Effect of CeO$_2$ Content on Microstructure and Properties of SiCp/Al-Si Composites Prepared by Powder Metallurgy

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Abstract: The effect of CeO$_2$ content on the microstructure and properties of SiCp/Al-Si composites prepared by powder metallurgy was studied, and the mechanism of CeO$_2$ in composites was deeply analyzed. The results show that the addition of the appropriate amount of CeO$_2$ can refine the Si particles and improve the tensile properties of the SiCp/Al-Si composites. As the CeO$_2$ content increases from 0 to 0.4 vol%, the particle size of the Si phase shows a tendency to decrease first and then increase, while the tensile strength, yield strength, and elongation of the composites show a trend of first increasing and then decreasing. When the CeO$_2$ content is 0.2 vol%, the refining effect of CeO$_2$ and the tensile properties of composites are the best. The fracture mode of SiCp/Al-Si composites with a rare earth addition is a mixed fracture. There are three main mechanisms for CeO$_2$ in SiCp/Al-Si composites. One is when CeO$_2$ serves as the nucleation substrate of Si phase to refine Si particles. The second is when CeO$_2$ reacts with the alloying elements in the aluminum matrix to form a new phase, CeCu$_2$Si$_2$, which can not only play a role of dispersion strengthening, but also improve the bonding strength between Al matrix and Si particles. The third is the pinning effect of CeO$_2$ and CeCu$_2$Si$_2$ particles on grain boundaries or phase boundaries to refine aluminum grains.

Keywords: powder metallurgy; CeO$_2$; microstructure; tensile properties

1. Introduction

Al-Si alloys are widely used as lightweight materials in aerospace, automotive parts, and other fields due to their excellent casting properties, high strength, and strong corrosion resistance [1,2]. SiCp has the characteristics of isotropy, low expansion coefficient, and high strength, which are ideal reinforcing materials for preparing metal matrix composites [3,4]. SiCp/Al-Si composites combine the advantages of SiC and Al-Si alloys in strength, expansion, and wear resistance [5,6]. Li et al. [7] studied the effect of the SiCp orientation anisotropy on the tensile properties of spray-formed SiCp/Al-Si composites compared with that of the matrix alloy without reinforcement particles. The results showed that the addition of SiCp improved the tensile properties of the Al-Si alloy. Zhou et al. [8] fabricated SiCp/Al composites based on different matrix elements, Mg and Si, content by pressureless infiltration. The results showed that adding the Mg element to the matrix increased the coefficient of thermal expansion (CTE) of SiCp/Al composites and adding the Si element to the matrix could control the formation of harmful interface products Al$_4$C$_3$.

For Al-Si cast alloys, the size and morphology of silicon play a decisive role in the properties of the alloys [9]. The eutectic silicon in the unmodified alloy is usually thick and lamellar, which tends to produce stress concentration at the tip of eutectic silicon, thereby reducing the elongation of the alloy. Rare earth elements are often used as modifiers because of their high chemical activity. Among them, Ce, La, and Y are the most commonly used rare earth elements in aluminum alloy [10,11]. In the case of Al-Si alloys, tiny amounts of rare earth elements can transform the second phase (Si phase) from a thick...
plate to a fine fibrous shape. The particle size of the Si phase becomes smaller after further heat treatment (solution aging), and the performance of the alloy has been greatly improved [12,13]. At present, rare earth is often introduced into Al-Si matrix composites in the form of rare earth compounds. In the Al-Si matrix composites prepared by the casting method, rare earth is usually added in the form of ReH$_2$, the Re-Al series master alloy, and ReO$_2$ [14,15]. Sharma et al. [16] prepared the Al-11Si-20Cu brazing alloy containing La$_2$O$_3$ by the electromagnetic induction casting process and found that the addition of La$_2$O$_3$ significantly improved the filler brazeability, microhardness, joint tensile shear strength, and elongation of the composites. Elgallad et al. [17] found that adding rare earth elements, La or Ce, to the Al-Si alloy increased the melting temperature of the alloy and caused partial modification of the eutectic Si particles. Liu et al. [18] added different contents of CeO$_2$ and Y$_2$O$_3$ (2 vol% and 3 vol%) to Ti/Al$_2$O$_3$ composites prepared by vacuum hot pressing sintering to restrain the interface reaction. The results indicated that rare earth oxides effectively reduced the thicknesses of the reaction layers and improve the performance of the composites.

Powder metallurgy is one of the earliest solid forming methods for preparing particle reinforced aluminum matrix composites, and the process is relatively mature [19–21]. However, the research on particle reinforced aluminum matrix composites with rare earth mostly focuses on the preparation of composites by the liquid phase method. There are few reports on the application of rare earth added in Al-Si matrix composites prepared by powder metallurgy, and less attention has been paid to the mechanism of rare earth in Al-Si matrix composites. In this paper, SiCp/Al-Si composites with different CeO$_2$ volume fraction were prepared by the powder metallurgy method. The effect of CeO$_2$ content on the microstructure and properties of the composites was investigated. Additionally, the mechanism of CeO$_2$ in the SiCp/Al-Si composite was also explored.

2. Materials and Methods

In this paper, SiCp/Al-Si composites with different CeO$_2$ contents prepared by powder metallurgy were used as the research object. Al-12Si alloy powder with a particle size of 7 µm was used as the matrix. Table 1 shows its chemical composition. SiCp, with an average particle size of 5 µm and a volume fraction of 20%, was selected as reinforcement. The additive used in the experiments was CeO$_2$ powder, with a particle size of about 1–20 µm, and its addition amount was 0, 0.1 vol%, 0.2 vol%, 0.3 vol%, and 0.4 vol%, respectively. The experimental preparation process was powder mixing, cold pressing, sintering, hot extrusion, and heat treatment. The specific technological parameters were as follows: QM-BP planetary ball mill (Shenhua Biotechnology, Guangzhou, China) was used for dry mixing, the grinding ball was a stainless-steel ball, the dispersant was stearic acid, the ball material ratio was 4:1 (mass ratio), the ball mill speed was 240 r/min, and the mixing time was 6 h. The billet, with a diameter of 78 mm, was then cold-pressed in a hydraulic machine (Zhengxi, Chengdu, China) with a pressure of 500 Mpa. After that, the billet was heated in a tube furnace (NBD, Zhengzhou, China) with a sintering temperature of 530 °C, a sintering time of 4 h, a heating rate of 2 °C/min, and a protective atmosphere of nitrogen (N$_2$). The billet was then hot extruded into the bar, with an extrusion ratio of 15.6:1 and an extrusion speed of 1 mm/s at about 500 °C. Finally, the hot extruded samples were annealed at 300 °C for 3 h, solution treated at 510 °C for 2 h, water quenched, and then immediately aged at 170 °C for 5 h.

Table 1. Chemical compositions of Al-12Si alloy (wt%).

| Component | Si  | Cu  | Mg  | Mn  | Al   |
|-----------|-----|-----|-----|-----|------|
| Content   | 12.0| 1.4 | 0.7 | 0.6 | Bal. |

The microstructures of the samples were observed by JSM-5610LV scanning electron microscopy (SEM, JEOL, Tokyo, Japan), with energy dispersive spectroscopy (EDS, Kevex,
Texas, TX, USA) and transmission electron microscopy (TEM, JEOL, Tokyo, Japan). The preparation method of the TEM samples was to first cut the material into a thin slice with a thickness of 0.3 mm and then manually polish the slice to a thickness of about 50 µm with sandpaper. Next, it was punched into thin slices with a diameter of 3 mm and finally thinned on the Gatan-691 ion thinner. The tensile properties of the composites were tested by the Shimazu AG-1250kN precision universal tensile testing machine (Shimazu, Tokyo, Japan), with an initial strain rate of 1.1 × 10^{-3} s^{-1} at room temperature. The size of tensile sample was shown in Figure 1, and the tensile results were the average values of three samples for each tested condition.

![Figure 1. Schematic diagram of tensile sample (mm).](image)

3. Results and Discussion

3.1. Effect of CeO$_2$ Content on Microstructure of SiCp/Al-Si Composites

Figure 2 shows the microstructure of SiCp/Al-Si composites with different CeO$_2$ volume fraction. According to the energy spectrum analysis in Figure 3, the black phase with irregular shapes and sharp edges in Figure 2 is SiC. The gray phase with regular shapes, mostly round and elliptical, and smooth edges was Si. The white, spotty, or flocculent phases were ferric or cerium-containing phases. The Fe element in the Fe phase may have come from the impurity elements in the Al matrix or have been mixed in ball milling.

Figure 4 shows the number density distribution histogram and the average size of the Si phase in the composites with different CeO$_2$ contents. According to the normal distribution, as the size of the Si phase particles increases, the number density of the particles decreases gradually. Combining Figures 2 and 4, it can be seen that, when CeO$_2$ was not added, the precipitated Si particles were thick, unevenly distributed, and seriously agglomerated. When the addition amount of CeO$_2$ was low, the size of Si phase decreased significantly, and the distribution uniformity increased with the increase of CeO$_2$ content. When the content of CeO$_2$ was 0.2 vol%, the size of Si phase was the smallest and the distribution was the most uniform. At this time, the white cerium phase was mostly punctate and evenly distributed. When the CeO$_2$ content exceeded 0.2 vol%, the white cerium phase agglomerated and became larger in size. In addition, the size of the Si phase gradually increased.

The addition of CeO$_2$ can refine the Si phase and make its distribution more uniform. Firstly, CeO$_2$ can be used as the heterogeneous nucleation site of Si phase, which increases the number density of Si phase, thus refining the Si particle. When the content of CeO$_2$ was low, CeO$_2$ could be used as the nucleation substrate to refine Si phase effectively. When the CeO$_2$ content was 0.1 vol%, the content of CeO$_2$ was insufficient and the refining was not sufficient. When the CeO$_2$ content was 0.2 vol%, the addition amount of CeO$_2$ was appropriate and the refining effect was most obvious. When the CeO$_2$ content exceeded 0.2 vol%, CeO$_2$ agglomerated, thereby deteriorating the refining effect. When the CeO$_2$ content was 0.4 vol%, the silicon phase was coarse and agglomerated, which was almost the same as the structure without CeO$_2$, and the refinement effect was the worst. Secondly, the addition of an appropriate amount of CeO$_2$ can make the Si phase distribution more uniform. This
may be because the dispersed rare earths can provide a large base for the growth of Si phase and attract a large number of Si elements, so that the Si element required for the agglomeration of Si phase is insufficient, and thus reduce the agglomeration tendency of Si phase, and the uniformity of Si phase distribution could be improved accordingly.

Figure 2. The SEM images of SiCp/Al-Si composites with different CeO2 volume fraction: (a) 0; (b) 0.1 vol%; (c) 0.2 vol%; (d) 0.3 vol%; (e) 0.4 vol%.
Figure 2. The SEM images of SiCp/Al-Si composites with different CeO\textsubscript{2} volume fraction: (a) 0; (b) 0.1 vol%; (c) 0.2 vol%; (d) 0.3 vol%; (e) 0.4 vol%.

Figure 3. The energy spectrum diagram of SiCp/Al-Si composites with different CeO\textsubscript{2} volume fraction: (a) the EDS analysis of region A in Figure 2a; (b) the EDS analysis of region B in Figure 2a; (c) the EDS analysis of region C in Figure 2a; (d) the EDS analysis of region D in Figure 2b.

Figure 4 shows the number density distribution histogram and the average size of the Si phase in the composites with different CeO\textsubscript{2} contents. According to the normal distribution, as the size of the Si phase particles increases, the number density of the particles decreases gradually. Combining Figures 2 and 4, it can be seen that, when CeO\textsubscript{2} was not added, the precipitated Si particles were thick, unevenly distributed, and seriously agglomerated. When the addition amount of CeO\textsubscript{2} was low, the size of Si phase decreased significantly, and the distribution uniformity increased with the increase of CeO\textsubscript{2} content. When the content of CeO\textsubscript{2} was 0.2 vol%, the size of Si phase was the smallest and the distribution was the most uniform. At this time, the white cerium phase was mostly punctate and evenly distributed. When the CeO\textsubscript{2} content exceeded 0.2 vol%, the white cerium phase agglomerated and became larger in size. In addition, the size of the Si phase gradually increased.

Figure 4. Cont.
Figure 4. The number density distribution histogram and the average size of precipitated Si particles in SiCp/Al-Si composites with different CeO$_2$ contents: (a) 0; (b) 0.1 vol%; (c) 0.2 vol%; (d) 0.3 vol%; (e) 0.4 vol%; (f) the average size of precipitated Si particles.

3.2. TEM Analysis of SiCp/Al-Si Composites

The matrix Al-12Si-Cu-Mg is a typical heat-treatable aluminum alloy, in which the main precipitates are Mg$_2$Si, Al$_2$Cu, Al$_2$CuMg, Al$_5$Cu$_2$Mg$_8$Si$_6$, and Al(Si, Fe)Mn phases [22,23]. Figure 5 shows the TEM images and corresponding selected-area electron diffraction (SAED) patterns of SiCp/Al-Si composites without CeO$_2$ after heat treatment. Some dispersed and coarse second-phase particles could be seen in the SiCp/Al-Si composites prepared by powder metallurgy, as shown in Figure 5. The results of SAED patterns show that these large round and rod-like particles may have been Al$_4$Cu$_9$, Al$_2$Cu, Al$_{19}$Mn$_4$, or Al$_5$Cu$_6$Mg$_2$, and not Mg$_2$Si, Al$_5$Cu$_2$Mg$_8$Si$_6$, or Al(Si, Fe)Mn dispersoids. It can be seen that, in the SiCp/Al-Si composites, there were more compounds formed between Al-Cu, Al-Cu-Mg, and Al-Mn, while the particles containing Si or Fe were not found. This may be due to the sintering temperature (530) of the composites prepared by powder metallurgy, which was lower than the molten temperature of the cast Al-Si-Cu-Mg alloy. The atom diffusion ability of the composites was weaker than that of the cast alloy. In addition, affected by heat, vacancy concentration, internal stress, and other factors, it is more difficult for Si and Fe elements to combine with other elements to form compounds compared with Al, Cu, Mg, and Mn in the low-temperature aging process.
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Figure 5. TEM images of SiCp/Al-Si composites without CeO$_2$: (a) the precipitated phase Al$_{19}$Mn$_4$; (b) diffraction patterns of Al$_{19}$Mn$_4$; (c) the precipitated phase Al$_4$Cu$_9$; (d) diffraction patterns of Al$_4$Cu$_9$; (e) the precipitated phase Al$_2$Cu; (f) diffraction patterns of Al$_2$Cu; (g) the precipitated phase Al$_5$Cu$_6$Mg$_2$; (h) diffraction patterns of Al$_5$Cu$_6$Mg$_2$. 
Figure 6 shows the TEM images and corresponding selected-area electron diffraction patterns of the SiCp/Al-Si composites with CeO₂. It can be seen from Figure 6 that CeO₂ existed at the grain boundaries of matrix, and a new phase CeCu₂Si₂ was formed.

### 3.3. Effect of CeO₂ Content on Tensile Properties of SiCp/Al-Si Composites

Figure 7 shows the tensile properties curve of composites with different CeO₂ contents. With the increase of CeO₂ content, the tensile strength, yield strength, and elongation all showed a trend of first increasing and then decreasing. The tensile strength, yield strength, and elongation of the composites reached the peak values of 376.9 MPa, 345.8 MPa, and 4.09%, respectively, when the CeO₂ content was 0.2 vol%, which were then increased by about 16.3%, 23.3%, and 37.7%, respectively, compared with that without CeO₂.

![Figure 6. TEM images of SiCp/Al-Si composites with 0.2 vol% CeO₂ content: (a) the precipitated phase CeCu₂Si₂; (b) diffraction patterns of CeCu₂Si₂; (c) CeO₂-Si and CeO₂-Al interface; (d) diffraction patterns of CeO₂; (e) diffraction patterns of the precipitated Si; (f) diffraction patterns of Al.](image)

![Figure 7. Tensile properties of SiCp/Al-Si composites with different CeO₂ contents: (a) tensile strength and yield strength; (b) elongation.](image)
On the one hand, explained from the aspect of the matrix Al-Si alloy, the relationship between the strength of Al-Si alloy and the size of Si particles can be represented as:

\[
\sigma \propto \frac{F_V}{D(1 - F_V)}
\]

(1)

in which \(\sigma\) is the strength of the alloy and \(F_V\) and \(D\) denote the volume fraction and average diameter of Si particles, respectively. For the SiCp/Al-Si composites, it is assumed that SiC particles are equivalent to Si particles and the strength of the composites is proportional to the volume fraction of Si particles and inversely proportional to the average diameter of Si particles.

On the other hand, it can also be explained in terms of the dislocation density strengthening mechanism of the SiCp/Al-12Si composite. Dislocation density strengthening means that, when the material is cooled from the preparation or heat treatment temperature, due to the large difference in thermal expansion coefficient between the reinforcing particles and the matrix, thermal mismatch strain is generated inside the aluminum matrix, which generates a large number of dislocations, thereby improving the strength of the material. Assuming that the shape of the reinforcing particles is cubic, the increment of the yield strength caused by the increase of the dislocation density can be estimated by the following equation:

\[
\Delta\sigma_d = kG_p b \left( \frac{12\Delta\alpha\Delta TV_p}{bd_p} \right)^{1/2}
\]

(2)

In Equation (2), \(k\) is the coefficient; \(G_p\) is the elastic modulus of the reinforced particles; \(b\) is the Burgers vector; \(\Delta\alpha\) is the difference in thermal expansion coefficient between the matrix and the reinforced particles; \(\Delta T\) is the temperature difference; \(d_p\) is the size of the reinforced particles. It is also assumed that the Si particles are equivalent to SiC particles, and it can be seen from Equation (2) that the increment in the yield strength of the composites has a negative correlation with the reinforced particle size \(d_p\).

Therefore, from the above two aspects, it can be concluded that the strength of the composites has a negative correlation with the Si phase particles size, that is, the smaller the Si phase particle size, the higher the strength of the composites. This can be verified from the change law of tensile strength and yield strength in Figure 7a. When the CeO\(_2\) content was 0.2 vol\% (the average diameter of Si particles is the smallest), the tensile properties of the composites were the best.

The strengthening mechanism of composites can be analyzed from the following three aspects. Firstly, the distribution uniformity of the Si particle in the composites was considered. The existence of Si particles made the dislocation movement difficult, which can prevent the plastic deformation of the Al matrix, thereby increasing the strength. The hindering effect of Si particles on dislocation enhanced with the increase of its distribution uniformity. At this time, the stress concentration degree decreased gradually, and the stress limit required for fracture became slow, thus improving the strength and ductility (elongation) of composites. Secondly, the size of Si particles was one of the main factors affecting the strength of composites. On the one hand, the large-size Si particles were easy to crack during the stress process due to their brittleness and became the crack initiation site for the composite fracture, thus reducing the strength and elongation of the material. On the other hand, the smaller the particle size of Si phase, under the condition of a certain Si phase content, the number of Si phase particles will increase greatly. The phase interface between Al and Si then increased greatly, and the obstacle to dislocation slip was enhanced so as to improve the strength. Finally, the CeO\(_2\) content also had a great influence on the strength of composites. When the volume fraction of CeO\(_2\) exceeded 0.2\%, the agglomeration phenomenon of CeO\(_2\) was intensified. The internal structure of the agglomerated CeO\(_2\) was loose, which could not effectively bear the stress. At the same time, the ability to transfer stress was also poor. In addition, agglomerated CeO\(_2\) was
irregular in shape, which easily became the crack initiation site in the process of plastic deformation, thus reducing the strength of the material.

3.4. Fracture Behavior of SiCp/Al-Si Composites

Macroscopically, there was no obvious plastic deformation of the composites before tensile fracture. From the tensile properties measured above, it can be seen that the elongation of the composites was between 2.97% and 4.09%, so the fracture form was brittle. However, from a microscopic point of view, with the change of the CeO$_2$ volume fraction, its fracture behavior also had a certain difference. Figure 8 shows the SEM images of the fracture surface of the composites with different volume fractions of CeO$_2$. Among them, Figure 8a shows the fracture morphology of the composites without CeO$_2$. There were a large number of Si phase particles or large-size SiCp cleavage sections, cavities formed by the peeling of SiC particles and the tearing edges formed around the cavities on the fracture. In addition, there were small toughening nests generated by the fracture of the Al matrix distributed around Si and SiC. With the increase of CeO$_2$ volume fraction, the section size of Si phase decreased and the number of toughening nests and tearing edges increased, reaching the peak when the CeO$_2$ content is 0.2 vol%. At this time, the cross section of the Si phase particles was the smallest, and the number of toughening nests and tearing edges was the largest. Thereafter, as the content of CeO$_2$ continued to elevate, the cross-section size of the Si phase particles increased, and the number of toughening nest and tearing edges reduced.

On the one hand, the fracture behavior of the tensile specimens was mainly related to the size of the Si phase particles. The cleavage section was mainly produced by the brittle fracture of Si and SiC particles, and the addition of an appropriate amount of CeO$_2$ could refine the Si phase particles, so that the size of the cleavage section formed by the Si particles was reduced and the number of tearing edges and small toughening nests around the Si particles increased accordingly. On the other hand, SiC particles could be drawn, while Si particles mainly underwent cleavage fracture, which was mainly caused by the bonding strength of the interface. The average size of SiCp was 5 μm; the size was small and the internal defects were few, so the particle fracture strength was high. The interface bonding strength between SiCp and Al was less than the fracture strength of SiCp, so cracks were formed along the interface junction and then fractures occurred. The Si particles were better combined with Al, and the interface bonding strength was greater than the fracture strength of Si particles, so the Si particles had cleavage fracture. Furthermore, the fracture of the tensile specimen started from the fracture of Si particles and SiCp. As the tensile stress increased, stress concentration occurred around the reinforcement particles and the Si particles and SiCp were fractured, forming the crack source. The cracks then propagated into the Al matrix and connected to each other, which eventually lead to the occurrence of fracture behavior. There is research showing that the small Si particles have an impediment to the crack growth [24], so the refinement of Si particles can improve the fracture strength and plasticity of the material by hindering the growth of cracks. The uniform distribution of Si particles relatively reduced the stress concentration, thereby hindering fracture.

In a nutshell, the fracture mode of the 20 vol% SiCp/Al-12Si composites with rare earth addition was a mixed fracture: brittle cleavage fracture of the Si phase and a few SiC particles, the tearing of Si and SiC particles with the matrix at the matrix interface, and ductile fracture in Al matrix far away from Si and SiC particles.
3.5. Analysis of the Mechanism of CeO$_2$ in SiCp/Al-Si Composites

As can be seen in Figure 4f, the addition of CeO$_2$ significantly refined the precipitated silicon phase. During the sintering process, the Si solute was precipitated from the supersaturated solid solution Al matrix. The formation of Si phase included two stages: nucleation and growth. The higher the nucleation rate and the lower the growth rate, the smaller the size of Si particles. The high energy locations, such as grain boundaries, high-density dislocations, and second-phase particles, are preferentially heterogeneous nucleation sites for the silicon phase [25–27]. The nucleation rate of heterogeneous nucleation depended on the interface energy between the substrate and the nucleation phase. The nucleation resistance decreased with the decrease of interface energy, which was conducive to heterogeneous nucleation and increased the nucleation rate.
According to lattice mismatch theory [28], as the mismatch degree between substrate and nucleation phase decreases, the lattice matching degree between substrate and nucleation phase increases, so that the energy caused by lattice mismatch at the interface reduces, that is, the interface energy between substrate and nucleation phase reduces. The interface energy is the resistance to the nucleation of the silicon phase. Al, Si, and CeO2 have face-centered, diamond, and fluorite-type (CaF2) cubic structures, respectively, all of which belong to the cubic crystal system and face-centered cubic lattice. Therefore, the one-dimensional mismatch degree can be used to reflect the nucleation effect of the substrate and CeO2 on the Si phase. The one-dimensional lattice mismatch degree (δ) can be expressed as:

$$\delta = \frac{|\alpha_s - \alpha_n|}{\alpha_n}$$  \hspace{1cm} (3)

where $\alpha_s$ is the lattice constant of the substrate and $\alpha_n$ is the lattice constant of the nucleation phase. From the calibrated diffraction spectrum in Figure 6, it can be seen that the lattice constants of the cubic system Al, Si, and CeO2 phase were 0.4050 nm, 0.5430 nm, and 0.5411 nm, respectively. Substituting into Equation (3), the one-dimensional mismatch of the Al substrate and Si phase ($\delta_1$) and the CeO2 substrate and Si phase ($\delta_2$) were calculated to be 0.254 and 0.0035. $\delta_2$ is much smaller than $\delta_1$, and the difference between the two is two orders of magnitude. According to the lattice mismatch degree, it can be seen that the interface between the Al substrate and Si phase was a non-coherent interface, while the interface between the CeO2 substrate and Si phase was a coherent interface. The interface energy of the non-coherent interface was greater than that of the coherent interface (as shown in Table 2). That is, the nucleation resistance was lower with CeO2 as the substrate for Si than with Al as the substrate, and the heterogeneous nucleation effect was better. Therefore, adding CeO2 to the SiCp/Al-Si composites, CeO2 can provide a large number of nucleation substrates to refine the Si particles.

### Table 2. The relationship among interface structure, lattice mismatch degree, and interface energy.

| Interface Structure      | Lattice Mismatch Degree | Interface Energy |
|--------------------------|-------------------------|-----------------|
| Coherent Interface       | $\delta \leq 0.05$      | 0.1 J/m²        |
| Semi-coherent Interface  | 0.05 $\leq \delta \leq 0.25$ | 0.5 J/m²       |
| Non-coherent Interface   | $\delta \geq 0.25$      | 1.0 J/m²        |

The rare earth (CeO2) interacted with the alloying elements in the aluminum matrix to form the rare earth compounds (Figure 6a). The particles were small, which can impede the movement of dislocations and exert a certain dispersion strengthening effect. At the same time, the new phase CeCu2Si2, located at the interface of Al and Si, can improve the bonding strength between Al and Si particles.

According to Figure 6a,c, it can be seen that CeO2 dispersoids existed at the grain boundary or phase boundary, which significantly reduced the mobility of the interface and hindered movement of the aluminum grain boundary. In the process of sintering, hot extrusion, and heat treatment, it can hinder the growth of the aluminum grains to a certain extent and refine the grains, thereby simultaneously improving the strength and plasticity of the composites.

### 4. Conclusions

1. The addition of an appropriate amount of CeO2 can refine the Si particles, reduce the agglomeration of Si phase, and improve its distribution uniformity in the SiCp/Al-Si composites. When the CeO2 volume fraction was 0.2%, the Si phase particle size was the smallest and the distribution uniformity was the best.

2. The main precipitates in SiCp/Al-Si composites without CeO2 were Al19Mn4, Al4Cu9, Al2Cu, Al5Cu6Mg2, and a new phase of CeCu2Si2 was formed after adding CeO2 in
the composites. CeO$_2$ was mainly located at the grain boundary or phase boundary of the composites.

(3) The addition of appropriate content of CeO$_2$ can improve the tensile properties of composites. When the CeO$_2$ content was 0.2 vol%, the tensile properties of the composites were the best.

(4) The fracture mode of the 20 vol% SiCp/Al-12Si composites with rare earth addition is a mixed fracture: brittle cleavage fracture of the Si phase and a few SiC particles, the tearing of Si and SiC particles with the matrix at the matrix interface, and ductile fracture in the Al matrix far away from Si and SiC particles.

(5) There are three main mechanisms of CeO$_2$ in SiCp/Al-Si composites. Firstly, CeO$_2$ serves as the nucleation substrate of Si phase to refine Si particles; secondly, CeO$_2$ reacts with the alloying elements in the aluminum matrix to form a new phase CeCu$_2$Si$_2$, which can exert a certain dispersion strengthening effect and improve the bonding strength between Al and Si particles; thirdly, the pinning effect of CeO$_2$ and CeCu$_2$Si$_2$ particles on grain boundaries or phase boundaries to refine aluminum grains.

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References
1. Chi, B.; Shi, Z.; Wang, C. Crystallization behavior, Al-Ce intermetallic formation, and microstructure refinement of near-eutectic Al-Si alloys by rare-earth element additions. *Int. J. Mater. Res.* 2020, 111, 938–952. [CrossRef]
2. Liu, X.; Sekizawa, K.; Suzuki, A. Compressive Properties of Al-Si Alloy Lattice Structures with Three Different Unit Cells Fabricated via Laser Powder Bed Fusion. *Materials* 2020, 13, 2902. [CrossRef] [PubMed]
3. Laghari, R.A.; Li, J.G.; Wu, Y. Study of Machining Process of SiCp/Al Particle Reinforced Metal Matrix Composite Using Finite Element Analysis and Experimental Verification. *Materials* 2020, 13, 5524. [CrossRef] [PubMed]
4. Zhu, S.Z.; Ma, G.N.; Wang, D. Suppressed negative influence of natural aging in SiCp/6092Al composites. *Mater. Sci. Eng.* 2019, 767, 138422. [CrossRef]
5. Yang, H.; She, X.W.; Tang, B.B. Study of the Microstructure and Ring Element Segregation Zone of Spray Deposited SiCp/7055Al. *Materials* 2019, 12, 1299. [CrossRef]
6. Liu, Y.; Li, G.; Jiang, W. Effects of Cu-Coated SiC Content on Microstructure and Properties of Laser Cladding SiCp/Al-Si Composite Coatings. *Materials* 2019, 12, 1537. [CrossRef]
7. Li, W.; Chen, J.; He, J.J. Effect of the Sic Particle Orientation Anisotropy on the Tensile Properties of a Spray-Formed Sicp/Al-Si Composite. *Strength Mater.* 2014, 46, 221–228. [CrossRef]
8. Zhou, X.L.; Zou, A.H.; Hua, X.Z. Influence of Mg and Si in the Aluminum on the Thermo-Physical Properties of Pressureless Infiltrated SiCp/Al Composites. *Mater. Sci. Forum* 2009, 610, 546–553. [CrossRef]
9. Gu, T.; Pan, Y.; Lu, T. Effects of boron addition on the morphology of silicon phases in Al-Si casting alloys. *Mater. Charact.* 2018, 141, 115–119. [CrossRef]
10. Wang, S.; Zhou, N.; Song, D. Effects of La and Ce Mixed Rare Earth on Microstructure and Properties of Al-Mg-Si Aluminum Alloy. *Mater. Sci. Forum* 2017, 898, 367–371. [CrossRef]
11. Li, Q.; Li, B.; Li, J. Effect of yttrium addition on the microstructures and mechanical properties of hypereutectic Al-20Si alloy. *Mater. Sci. Eng. A* 2018, 722, 47–57. [CrossRef]
12. Hu, G.Y.; Zhu, C.J.; Xu, D.F.; Dong, P.X.; Chen, K.H. Effect of cerium on microstructure, mechanical properties and corrosion properties of Al-Zn-Mg alloy. *J. Rare Earths* 2021, 39, 208–216. [CrossRef]
13. Guan, L.Y.; Li, B.L.; Qi, P. Effect of Heat Treatment on the Microstructure and Property of Al-Si-Mg Alloy. *Mater. Sci. Forum* **2016**, *850*, 768–772. [CrossRef]

14. Han, H.; Wang, A.; Xie, J. Effects of CeO$_2$ on microstructure, friction and wear properties of SiCp/Al-Si composites. *Energ. Mater. Res.* **2016**, *5*, 88–94. [CrossRef]

15. Lu, J.; Yang, B.; Li, H. The effects of addition of La$_2$O$_3$ on the microstructure and mechanical properties of carbon/carbon composites. *Mater. Sci. Eng., A* **2014**, *610*, 350–354. [CrossRef]

16. Sharma, A.; Roh, M.H.; Jung, J.P. Effect of La$_2$O$_3$ Nanoparticles on the Brazability, Microstructure, and Mechanical Properties of Al-11Si-20Cu Alloy. *J. Mater. Eng. Perform.* **2016**, *25*, 1–8. [CrossRef]

17. Elgallad, E.M.; Doty, H.W.; Alkahtani, S.A. Effects of La and Ce Addition on the Modification of Al-Si Based Alloys. *Adv. Mater. Sci. Eng.* **2016**, **2016**, 5027243. [CrossRef]

18. Liu, M.; Wang, Z.; Luan, X. Effects of CeO$_2$ and Y$_2$O$_3$ on the interfacial diffusion of Ti/Al$_2$O$_3$ composites. *J. Alloys Compd.* **2016**, *656*, 929–935. [CrossRef]

19. Christensen, B.D.; Donaldson, I.W.; Bishop, D.P. Effects of process variables on the mechanical and physical properties of an Al–Cu–Mg powder metallurgy alloy. *SN Appl. Sci.* **2019**, *1*, 511. [CrossRef]

20. Qiu, T.; Wu, M.; Du, Z. Microstructure evolution and densification behaviour of powder metallurgy Al–Cu–Mg–Si alloy. *Powder Metall.* **2020**, *63*, 54–63. [CrossRef]

21. Zare, R.; Sharifi, H.; Saeri, M.R. Investigating the effect of SiC particles on the physical and thermal properties of Al6061/SiCp composite. *J. Alloys Compd.* **2019**, *801*, 520–528. [CrossRef]

22. Toschi, S. Optimization of A354 Al-Si-Cu-Mg alloy heat treatment: Effect on microstructure, hardness, and tensile properties of peak aged and overaged alloy. *Metals* **2018**, *8*, 961. [CrossRef]

23. Sadeghi, I.; Wells, M.A.; Esmaeili, S. Effect of particle shape and size distribution on the dissolution behavior of Al$_2$Cu particles during homogenization in aluminum casting alloy Al-Si-Cu-Mg. *J. Mater. Process. Technol.* **2018**, *251*, 232–240. [CrossRef]

24. Chen, Z.W.; Abraham, F.; Walker, J. Tensile Fracture Behavior of Friction Stir Processed Al-7Si-0.3Mg Cast Alloy. *Mater. Sci. Forum* **2012**, *706–709*, 971–976. [CrossRef]

25. Zhang, X.X.; Wang, D.Z.; Yao, C.K. Nucleation and growth behavior of primary silicon in alumina fiber reinforced hypereutectic Al-Si composite. *J. Mater. Sci. Lett.* **2002**, *21*, 921–922. [CrossRef]

26. StJohn, D.; McDonald, S.; Darlapudi, A. A New Perspective on the Nucleation, Growth Morphology and Modification of the Silicon Phase During the Formation of Eutectic Al-Si Grains. *JOM* **2019**, *71*, 391–396. [CrossRef]

27. Zhang, Y.; Zheng, H.; Liu, Y. Cluster-assisted nucleation of silicon phase in hypoeutectic Al–Si alloy with further inoculation. *Acta Mater.* **2014**, *70*, 162–173. [CrossRef]

28. Toth, G.I.; Tegze, G.; Fuszttai, T. Heterogeneous Crystal Nucleation: The Effect of Lattice Mismatch. *Phys. Rev. Lett.* **2012**, *108*, 025502. [CrossRef]