Research Article

Influence of Manganese Content on the Dissolution of the Fe₃C Iron Carbide Phase (Cementite) during a Graphitization Anneal of Spheroidal Graphite Cast Iron

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The transformation of iron carbide cementite was investigated on spheroidal graphite containing different contents of manganese. The isothermal maintain were carried out at 600, 650, 700, and 750°C for periods of up to one hour. It was observed that the kinetics of graphitization is slowed even more than cast iron rich in manganese.

1. Introduction

Graphitization heat treatment aims mainly at softening the structure by transforming the ferrite matrix. The corresponding treatment in the case of cast iron is usually time consuming and costly. This explains the number of studies devoted to the influence of the addition of alloying elements on the processes involved in the graphitization [1].

Copper, nickel, and silicon are commonly considered part graphitization. The effect of the molybdenum and/or manganese differs because of their power stabilizing against the carbides [2–4]. Thus, these elements cause a slowing of the kinetics of graphitization. The influence of manganese after the graphitization process of spheroidal graphite cast iron will be specifically studied.

2. Materials

In Table 1 are collected the composition of the studied spheroidal graphite cast iron and hardness in the state of reception. Values of carbon content—measured using a LECO CS 244 type dosing—show that it is a hypoeutectic cast iron ($1.7 < C < 4.3$).

In their “as received state” the samples under study have a ferrite-perlitic structure. Thus, the perlitic cementite leads to

the formation of graphite, according to the following decomposition reaction (R):

This graphitization—similar to the bainitic or martensitic structure—is called secondary (as opposed to primary graphitization developed, either in the liquid metal or in the austenite supersaturated in carbon).

The results obtained confirm the retarding effect exerted by manganese on the kinetics of graphitization of spheroidal graphite cast iron? In fact, we have the following.

- (i) As shown in Figures 1(a) and 1(b), the magnitude of the dilatometric expansion corresponding to the reaction (R) decreases as the manganese content increases from 0.9 to 2.15 wt%.
- (ii) The dilatometric curves recorded during isothermal heat treatment applied to the cast iron containing 2.15 wt% (Figure 1(a)) show the importance of the temperature parameter (θ_g) on the process of graphitization. Indeed, we note that cementite graphitized even faster than θ_g is close to A_{c1} . In addition, early maintenance develops a contraction whose amplitude and duration increase when θ_g decreases: this contraction is related to the coalescence of pearlite,

FIGURE 1: Dilatometric behavior while maintaining materials at different temperatures θ_g : (a) material with 2.15% Mn; (b) material with 0.7% Mn.

FIGURE 2: Micrographic controls after holding for one hour at different temperatures of the cast iron with 2.15% Mn.

in which the cementite lamellae tend to fragment then gather in small globules.

After treatment for one hour at different temperatures θ_g , the microscopic examination shows (Figure 2) that the amount of ferrite formed is more consistent when temperature θ_g was high. Furthermore, pearlite preferentially occupies the remaining internodes areas, which are substantially richer in manganese. Note that, before decomposing, pearlite tends to take a globular form at the interfaces ferrite/pearlite. The same dilatometric test—and micrographic examinations carried out on the cast iron with 0.9 wt% Mn of content—clearly shows that lower manganese content allows the graphitization to progress more rapidly. In particular, the dilatometric curves of Figure 1(b) confirm that with temperature θ_g and holding time given, the amplitudes of expansions observed are higher in the case of 0.9% Mn cast iron.

TABLE 1: Composition in weight percent of the spheroidal graphite cast iron studied.

C	Si	Mn	Mg	S	P	Cu	HV _{300N}
3.34	2.57	2.15	0.04	0.008	0.02	0.04	290
3.12	2.00	0.90	0.04	0.013	0.020	0.02	220

Similarly, the micrographic controls carried out after one hour of isothermal heat treatment (Figure 3) shows that if the manganese content is 0.9 wt%, it forms more ferrite, while the amount of pearlite, not yet graphitized, is less important.

The comparison of hardness measurements carried out at the end of such isothermal treatment (Figure 4) for both levels of manganese considered shows that it produces a continuous decrease of this characteristic when the temperature θ_g increases. Note that the curve on the ductile cast iron containing 0.9% Mn is from 40 to 50 Vickers points below

FIGURE 3: Micrographic controls after holding for one hour at different temperatures of the cast iron with 0.9% Mn.

FIGURE 4: Variation of hardness after one hour of graphitization with temperature θ_g .

the one containing 2.15% Mn. What is more, the curve reflecting the evolution of the hardness of the cast iron with 2.15% Mn shows an increase from $\theta_g = 700^\circ\text{C}$. This results in the formation of some amount of austenite, which changes into martensite during the final cooling; hence the hardening at the end found after return to the ambient temperature. This transformation is confirmed by the fact there is a martensite starting point M_s in dilatometry (Figure 1(a) inset).

3. Discussion and Conclusion

With the increases of the content of manganese in cementite, it becomes more stable: therefore its decomposition kinetics (in iron and graphite) is slowed down. When the proportion of iron atoms substituted by manganese atoms increases,

FIGURE 5: Relationship between the Gibbs energy of formation and manganese content of cementite complex.

the Gibbs energy of formation of complex cementite decreases steadily (Figure 5).

Indeed, manganese is likely to fit into the primary carbide. This is because the physical characteristics of manganese are very similar to those of iron (Table 2).

Furthermore, the lattice carbide Mn_3C is isomorphic to that of the carbide Fe_3C and their lattice parameters are very similar (Table 3).

TABLE 2

	Atomic number	Density (g/cm ³)	Electronic structure
Mn	25	7.43	(A) 3d ⁵ 4s ²
Fe	26	7.85	(A) 3d ⁵ 4s ²

TABLE 3

	Symmetry	Parametres (Å)
Mn ₃ C	Orthorhombic	$a = 4.530; b = 5.080; c = 6.772$
Fe ₃ C	Orthorhombic	$a = 4.523; b = 5.088; c = 6.743$

In conclusion, all the results confirm that the kinetics of graphitization of the cementite is further slowed when the melt is rich in manganese, while, also, recent studies show that the structure of the matrix can play a role in this development [5].

References

- [1] K. He, A. Brown, R. Brydson, and D. V. Edmonds, "Analytical electron microscope study of the dissolution of the Fe₃C iron carbide phase (cementite) during a graphitisation anneal of carbon steel," *Journal of Materials Science*, vol. 41, no. 16, pp. 5235–5241, 2006.
- [2] S. Drapal, "Contribution à la théorie de décomposition de la cémentite dans les malléables," *Mémoires Scientifiques de la Revue de Metallurgie*, vol. 59, no. 4, p. 263, 1962.
- [3] J. Y. Park, K. Taek Choi, J. A. Szpunar, K. Hwan Oh, and H. Yong Ra, "Effect of Mn negative segregation through the thickness direction on graphitization characteristics of strip-cast white cast iron," *Scripta Materialia*, vol. 46, no. 3, pp. 199–203, 2002.
- [4] K. He, A. Brown, R. Brydson, and D. V. Edmonds, "An EFTEM study of the dissolution of cementite during the graphitisation annealing of a quenched medium carbon steel," *Journal of Physics*, vol. 26, no. 1, pp. 111–114, 2006.
- [5] S. A. Rounaghi and A. R. Kiani-Rashid, "A study on graphitisation during annealing of martensitic hypereutectoid steel," *Phase Transition*, vol. 84, no. 11-12, pp. 981–991, 2011.