

Article ID:1003 - 6326(1999)03 - 0524 - 06

Interactions of particles with solidifying front in $\text{Al}_2\text{O}_3/\text{Al-Si}$ composites^①

Wu Shusen(吴树森), Huang Naiyu(黄乃瑜), An Ping(安萍)

College of Materials Science and Engineering,

Huazhong University of Science and Technology, Wuhan 430074, P. R. China

Abstract: The behavior of ceramic particles at the solid/liquid interface and the distribution of particles in metallic matrix composites was studied with a zone unidirectional solidification method. Two kinds of particle dispersed composites, $\text{Al}_2\text{O}_3/\text{Al-12.6\%Sr-Sr}$ and $\text{Al}_2\text{O}_3/\text{Al-12.6\%Sr-Sr-Ca}$ containing Al_2O_3 particles in volume fraction 2% ~ 5% were used. In the $\text{Al}_2\text{O}_3/\text{Al-Sr-Sr}$ composites, the particles were pushed by the solidifying front, and did not uniformly distribute in the solid. But in the $\text{Al}_2\text{O}_3/\text{Al-Sr-Sr-Ca}$ composites, the particles were engulfed by the solidifying front and uniformly distributed in the solid. The particles engulfing into the solid was realized only by Sr and Ca addition at the same time. As the interfacial energy between solid and particle was decreased in this case, the Al_2O_3 particles acted as the substrates of heterogeneous nucleation for the Si phases, which made the particles to be engulfed.

Key words: metallic matrix composites; solidification; particle size distribution

Document code: A

1 INTRODUCTION

As the particle reinforced aluminum matrix composites are superior in strength and wear resistance, the applications of the composites have been advanced in many aspects, such as in automobile parts and sports articles^[1~3]. However, for the massive production of the composites, the liquid metal processes, including the casting process, are necessary. There exists an important problem of how to make the particles distribute uniformly in the solidified solid. As we know, most of the ceramic particles are pushed by the solidifying interface, and segregate at grain boundaries^[1]. It is very difficult to obtain a uniform distribution of particles under the condition of gravity casting. If particles can be engulfed by the solidifying front, a uniform distribution of particles can be obtained^[4]. On the other hand, if particles are pushed by the solidifying front, particles will segregate at the last freezing part or grain boundaries. Here the term "engulfed" is used when a particle is incorporated in a planar interface. The term "entrapped" is

used when the particle is incorporated by a non-planar (e.g. dendritic) interface which grows around it^[5].

Previous studies^[6~7] showed that if the interfacial energy between a ceramic particle and a solid phase can be decreased, and the contact angle between particle and solidifying front is less than 90° , the particle will be engulfed by the solidifying front and uniformly distributes in solid. On the other hand, the particles will be pushed into the liquid by the solidifying front when the contact angle is greater than 90° . The interaction of Al_2O_3 particles with the solid (S)/liquid (L) interface of eutectic Al-Si alloys and the particle distribution were investigated in this study. The effect of trace elements on the interaction has also been discussed. The reason to select the eutectic Al-Si alloy as the matrix alloy is that a relatively planar S/L interface morphology similar to that in single phase pure melt solidification can be obtained. This is favorable to discuss the interaction of particles with a solidifying front. Moreover, the Al-Si alloy is one of the major cast light metals.

① Received Sep. 7, 1998; accepted Oct. 28, 1998

2 EXPERIMENTAL TECHNIQUE

The DURALCAN composites W6A20A (6061 aluminum alloy reinforced with Al₂O₃ particles in volume fraction 20 %) was used as master material for making the composite samples. In order to purify its alloying elements, a dilution of the composites was done by melting, agitating and holding for the settling of the Al₂O₃ particles. Pure Al (99.99 %) was added to the residual melt after the upper part of the melt was poured. This process was repeated three times in order to obtain the Al₂O₃/Al composites that contained a very small amount of impurities. By adding pure silicon (99.999 %) and trace Sr and Ca to these composites, the Al₂O₃p/Al-12.6 % Si-Sr composites and Al₂O₃p/Al-12.6 % Si-Sr-Ca composites were prepared. The chemical compositions of matrix of W6A20A and the two composites are shown in Table 1. The only difference of the two composites was trace Ca added in the latter. The volume fraction of Al₂O₃ particles in the composites is 2 % ~ 5 %, and the average diameter of Al₂O₃ particles is 30 μm.

If the ordinary UDS method is used to study the solidification process of composites, the particles, such as that in Al₂O₃p/Al, will sedimentate before solidification because of the difference in specific gravity between the particles and the liquid, which will lead to difficulty in maintaining the steady state unidirectional solidification, and be also unfavorable for discussing the behavior of particles at the interface. Therefore, a zone UDS method^[8] was utilized in this experiment. The melting zone was maintained in a short length of 30 ~ 40 mm during the experiment so that the excessive accumulation of particles in front of S/L interface might be avoided. The sample was fixed in this experiment, and the electric furnace was moved up-

ward.

High purity alumina tubes (99.9 % Al₂O₃) were used as the crucible in the experiment for avoiding the chemical reaction between the melt and the crucible. The sample was quenched in water when it solidified to about 20 ~ 40 mm length. The sample was then analyzed by means of optical microscope, SEM and EPMA.

3 RESULTS

The distribution of Al₂O₃ particles near the S/L interface in Al₂O₃p/Al-Sr-Sr composites is shown in Fig.1, in which the solidification direction was upwards at a solidification rate of 2.22×10^{-3} mm/s. The particles were rejected and pushed by the solidifying front, and accumulated in the liquid in front of the interface. There were no particles in the solid near the interface. The particles were still pushed at the maximum freezing speed of 6.67×10^{-3} mm/s in the experiment. However, when too many of the pushed Al₂O₃ particles accumulated in front of the S/L interface, the movement of particles was impeded by the bridging effect of the accumulated particles, and the particles were mechanically entrapped into solid to form a band structure. Fig.2 shows the band structure containing Al₂O₃ particles at the solidification rate of 4.44×10^{-3} mm/s. Of course, this is not a uniform distribution. The eutectic structure of Al-Si alloy was very fine in this case as the freezing velocity was high.

On the other hand, in the case of the Al₂O₃p/Al-Sr-Sr-Ca composites, the Al₂O₃ particles were engulfed by the solidifying front at a very low solidification rate of 5.56×10^{-4} mm/s, as shown in Fig.3. There was no particle accumulation in front of the interface. Some particles were just at the interface and entering into the solid. To confirm the influence of the

Table 1 Chemical composition of matrix of composite specimens (%)

Matrix	Si	Fe	Cu	Mn	Mg	Cr	Zn	Sr	Ca
W6A20A	0.4 ~ 0.8	< 0.70	0.15 ~ 0.40	< 0.15	0.80 ~ 1.20	0.04 ~ 0.35	< 0.25	< 0.01	< 0.01
Al-Sr-Sr	12.6	< 0.05	< 0.04	< 0.01	< 0.01	< 0.001	< 0.001	< 0.09	< 0.005
Al-Sr-Sr-Cr	12.6	< 0.05	< 0.04	< 0.01	< 0.01	< 0.001	< 0.001	< 0.09	< 0.10



Fig.1 Distribution of particles at solid/liquid interface in $Al_2O_3p/ Al-Si-Sr$ composites (Upward solidification , $R = 2.22 \times 10^{-3} \text{ mm/s.}$)

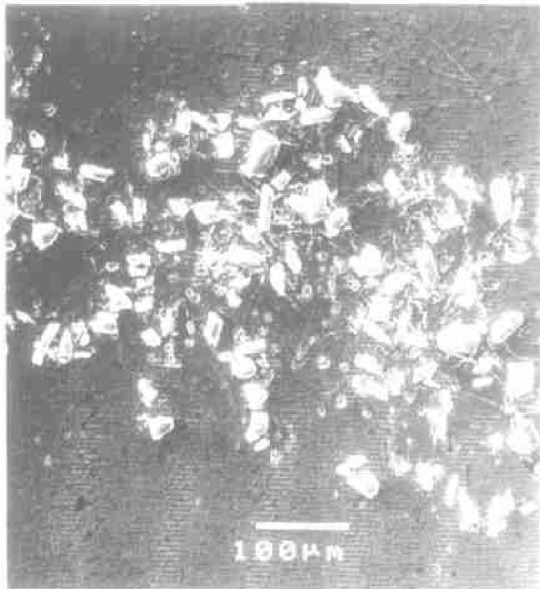


Fig. 2 Distribution of particles in solid of $Al_2O_3p/ Al-Si-Sr$ composites ($R = 4.44 \times 10^{-3} \text{ mm/s}$)

solidification rate on the engulfment , many experiments were carried out . The experimental results show that the increase in the solidification rate assisted the engulfment when particles could be engulfed . The Al_2O_3 particles in $Al_2O_3p/ Al-Si-Sr-Ca$ composites were uniformly distributed in the solid , as shown in Fig . 3 . These particles were either surrounded by the α Al phase or touched by the Si phase .



Fig. 3 Distribution of particles at solid/liquid interface in $Al_2O_3p/ Al-Si-Sr-Ca$ composites ($R = 5.56 \times 10^{-4} \text{ mm/s}$)

4 DISCUSSION

In order to discuss the mechanism of particle engulfment , the microstructures and distribution of trace elements were analyzed . According to the EPMA , the levels of Sr and Ca in the melt were clearly higher than those in the α Al phase in $Al_2O_3p/ Al-Si-Sr-Ca$ composites . Moreover , the levels of Sr and Ca in the interface between Si phase and α Al phase were comparatively higher than those in the α Al phase . Namely , Sr and Ca , which were rejected by the solidifying α Al phase and Si phase during the eutectic solidification of Al-Si alloys , accumulated in liquid phase , or adsorbed at the boundaries between Si phase and α Al phase and at the surface of the

Al_2O_3 particles.

The spectra peak curves of the EDX analysis for the Al_2O_3 particle in the $\text{Al}_2\text{O}_3/\text{Al-Sr-Sr-Ca}$ composites are shown in Fig. 4. There were almost no other elements except Al_2O_3 in the central part of the particle. But in the edge area, Si, Sr and Ca were obviously observed. This shows that Si, Sr and Ca in the melt have penetrated into the surface of alumina particles. Namely, the chemical compositions of the Al_2O_3 particle surface have been changed. This means that the surface of the Al_2O_3 particles has been modified. In reference^[9], the wettability of aluminum melt with Al_2O_3 was improved by the addition of 3% Ca. There was a rich layer of Ca at the interface between Al_2O_3 and the Al-Ca melt, and a compound oxide of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ would be formed on the surface of alumina^[9]. The

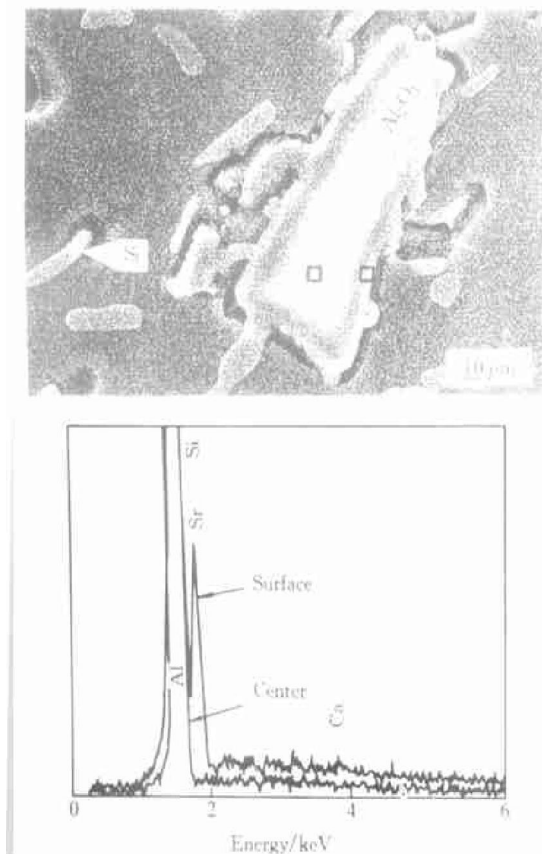
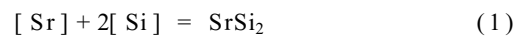


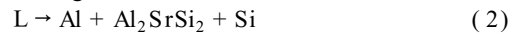
Fig.4 Comparison of chemical compositions of surface and center in an Al_2O_3 particle by EDS

alloying elements were comparatively more in this study, but the levels of Sr and Ca were very low. The oxide formed on the surface may be more complicated.

Moreover, some angular compounds were observed both in the solid and the liquid in the $\text{Al}_2\text{O}_3/\text{Al-Sr-Sr}$ composites. The compound contained only Sr and Si as confirmed by the EDX analysis. It should be SrSi_2 or the mixture of Si and SrSi_2 , as the Si amount was comparatively higher than that in the SrSi_2 . The following reactions easily occur in the Al-Sr-Sr system^[10]:



And during the eutectic reaction,



However, the intermetallic compound Al_2SrSi_2 is usually very small and it is difficult to analyze^[11]. The melting point of SrSi_2 is 1273 K, which is about 400 K higher than that of the eutectic Al-Si alloy. The solidification temperature of primary Si is also higher than the eutectic temperature. Therefore, the compound should be formed before the eutectic reaction by the segregation of Sr and Si in the Al-Sr-Sr alloy.

The chemical reactions are more complicated in the Al-Sr-Sr-Ca quaternary system, and there is still no phase diagram for reference. In the solidified samples of the $\text{Al}_2\text{O}_3/\text{Al-Sr-Sr-Ca}$ composites, few angular compounds were also observed in solid and liquid. Fig. 5 shows the X-ray area scanning results of the compounds, as denoted by the arrows, near the S/L interface. It shows that the compound contains Si, Sr and Ca and should be the intermetallic compound of Sr-Sr-Ca. The same small compounds ($< 1 \mu\text{m}$) were sometimes observed at the interface between the solid and Al_2O_3 crucible. That is to say, this intermetallic compound would also be formed at the surface of alumina particles.

As mentioned above, the Al_2O_3 surface was somehow modified with Sr + Ca addition in the $\text{Al}_2\text{O}_3/\text{Al-Si}$ composites, which promoted the engulfment of Al_2O_3 particles by the solid. From Fig. 3 and Fig. 4, it is obvious that every Al_2O_3 particle is covered or touched by Si phase. Many evidences in the experiments indicate that the Si

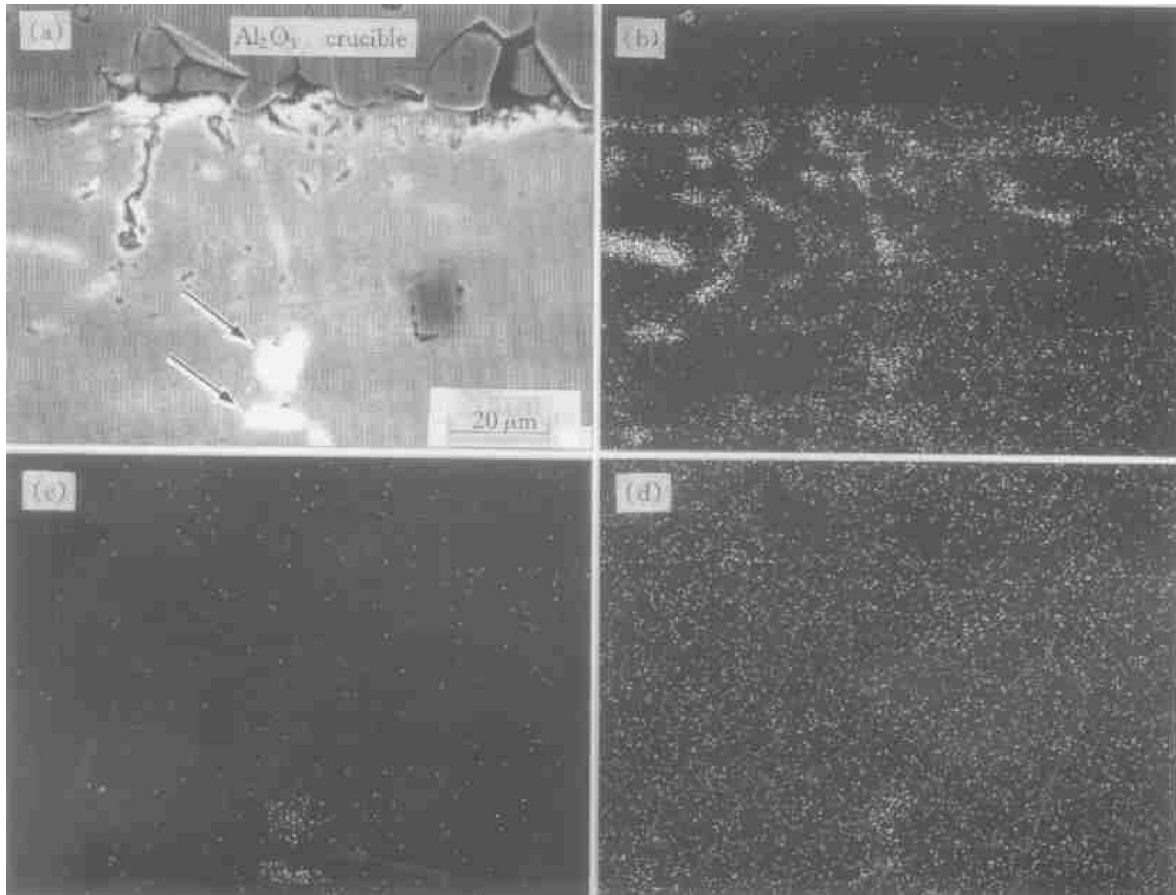


Fig.5 SEM compo images of compound in Al₂O₃p/ Al-Si-Sr-Ca composites
 (a) —BSE;(b) —Si;(c) —Ca;(d) —Sr

phase can nucleate and grow on the Al₂O₃ particle surface. Fig.6 shows the matrix structures near the S/L interface of the specimen. The outside of the specimen is the alumina crucible, which has the same composition with Al₂O₃ particles. It is obvious that Si phase in the periphery was coarser than that in the inner part, and Si phase grew from crucible surface to inner. The fine eutectic structure in the inner part of specimen resulted from the modification of Sr and Ca. Namely, Al₂O₃ particles promoted the nucleation and growth of Si phase, and acted as the substrate of heterogeneous nucleation. It also indicates that the interfacial energy between Si phase and Al₂O₃ particle was decreased with Sr and Ca addition. The change of the relationship of interfacial energies is the main reason for particle en-

gulfment^[12]. It is well known that Si phase is the leading phase in eutectic reaction of Al-Si alloy^[13], and α Al phase can grow out easily with the growth of Si phase. Because the Si phase could nucleate and grow on the alumina surface, Al₂O₃ particles were not pushed by the growing solid front, but engulfed into the growing solid. The uniform distribution of Al₂O₃ particles in the solid was realized. But in the Al₂O₃p/ Al-Si-Sr composites, Al₂O₃ particles did not become the nucleator of Si phase, and were still pushed by the solid front, and segregated at grain boundaries or formed band structures.

5 CONCLUSION

The interactions of Al₂O₃ particles with the

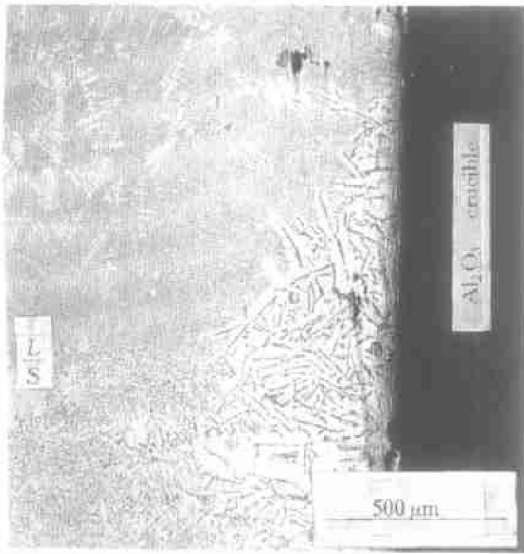


Fig.6 Microstructures of matrix alloy at S/L interface of $\text{Al}_2\text{O}_3\text{p}/\text{Al-Si-Sr-Ca}$ composites (Upward solidification, $R = 2.22 \times 10^{-3} \text{ m m/s.}$)

S/L interface of eutectic Al-Si alloys have been studied with the zone UDS method. In the $\text{Al}_2\text{O}_3\text{p}/\text{Al-Si-Sr}$ composites, Al_2O_3 particles are pushed by the solidifying front. When the movement of the particles is impeded by the accumulation of the particles, they are mechanically entrapped into solid to form band structures. But in the $\text{Al}_2\text{O}_3\text{p}/\text{Al-Si-Sr-Ca}$ composites, particles

are engulfed by the solidifying front and uniformly distributed in the solid. Sr and Ca addition in Al-Si alloy can promote the engulfment of Al_2O_3 particles

REFERENCES

- 1 Allison J E and Cole G S. JOM, 1993, (1): 19.
- 2 Zhang Erlin, Yan Bo, Zeng Songyan *et al.* Trans Nonferrous Met Soc China, 1998, 8(1): 92.
- 3 Zhang Fan, Li Xiaocui, Jin Chen *et al.* Trans Nonferrous Met Soc China, 1998, 8(3): 449.
- 4 Asthana R and Tewari S N. J Mat Sci, 1993, 28: 5414.
- 5 Stefanescu D M, Dindaw B K and Moitra A. Metall Trans A, 1988, 19(11): 2847.
- 6 Wu Shusen and Nakae H. Acta Metallurgica Sinica, 1998, 34(9): 939.
- 7 Nakae H and Wu Shusen. Key Eng Mater, 1997, 127: 503.
- 8 Wu Shusen and Nakae H. J Japan Found Eng Soc, 1997, 69(1): 3.
- 9 Choh T and Oki T. J Japan Inst Metals, 1987, 51(10): 1209.
- 10 Petzow G and Effenberg G. Ternary Alloys—A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams. Weinheim: VCH Verlagsgesellschaft (Press), 1990: 270.
- 11 Song K, Fujii H and Nakae H. J Japan Inst of Light Met, 1993, 43(8): 484.
- 12 Wu Shusen and Nakae H. J Japan Found Eng Soc, 1997, 69(9): 775.
- 13 Bell J A and Wingard W C. J Inst Metals, 1964/1965, 93: 318.

(Edited by He Xuefeng)