Eutectic decomposition in Ca-Si modified austenite medium Mn steel after solidification

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Austenite medium Mn steel is still a popular wear resistant material [1–3]. Its wear resistance increases with the increment of C content, while the toughness decreases greatly because a network and/or needle-like carbides appear in the austenite matrix [4]. It has been found that the diffusion-controlled precipitation of these carbides can be impeded; meanwhile some granular γ-$(Fe,Mn)_3C$ eutectics appear in the as-cast austenite medium Mn steel by employing a Si-containing agent modifier. The eutectics are formed among primary austenite dendrites at the later stage of non-equilibrium solidification [5]. Microstructure selection of austenite medium Mn steel modified with $Ca_{28}Si$ agent up to 1.5 wt% as a function of cooling rate was relatively well understood [6]. However, there is still a lack of knowledge on the details of microstructure selection of the steel modified with $CaSi_{28}$ agent over 1.5 wt%. C and Mn migration after solidification during cooling probably occurs by some processes such as *second* cementite ($(Fe,Mn)_3C_{II}$) formation and eutectoid transformation according to the Fe-C-Mn phase diagram [7]. Diffusion-controlled $(Fe,Mn)_3C_{II}$ and/or pearlite growth may proceed by C and Mn precipitation from eutectic, along with eutectic decomposition. The present work is focused on examining the microstructure selection of the austenite medium Mn steels modified with $Ca_{28}Si$ agent over 2.0 wt% and on studying the effects of modifier amounts and cooling rate on eutectic decomposition.

The austenite medium Mn steels were prepared by melting weighed quantities of pig iron, steel scraps, $FeMn_{80}$ alloy (Fe-80%Mn-1.0%Si-1.2%C), and $Ca_{28}Si$ agent (Fe-28%Ca-65%Si-2.4%Al-0.8%C). Allowing time for melt homogenization, molten alloy was poured into the prepared steel molds in the range of room temperature to $600\,^{\circ}C$ after de-oxidizing by aluminum. The steel mold is shown schematically in Fig. 1. One thermocouple was fixed in the hole marked by A. The nominal compositions of cast steels are presented in Table I.

Samples were ground, polished, and etched in a solution of 4 ml HNO_3 and 96 ml C_2H_5OH. Microstructure investigation was carried out by a video-image digital analysis system (VIDAS). Vickers durometer (VD) was used in this work to identify phases in austenite medium Mn steel. Micro-hardness of eutectic, cementite, and pearlite are Hv500–800, Hv1200–1400, and Hv260–450, respectively [6].

Fig. 2a shows the micrograph of the steel no. 1 solidified in the mold preheated at $600\,^{\circ}C$. Lots of white granules are well distributed in the austenite grain. VD analyses indicate that these granules are γ-$(Fe,Mn)_3C$ eutectic. Fig. 2b–d present the micrographs of the steel no. 2 solidified in the mold preheated at $600\,^{\circ}C$. Rosettes and other forms of $(Fe,Mn)_3C_{II}$/pearlite are dispersed throughout the austenite grains surrounded by inter-boundary $(Fe,Mn)_3C_{II}$/pearlite. A few eutectics can be seen in the austenite grains (see Fig. 2d). This means that Ca-Si modifier enhances the eutectic's decomposition into $(Fe,Mn)_3C_{II}$/pearlite.

$(Fe,Mn)_3C$ phase in eutectic, as an intermetallic compound, is relatively stable; however, γ phase in eutectic is unstable during cooling after solidification of the austenite medium Mn steel. Solid transformation of the γ phase occurs as shown in the following in accordance with the Fe-C-Mn phase diagram [7],

$$\gamma \rightarrow \gamma' + (Fe, Mn)_3C_{II}, \qquad (1)$$

and

$$\gamma' \rightarrow P. \qquad (2)$$
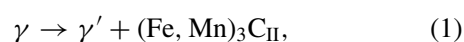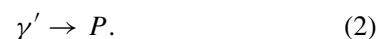
It therefore can be concluded that the diffusion-controlled eutectic decomposition is related to the C and Mn precipitation from γ phase in eutectic and diffusing to the nearest $(Fe,Mn)_3C$ phase in eutectic, along with the $(Fe,Mn)_3C_{II}$ growth (see Equation 1) probably followed by the pearlite formation (see Equation 2).

The precipitation tendency of C and Mn from γ phase in eutectic can be qualitatively forecast using the chemical potential. The chemical potential of an element i at a temperature T ($\mu_i(T)$), as the thermodynamic driving force for the precipitation of i on cooling, is related to its activity coefficient (f_i) by the expression [8]:

$$\mu_i = \mu_{0i}(T) + RT \ln f_i(\%i) \qquad (3)$$

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TABLE I Nominal composition of cast steels

Sample	Modifier (α_k) (wt%)	Nominal composition (wt%)							
		C	Mn	Si	Al	Ca	S	O	Fe
No. 1	Ca-Si/2.0	1.25	6.60	2.05	1.00	0.59	0.02	0.02	Bal.
No. 2	Ca-Si/3.5	1.25	6.60	3.70	1.06	0.92	0.02	0.02	Bal.
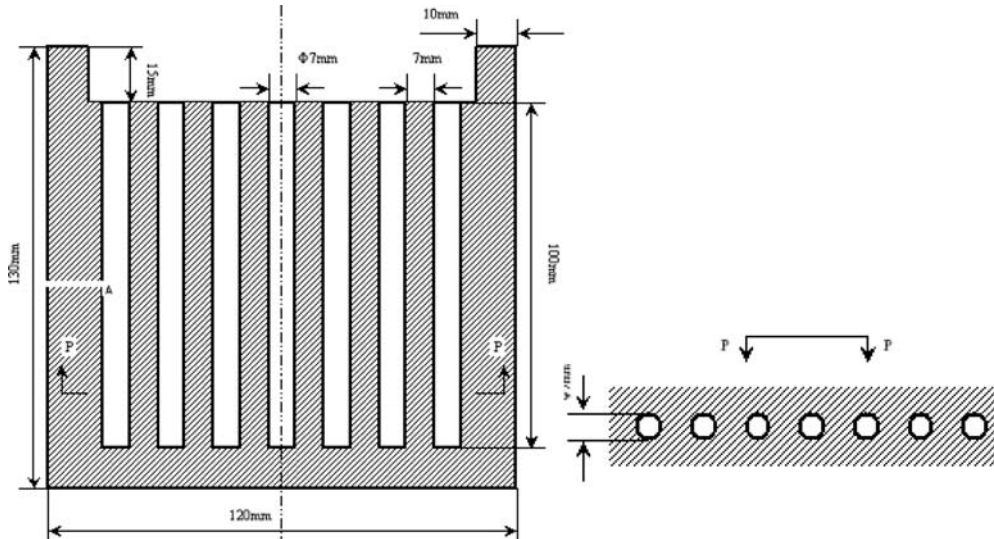
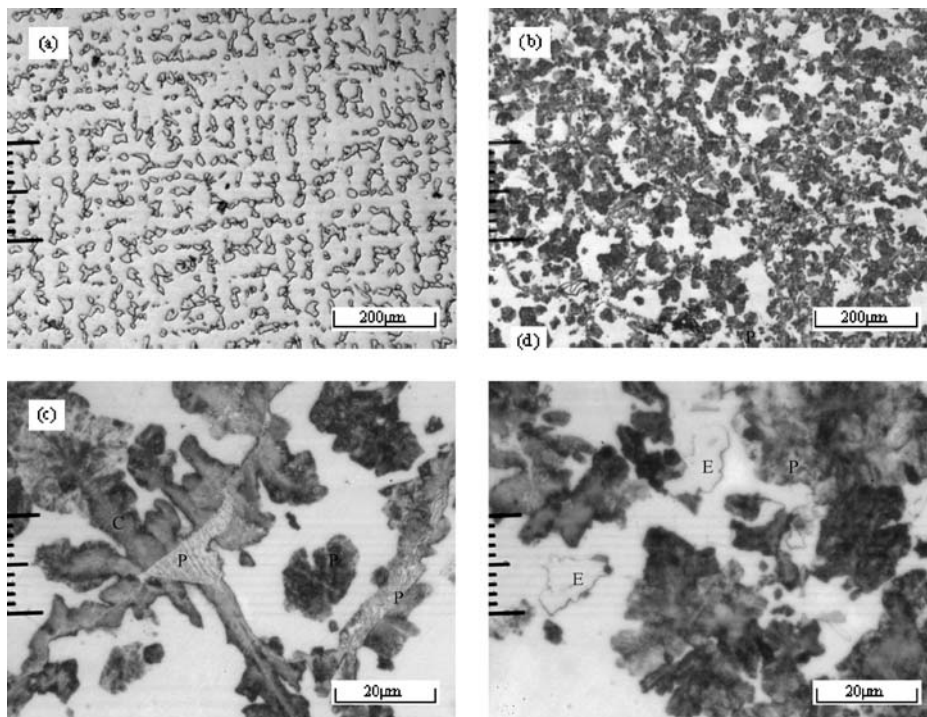*Figure 1* Schematic diagram of steel mold.

Figure 2 Effect of Ca-Si modifier on the eutectic decomposition: (a) as-cast microstructure of the steel no. 1 solidified in the mold preheated at 600 °C, (b)–(d) as-cast microstructure of the steel no. 2 solidified in the mold preheated at 600 °C. Eutectic is represented by E (Fe,Mn)$_3$C$_{II}$ cementite by C, and pearlite by P.

where ($\%i$) is the chemical composition of i, $\mu_{0i}(T)$ is the chemical potential of the pure element i at the temperature T.

According to the Wangner's equation [9],

$$\lg f_i = e_i^i(\%i) + e_i^j(\%j) + e_i^{j'}(\%j') + \cdots \quad (4)$$

where e_i^i, e_i^j, $e_i^{j'}$ are the interaction coefficients of activity:

$$e_j^i = \frac{M_j}{M_i}e_i^j + \frac{1}{230}\left(1 - \frac{M_j}{M_i}\right) \quad (5)$$

where M_i, M_j are atomic weights of i and j, respectively.
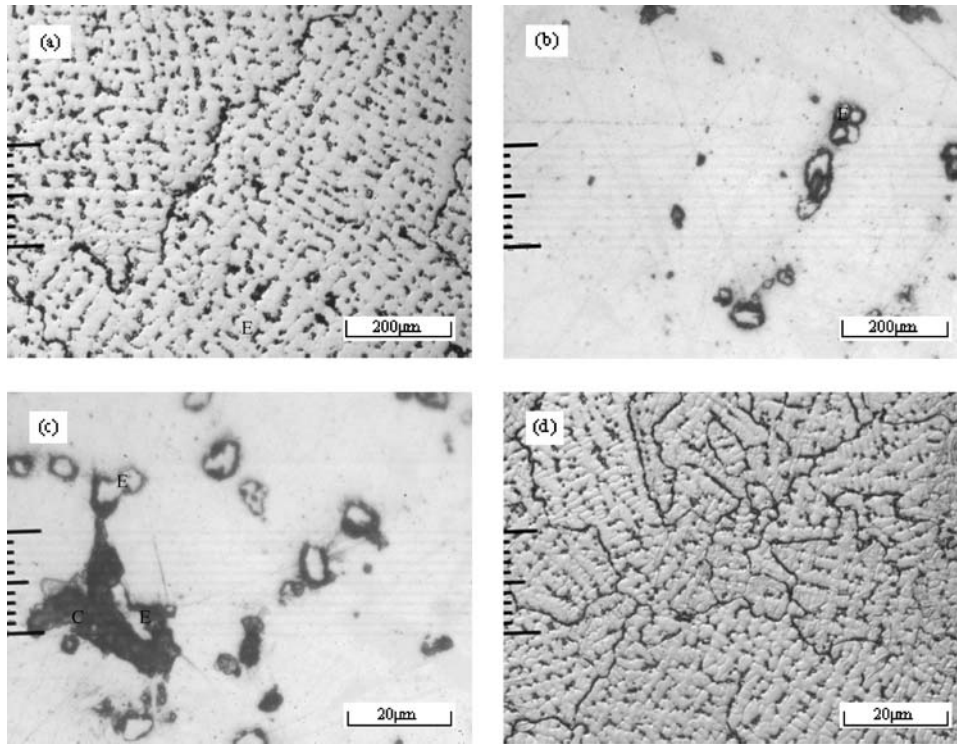
Figure 3 Effect of cooling rate on the eutectic decomposition: (a)–(c) as-cast microstructure of the steel no. 2 solidified in the mold preheated at 200 °C, (d) as-cast microstructure of the steel no. 2 solidified in the un-preheated mold. Eutectic is represented by E, and $(Fe,Mn)_3C_{II}$ cementite by C.

Combining $e_{Si}^c = 0.288$, $e_{Si}^{Mn} = 0.281$ [10] into Equation 5, e_c^{Si} and e_{Mn}^{Si} can be gained as 0.126 and 0.548. Clearly, μ_c and μ_{Mn} increase with increasing Si content in accordance with Equations 3 and 4. It indicates that C and Mn precipitation during cooling after solidification is enhanced because of the additional Si. Therefore, Si acts as an effective catalyst to accelerate $(Fe,Mn)_3C_{II}$ and pearlite formation (see Equations 1 and 2).

The Si content in eutectic is higher than that in austenite matrix [5]. Otherwise, the partition coefficient of Si in the $\gamma/(Fe,Mn)_3C$ phases is 0.97/0.03 [11]. These indicate that the highest Si-contained phase is the γ in eutectic, followed by the austenite matrix and $(Fe,Mn)_3C$ in eutectic. Therefore, $(Fe,Mn)_3C_{II}$ formation and eutectoid transformation (see Equations 1 and 2) occurs easily for the γ phase in the eutectic compared with the austenite matrix. As a result, the eutectic decomposes into $(Fe,Mn)_3C + (Fe,Mn)_3C_{II}$ + pearlite on cooling after solidification (see Fig. 2b-d). This also confirms that most of $(Fe,Mn)_3C_{II}$ and pearlite in the austenite grain probably nucleate in the γ phase of eutectic and grow by C and Mn migration, along with the eutectic decomposition.

Fig. 3a–c show the microstructures of the steel no. 2 solidified in the mold preheated at 200 °C. As shown in Fig. 3b, an eutectic is decomposed into four parts, along with the $(Fe,Mn)_3C_{II}$ growth from the middle of it. Fig. 3c shows another representative decomposed eutectic. Clearly, the eutectic would disappear at once, and a block of $(Fe,Mn)_3C_{II}$ appears nearby it. These demonstrate that some eutectics' decomposition into $(Fe,Mn)_3C_{II}$ does occur. However, pearlite phase is not observed throughout the microstructure, indicating that eutectoid transformation (see Equation 2) probably

does not proceed. Fig. 3d presents the microstructure of the steel no. 2 solidified in the un-preheated mold. Clearly lots of eutectics are well distributed among primary austenite dendrites. The microstructure is similar to that of the steel no. 1 solidified in the mold preheated at 600 °C (see Fig. 2a), but with inter-boundary $(Fe,Mn)_3C_{II}$ carbides. These carbides are formed on the subsequent cooling to the eutectoid temperature, along with the C and Mn precipitating from the austenite matrix and some eutectics nearby the boundary [6]. VIDAS analyses show that the ratio of eutectic decomposition is much lower than that in the steels solidified in the molds preheated at 200 °C (see Fig. 3a–c) and at 600 °C (see Fig. 2b–d). This demonstrates that cooling rate exerts a great influence on the eutectic decomposition. As mentioned above, eutectic decomposition depends on C and Mn precipitation from γ phase in the eutectic. Clearly the diffusion-controlled precipitation of C and Mn is impeded at a high cooling rate. Consequently, eutectic decomposition is difficult.

From these results, it becomes clear that eutectic decomposition may occur in the Ca-Si modified austenite medium Mn steel during cooling after solidification. The decomposition ratio is related to the modifier amounts and the cooling rate.

References
1. HE ZHENMING, JIANG QICHAN and XIE JINGPEI, *Wear* **120** (1987) 305.

2. J. QICHUAN, H. ZHENMING and C. DONGHUAN, *J. Mater. Sci. Lett.* **9** (1990) 616.

3. Z. M. XU, T. X. LI and J. G. LI, *Acta Metall. Sin.* (*ENGLISH LETTERS*) **14**(2) (2001) 79.

4. GAOFEI LIANG, ZHENMING XU, JIANGUO LI *et al.*, *Acta Metall. Sin.* **39**(5) (2003) 550 (in Chinese).

5. GAOFEI LIANG, ZHENMING XU, JIANGUO LI *et al.*, *J. Mater. Sci. Lett.* **22** (2003) 549.

6. GAOFEI LIANG, ZHENMING XU and JIANGUO LI, *J. Mater. Sci.* **39** (2004) 2569.

7. L. S. LI, "Cast Steel and Melting (in Chinese)" (Mechanical Technology Press, Beijing, China, 1981) p. 55.

8. H. Q. HU, "Solidification of Metal (in Chinese)" (Metallurgical Industry Press, Beijing, China, 1984) p. 54.

9. Q. C. JIANG, J. L. YAN, Q. F. GUAN *et al.*, *Acta Metall. Sin.* (*ENGLISH EDITION*) **6B**(2) (1993) 156.

10. C. BODSWORTH and H. B. BELL, "Physical Chemistry of Iron and Steel Manufacture," 2nd ed. (Longmans, London, 1972) p. 485.

11. L. S. LI, "Cast Alloy and Melting (in Chinese)" (Mechanical Technology Press, Beijing, China, 1989) p. 23.