \( T_2 \) temperature. With the addition of Ce, Ce reacts with Al and Cu to form an \( Al_3Ce_2Cu_{13} \) phase (\( T_3 \)), and then, the \( Al_2Cu_3 \) phase is formed by the remaining liquid. The main reactions during the solidification process are as follows:

\[ L \rightarrow \beta \]  
\[ L + \beta \rightarrow 1 - \text{phase} \]  
\[ L \rightarrow Al_3Ce_2Cu_{13} - \text{phase} \]  
\[ L \rightarrow Al_2Cu_3 \]  

The possible precipitation sequence is shown as follows: \( (6) \rightarrow (7) \rightarrow (8) \rightarrow (9) \), and the precipitation sequence of the phases might be primary \( \beta - \text{phase} \rightarrow 1 - \text{phase} \rightarrow Al_3Ce_2Cu_{13} - \text{phase} \rightarrow Al_2Cu_3 - \text{phase} \).

The analysis revealed that the addition of Ce contributes to the significant grain refinement and a high area fraction of the I-phase and \( Al_3Ce_2Cu_{13} \)-phase, possibly related to the enrichment of Ce in the liquid ahead of the growing interface of the I-phase during the cooling process. The calculation shows that the relative values of the
atomic radius difference between Ce and Cu, Ce and Al are 42.2% and 27%, respectively. So the solubility of Ce in Cu and Al is low. But Ce is a surface active element, and it easily aggregates at the solid-liquid interface, that results in the compositional undercooling in the diffusion layer.

In the liquid phase, with the change of solute concentration, the temperature distribution is:

\[ T_L = T_0 - MC_e \left( 1 + \frac{1}{K} \exp \left( -\frac{RX}{D} \right) \right) \]  

So,

\[ T_L^I = T_0 - MC_e CoCe \left( 1 + \frac{1}{K_{Ce}} \exp \left( -\frac{RX}{D_{Ce}} \right) \right) \]  

In formula 11:

\[ K_{Ce} \]-Balanced distribution coefficient of Ce
\[ MC_e \]-The slope of the liquid phase in the Al-Cu-Fe-Ce state diagram
\[ CoCe \]-The initial content of Ce in the alloy
\[ R \]-Crystal growth rate
\[ D_{Ce} \]-Diffusion coefficient of Ce in liquid phase
\[ T_L \]-Initial crystallization temperature of alloy
\[ T_L^I \]-Ce’s contribution to temperature in the liquid phase
\[ X \]-Distance to solid-liquid interface

Take the derivative of the distance X to get

\[ \frac{dT_L}{dX} = \frac{RMC_e CoCe (1 - K_{Ce})}{D_{Ce} K_{Ce}} \exp \left( -\frac{RX}{D_{Ce}} \right) \]  

So \( \frac{dT_L^I}{dX} \) is the contribution of Ce to the largest critical temperature gradient at the solid-liquid interface. It can be found from the formula 12, \( K_{Ce} < 1 \), so \( \frac{dT_L^I}{dX} > 0 \), with the addition of Ce, the slope of the relationship curve between the solute in the alloy and the temperature increases. The critical temperature gradient of the alloy solid-liquid interface increases. Thus, the composition undercooling of the alloy increases, and the growth rate of dendrite accelerates.

Rapidly growing dendrites often hinder their lateral growth due to the large amount of solute discharged during their growth. The protruding part makes the dendrites branch develop after entering the composition undercooling area. Due to the enrichment of solute, the melting point of dendrite neck is low. At this time, necking is formed at the beginning of the branch, which is easy to be fused by high temperature liquid and be involved in the liquid flow again. These necks can be the core of non-spontaneous nucleation, thus, the number of nuclei is increased and the grains are refined.

This compositional undercooling can reduce the diffusion rate of the \( \beta \)-phase and stimulate the formation of the \( \text{Al}_{13}\text{Ce}_2\text{Cu}_{13} \) phase along the \( I \)-phase boundaries, thereby restricting the growth of the \( I \)-phase. With the increase of the Ce addition amount from 0 to 2 at%, the \( (\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12})_{100-x}\text{Ce}_x \) alloys exhibit a smaller, denser, and uniform grain size, and the content of the amorphous phase increases due to the addition of the rare earth Ce, which is a trace element in the \( \text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12} \) alloy.

Therefore, the effects of the rare earth Ce enriched at the solid-liquid interface include: increasing the deformation resistance of the alloy, promoting the proliferation of dislocations, enhancing the hindrance of atomic movement, and enhancing the hindrance and restraint of the alloy matrix during the expansion process.

At the same time, with the increase of the undercooling degree, the solute diffusion rate is reduced, and the crystal grains are refined. The smaller the crystal grains, the more the grain boundaries, the stronger the hindering effect on dislocations, the stronger the restraining force of the expansion process of the matrix, and the lower the thermal expansion coefficient.

When the addition amount of cerium is 2 at%, the \( \text{Al}_{13}\text{Ce}_2\text{Cu}_{13} \) phase increases, as shown in figure 5d, the \( \text{Al}_{13}\text{Ce}_2\text{Cu}_{13} \) phase aggregates and grows, the pinning effect on dislocations decreases, and the bonding force between atoms weakens, thermal expansion performance declines. Meanwhile, due to the aggregation of the cerium-containing phase, the resulting compositional undercooling is weakened, and the formation of the quasicrystalline phase in the alloy will be affected to a certain extent. The reduction of the quasicrystalline phase also greatly affects the thermal expansion performance of the material.
In summary, the different Ce addition amounts contribute to the refinement and increase of the $I$-phase grains, thereby affecting the thermal expansion properties. The smaller thermal expansion properties of the ($Al_{63}Cu_{25}Fe_{12})_{99}Ce_{1}$ alloy are mainly attributed to the reduction in grain size and the high area fraction of the $I$-phase.

5. Conclusions

(i) With the increase in the Ce addition amount, the microstructure of the $Al_{63}Cu_{25}Fe_{12}$ alloy is clearly improved, and the morphology of the $\beta$-phase changes from a long-strip structure to a dendritic structure, and the morphology of the $I$-phase changes from a dendritic to an ellipsoid structure; meanwhile, the Ce addition amount promotes the grain refinement.

(ii) The added Ce preferentially reacts with Al and Cu, affording the $Al_{13}Ce_2Cu_1$ phase. Meanwhile, by the addition of Ce, the area fraction of the $I$-phase increases, and the $\lambda-Al_{13}Fe_4$ phase disappears.

(iii) The linear expansion coefficient of the $Al_{63}Cu_{25}Fe_{12}$ alloy first decreases at a Ce addition amount of 1 at%; on the contrary, it increases at a Ce addition amount of greater than 1 at%. The area fraction of the $I$-phase first increases at a Ce addition amount of 1 at%, but it decreases by the addition of more Ce. At a Ce addition amount of 1 at%, the area fraction of the $I$-phase in the alloy and the linear expansion coefficient of the alloy reach optimum values. Results revealed that the area fraction of the $I$-phase considerably affects the linear expansion coefficient of the $Al_{63}Cu_{25}Fe_{12}$ alloy.

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