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Effect of Ca-Si agent modifier on the granulation of γ+(Fe,Mn)$_3$C eutectic particle in an austenite steel

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An austenite medium Mn steel with granular γ+(Fe,Mn)$_3$C eutectic particles (abbreviated EAMC) has been produced with Ca-Si agent modifier in the as-cast state [1]. It is thought that the eutectic particles are formed in the molten pool among the primary austenite dendrites at the later stage of solidification. However, the effect of Ca-Si agent modifier on the granulation of the eutectic particles has not been clarified. Directional solidification of unmodified and Ca-Si agent modified Fe-3.47 wt%C-9.26 wt%Mn alloys has been carried out to elucidate the mechanism of eutectic granulation.

Different Fe-C-Mn alloys (expressed by EAMC, C3SC, C3W) were prepared by melting weighed quantities of pig iron, steel scraps, Fe-Mn alloy, and Ca-Si agent. After allowing time for melt homogenization, molten alloy was poured into the prepared bar molds (100 mm in length 7 mm ID and 8.5 mm OD). The nominal chemical compositions of the bars are presented in Table I.

Directional solidification was performed using a high temperature gradient Bridgman-type unit in protective argon atmosphere. Detailed descriptions of the unit were given in elsewhere [2]. Specimens were solidified under steady state conditions with a constant temperature gradient (approx. 80 $\mathrm{Kmm^{-1}}$) and different growth rate (2.18–500 $\mu\mathrm{ms^{-1}}$). After 30 mm steady growth, they were quenched by pulling them rapidly into Ga-In reservoir. The solidified samples were cut longitudinally, polished, etched, and then the metallographic investigation of the microstructure was performed with a video-image digital analysis system (VIDAS). A scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analysis (EDXA) was used for the chemical analysis of the distribution of the modifier ahead of S/L interface. A transmission electron microscope (TEM) was used to observe the morphology of eutectic particle in EAMC and the heterogeneous nucleus in front of S/L interface. TEM foils were prepared by the conventional twinjet polishing technique using an electrolyte of 10% perchloric acid in methanol at -30°C.

The microstructure of EAMC reveals that granular particles are well distributed in the austenite matrix. A representative metallographic structure is shown in Fig. 1a. TEM observation indicates that the granular particle is the γ+(Fe,Mn)$_3$C eutectic [1]. Two phases of the eutectic grow in the lamellar fashion, as shown in Fig. 1b. VIDAS analysis shows the roundness of the eutectic particles is in the range 0.65 to 0.95. The results analyzed with EDXA relevant to the matrix and the eutectic particle are shown in Table II.

Fig. 2a shows an optical micrograph of the growth interface at 2.18 μm/s in the C3W sample. A regular, cellular solidification front is observed across the sample, but no independent primary austenite colony exists ahead of S/L interface. Fig. 2b shows an optical micrograph of the growth interface at 2.18 μm/s in the C3SC sample. The interface is dendritic, and developed lateral branching of primary austenite dendrites into the quenched liquid ahead of interface is observed.

Fig. 3 shows the SEM micrographs and the corresponding Ca and Si line scan images on the C3W and C3SC samples. The image of calcium is not given in Fig. 3a because its content is too low to be detected with EDXA. It is seen that the quenched liquid ahead of S/L interface in the C3SC sample contains a higher level of Si and Ca than that in the C3W sample.

The equilibrium partition ratios of silicon and calcium are 0.83 and 0.56, respectively [3]. The constitutional supercooling develops when a higher level of silicon and calcium segregates ahead of the S/L interface and the liquidus temperature decreases with the increment of solute content [4]. It leads to the developed

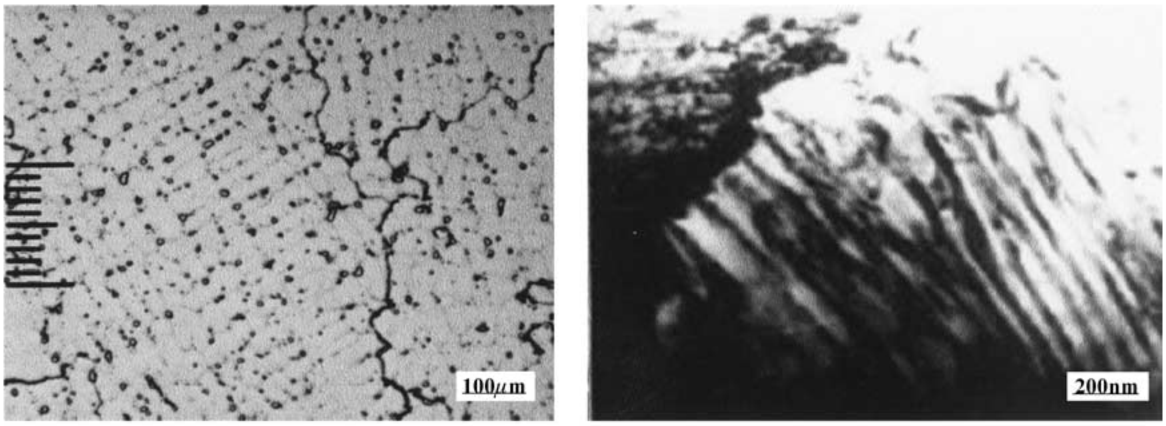
TABLE I Chemical composition of the studied alloys

		Composition (wt%)							
Sample	Modify	C	Mn	Si	Al	Ca	S	O	Fe
EAMC	Yes	1.25	6.58	1.75	1.08	0.13	0.02	0.02	Bal.
C3SC	Yes	3.47	9.26	1.25	0.41	0.54	0.02	0.02	Bal.
C3W	No	3.47	9.26	0.54	0.25	0.03	0.03	0.03	Bal.

TABLE II Chemical composition of matrix and eutectic

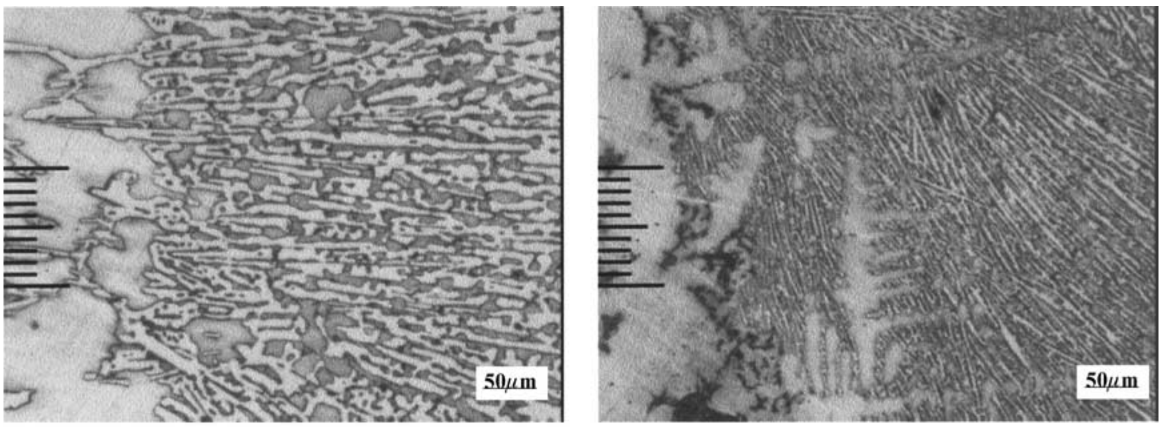
	Composition (wt%)					
Micro-area	C	Mn	Si	Al	Ca	Fe
Matrix	1.21	6.38	1.75	1.09	0.13	Bal.
Eutectic	3.57	9.34	1.81	0.54	0.05	Bal.

The value is the average of five points.



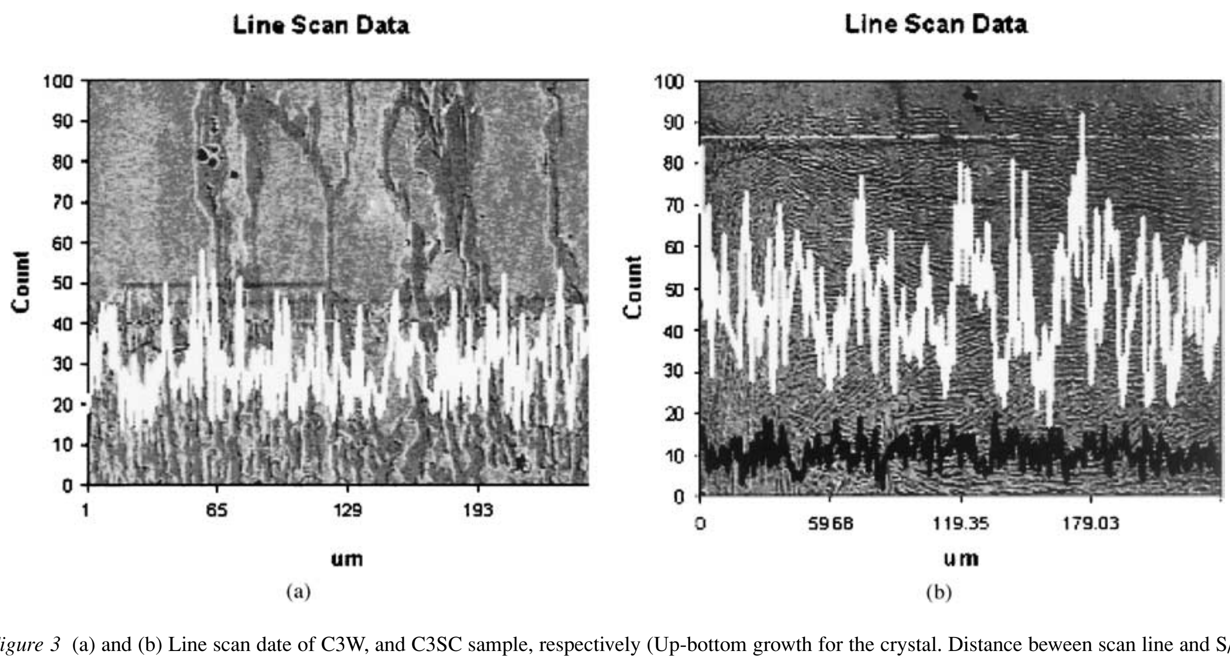
(a) (b)

Figure 1 (a) Metallographic structure of EAMC (optical micrograph) and (b) morphology of the eutectic (TEM). The white phase is the γ-Fe, and the black phase is the cementite.



(a) (b)

Figure 2 (a) and (b) Metallographic structure of directional solidified C3W, and C3SC, respectively. The crystal grows from left to right.



(a) (b)

Figure 3 (a) and (b) Line scan date of C3W, and C3SC sample, respectively (Up-bottom growth for the crystal. Distance beween scan line and S/L interface is fixed at 10 μm, and the scan rate of SEM is fixed at 1900–2000 CPS).

lateral branching of primary austenite dendrites, as shown in Fig. 2b.

TEM observation shows that some CaS particles exist in the quenched liquid ahead of S/L interface. The morphology of a CaS particle is given in Fig. 4. CaS particles can be as the heterogeneous nucleus of primary austenite dendrites [5]. As a result, the branches of the primary austenite dendrites into the liquid ahead of S/L interface develop because low supercooling is required.

Fig. 5a shows an optical micrograph of the directional structure in the C3W sample at 159 μm/s.

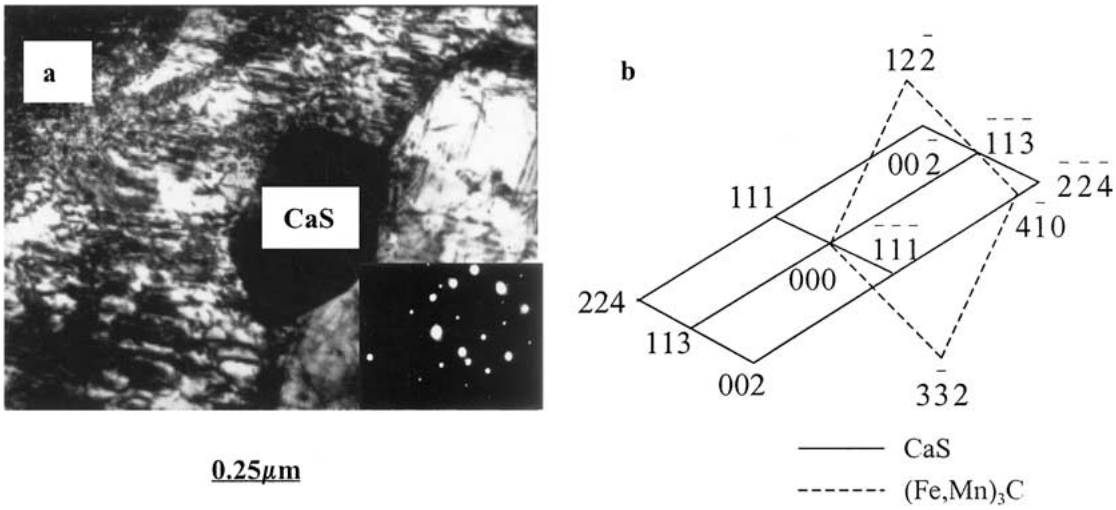


Figure 4 (a) Growth of the eutectic on CaS particle (TEM) and (b) indexing of the diffraction pattern for $B_{\text{CaS}} = [\bar{1}10]$, $B_{(\text{Fe,Mn})_3\text{C}} = [289]$.

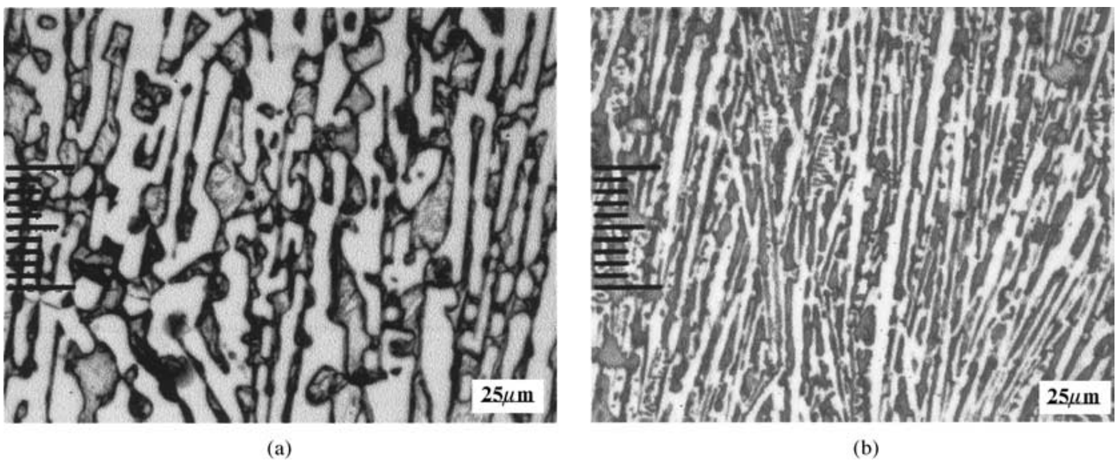


Figure 5 (a) and (b) Metallographic structure of directional solidified C3W, and C3SC, respectively (Bottom-up growth for the crystal).

The morphology of γ+(Fe,Mn)$_3$C eutectic reveals as typical non-faceted/faceted (NF/F) ledeburitic eutectic structure. Growth proceeds preferentially by edgewise growth of (Fe,Mn)$_3$C plates, with slight orientation changes during growth permitting the plates to spread in a fanlike fashion. Spaces between these fanlike (Fe,Mn)$_3$C plates fill in with a rodlike structure so that the final structure processes two different eutectic morphologies [6]. Fig. 5b shows an optical micrograph of the directional structure in the C3SC sample at 159 μm/s. Lamella of the γ-Fe phase are distributed in the (Fe,Mn)$_3$C matrix. The austenite and leading (Fe,Mn)$_3$C phases inter-grow parallel, like a regular, non-faceted/non-faceted eutectic.

The distribution of Si and Ca in front of the S/L interface is likely to be that shown in Fig. 3a and b. It indicates that the concentration of modifier retard the lateral growth preferentially of (Fe,Mn)$_3$C phase. It may result from two reasons as follows. The first is the reduction in surface energy and surface energy anisotropy, concomitant of solute absorption at the interphase boundary [7], after Ca-Si agent modifier is added. Secondly, it is known that the intergrowth zone is skewed toward (Fe,Mn)$_3$C side in the Fe-C-Mn system as a result of the nature of the F/NF eutectic in the conventional iron (no modifier). The added Ca-Si modifier enhances the segregation of C and Mn [1]. This shall enlarge the intergrowth zone toward the γ side. As a consequence, the (Fe,Mn)$_3$C phase cannot display its faceted feature but inter-grows with γ-Fe phase in a NF/NF fashion, as shown in Fig. 5b.

It may be expected that γ+(Fe,Mn)$_3$C phases in the normal EAMC casting display the similar growth characteristic as directional solidification. The γ-Fe and leading (Fe,Mn)$_3$C phases grow in the NF/NF fashion at the later stage of solidification, and quickly surrounded by the developed lateral branches of primary austenite dendrites (Fig. 2b). Thus, the eutectic particles shall grow into a granular form.

The granulation mechanisms of γ+(Fe,Mn)$_3$C eutectics in EAMC can be explained by (1) developed lateral branching of primary austenite dendrite attributed to the segregation of a higher level of Ca-Si modifier and the existence of CaS particles, and (2) non-faceted/non-faceted (NF/NF) growth fashion of γ and (Fe,Mn)$_3$C phases.

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