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Thermal Analysis of Fe-Carbide and Fe-C Mixtures

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Abstract

Differential thermal analysis (DTA) was employed to monitor changes which occurred during heating of Fe-carbide and Fe-C mixtures. The DTA curves showed a relationship between endothermic peaks and phase transformations given in the Fe-C phase diagram. The transformations included (i) magnetic Fe to non-magnetic Fe, (ii) pure α-Fe to pure γ-Fe, (iii) $\gamma + Fe_3C \rightarrow$ Liquid and (iv) pure γ-Fe to pure δ-Fe. Melting of the Fe-SiC powder compacts when sintered at temperatures higher than 1200°C was revealed and indicated by the endothermic peak of 1230°C. This peak corresponded to the transformation of $\gamma + Fe_3C \rightarrow$ Liquid. That meant that decomposition of SiC particles had occurred, and Si and C atoms subsequently diffused into iron particles. DTA curves of the Fe-TiC, Fe-WC and Fe-VC mixtures did not show peaks corresponding to melting. This indicated that TiC, WC and VC were stable when they were brought into contact with iron at elevated temperatures.

Key words: Differential thermal analysis, Iron, Carbides

Introduction

The powder metallurgical route, consisting of compaction and sintering steps, is a promising process for producing particulate-reinforced composites. Incorporation of carbide particles (SiC and TiC) into stainless steel 316L matrix has been previously investigated.[1] The sintered 316L-carbide materials showed improved yield strength and hardness. An addition of SiC also improved ductility of the sintered materials. In contrast, TiC addition reduced the materials' strain at break. It has been noticed that the 316L-SiC compacts could not be sintered at temperatures higher than 1200°C, due to melting of the powder compacts. A similar result was also reported in the 316L-SiC materials which were sintered at 1150°C for 60 minutes, resulting in molten metal oozing out of the compact.[2] The current interest in iron-based composites centers on developing wear resistant materials by addition of reinforcing hard ceramic particles since iron undergoes various transformations that can give a range of structures according to the desired strength properties. When the reinforcing agent is SiC, a structure modification of pure iron will occur if the conditions of the experiments lead to decomposition of the particulate (or fiber) and the dissolution of C and Si in the matrix. Fe-SiC metal matrix composites, produced by HIP, have shown increased ultimate tensile strength and yield strength.[3]

Explanations of material strengthening by carbide reinforcements in the sintered 316L-carbide materials were not easy to provide due to the nature of high alloyed 316L powders and the characteristics of sintered materials. To reduce the factor of high alloying, pure Fe powders which were embedded by either foreign particles or non-reactive Al_2O_3 and reactive SiC were selected for making a matrix.[4] The pure iron matrix composites were prepared via conventional powder metallurgy. This work aimed at investigating some basic behaviors of the sintered Fe-Al_2O_3 and Fe-SiC materials. The presence of non-reactive (Al_2O_3) and reactive (SiC) hard particles affected properties of sintered Fe-base composites. With constant compacting and sintering conditions, the addition of Al_2O_3 particles caused a reduction of sintered densities. Tensile strengths, elongation and hardness of the sintered Fe-Al_2O_3 materials decreased with increasing Al_2O_3 particle amounts. The presence of Al_2O_3 particles might prohibit sintering processes between the Fe powder particles. In contrast, addition of SiC particles resulted in a reaction between Fe and SiC particles. Sintered

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density of the sintered Fe-SiC composites was significantly lower than that of the sintered Fe-Al_2O_3 materials. However, tensile strengths and hardness, except elongation, of the sintered Fe-SiC composites were significantly improved.

Sintering behaviors of the compacts, made from pure Fe and carbide powders (SiC, TiC, VC and WC), have recently been investigated and reported.[5-8] It was found that the compacts containing carbides excluding SiC could be sintered at temperatures beyond 1200°C.[5, 8] Different carbide types showed different stabilities when they were mixed with Fe powders. Traditionally, thermal analysis, combined with microstructural examination and other experimental methods, provides transformation information of the material being heated and/or cooled. In order to understand interactions between Fe and carbide or particles during heating, differential thermal analyses (DTA) of mixtures between pure Fe powders and carbides have been carried out. Different graphite contents were also mixed with Fe powders and examined by DTA. Experimental results have been interpreted with the support of evidence including microstructures and chemical analysis results of the sintered materials given in the literatures.[5, 8]

Materials and Experimental Procedures

Pure iron powders were mixed with either 10 wt% carbides (SiC, TiC, VC and WC) or with varied contents of graphite (0.80, 2.06 and 3.20 wt%) for 1 hour using a twin cone mixing machine. Suppliers of iron and carbide powder are listed in Table 1.

Table 1. Suppliers of iron and carbide powder

Powder	Supplier
Fe	Hoganas, Belgium
SiC	Sigma-Aldrich
TiC	Sigma-Aldrich
VC	Changsha Asian Light Economic Trade Co.,Ltd
WC	Buffalo WC

The mixtures were examined using differential thermal analysis technique with a heating rate of 10°C/min under N_2 atmosphere in a temperature range between 30-1400°C. The obtained DTA curves were interpreted by matching the endothermic peaks with the transformation temperatures in the Fe-C phase diagrams.[9] Microstructures and chemical analysis results of the sintered Fe-SiC materials were used as evidences of SiC particle decomposition. [5, 8]

Results and Discussion

DTA of Fe-C Mixtures

The Fe-C mixtures were prepared with different compositions, corresponding to eutectoid Fe-0.80 wt. % C, highest solid solution of Fe-2.06 wt. %C, and eutectic Fe-3.20 wt. %C. These three Fe-C mixtures showed similar DTA curves (Figure 1) with endothermic peaks at 771, 930 and 1160°C (Table 2).

DTA of Fe-Carbide Mixtures

The Fe-carbide mixtures were prepared with a constant composition (10 wt. %). The Fe-TiC, Fe-VC and Fe-WC mixtures showed DTA curves (Figure 2) with two endothermic peaks at about 770 and 920°C (Table 2). The Fe-SiC showed an additional strong endothermic peak at 1227°C.

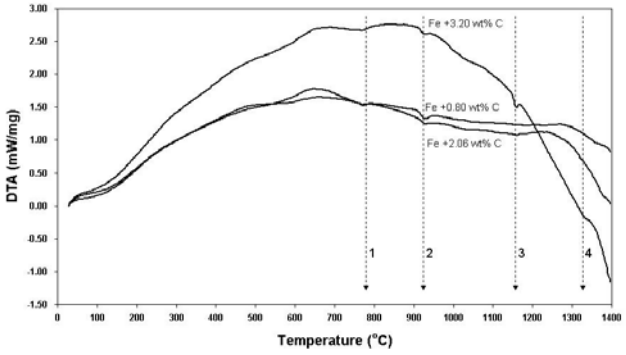

Figure 1. DTA curves of Fe-C mixtures

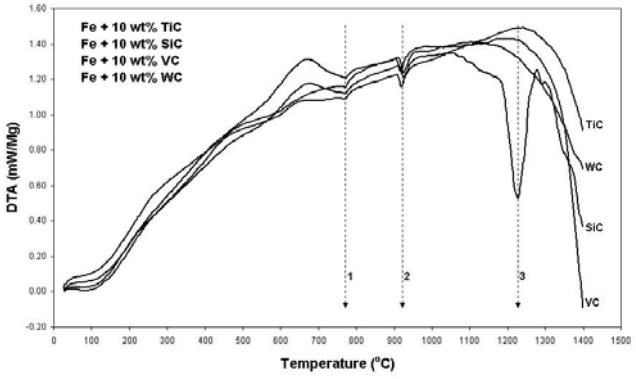

Figure 2. DTA curves of Fe-carbide mixtures

Table 2. Endothermic temperatures of Fe-C and Fe-carbide mixtures

Materials	Endothermic Temperature (°C)			
	1st peak	2nd peak	3rd peak	4th peak
Fe-0.80 C	771	930	-	1390
Fe-2.06 C	771	930	1160	-
Fe-3.20 C	771	930	1160	-
Fe-10 SiC	769	926	1227	-
Fe-10 TiC	768	920	-	-
Fe-10 VC	770	919	-	-
Fe-10 WC	769	926	-	-

Interpretation of Fe-C DTA Curves

In the starting mixtures, Fe and graphite (C) particles were in contact with one another. During heating, carbon atoms would diffuse into Fe particles to form a solid solution of Fe-C. In case of complete diffusion, the three Fe-C mixtures would turn to Fe-0.80 C and Fe-2.06 C steels and Fe-3.20 C iron after heating to 1400°C. In reality, the Fe-C mixtures were slowly heated from 300 to 1400°C because complete carbon diffusion during the thermal analysis run was impossible. Thus, transformations occurred during DTA run were resulted from changes of very low carbon iron. Matching Fe-C DTA endothermic peaks (Figure 1) with Fe-C phase diagram (Figure 3) indicated that 3 transformations were possible. They included (i) magnetic Fe to non-magnetic Fe, marked "1" in Figure 3, (ii) pure α-Fe to pure γ-Fe, marked "2" in Figure 3, and (3) pure γ-Fe to pure δ-Fe, marked "4" in Figure 3.

Interpretation of Fe-carbide DTA Curves

In the starting mixtures, Fe and carbide particles were in contact with one another. The stability of carbide particles would affect transformations of pure iron powder particles. In case of carbide decomposition, its constituent atoms would diffuse into Fe powder particles to form a solid solution. In case of stable carbides, transformations occurred during DTA run would be resulted from changes of pure iron powder particles only. DTA endothermic peaks of Fe-TiC, Fe-VC and Fe-WC (Figure 2) were similar to the case of Fe-C mixtures. Only 2 transformations, namely (i) magnetic Fe to non-magnetic Fe, marked "1" in Figure 3, and (ii) pure α-Fe to pure γ-Fe, marked "2" in Figure 3, were observed. For the Fe-SiC mixture, the strong endothermic peak at 1227°C (Figure 2) coincided with the transformation of $\gamma + Fe_3C \rightarrow$ Liquid, marked "3" in Figure 3. That meant during heating, SiC particles decomposed into silicon and carbon atoms which diffused into Fe powders particles. The localized concentration of carbon in Fe particles would reach eutectic composition. That composition caused Fe-C material to melt at temperatures above 1200°C.

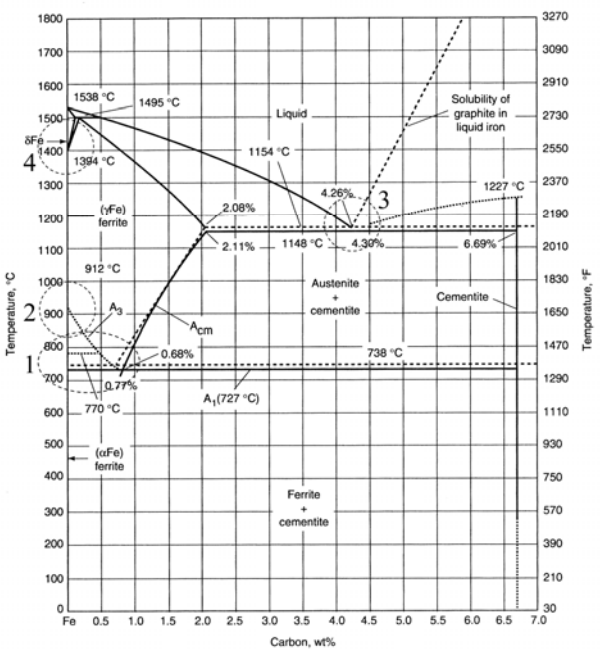

Figure 3. Fe-C phase diagram[9]

Evidence Supporting the Above Interpretations

Sintering of stainless steel 316L-SiC powder compacts at temperatures above 1200°C resulted in molten metal oozing out of the compact.[1, 2] The sintered SiC reinforced Fe-base composites showed evidence of reaction between Fe and SiC particles.[4, 5, 8] In the sintered Fe-SiC materials that were not melted, three different microstructural features were observed (Figure 4(b) and (c)). The light zones represent ferritic iron. The light grey zones represent lamellar structure of pearlite phase. The dark zones represent voids surrounding the remaining SiC particles, or the voids may have been caused by decomposed SiC particles. It was observed that the sizes of the pearlite zone, and the void, increased with increasing sintering temperatures. This indicates that decomposition of SiC particles was thermally activated. After decomposition, Si and C atoms would diffuse into Fe powder particles to form a solid solution. During cooling in the sintering furnace, the solid

solution of austenite Fe-C transformed into pearlite structure (alternate ferrite and cementite layers). Decomposition of SiC particles resulted in a growth of the voids surrounding the SiC particles and also resulted in a decrease of the SiC particle size.

For sintering of the Fe-SiC compacts at temperatures higher than 1200°C, some SiC particles decomposed into Si and C atoms that could diffuse into the Fe particles as shown by elemental mapping images (Figure 5). The strong endothermic peak at 1227°C, marked "3" in Figure 2, indicates a fast diffusion of Si and C into Fe powder particles. It was reported that the diffusion coefficient of Si increased appreciably when diffused simultaneously with C in the same direction, while it decreased markedly in the opposite direction.[10] In our work, diffusion of Si and C was in the same direction (from the decomposed SiC particles to the adjacent Fe powder particles). Therefore distribution of Si and C in the Fe matrix (Figure 5) is not uncommon. Formation of low melting point eutectic (Fe, Si)-C is probably attributable to fast diffusion of Si and C atoms into Fe powder particles.

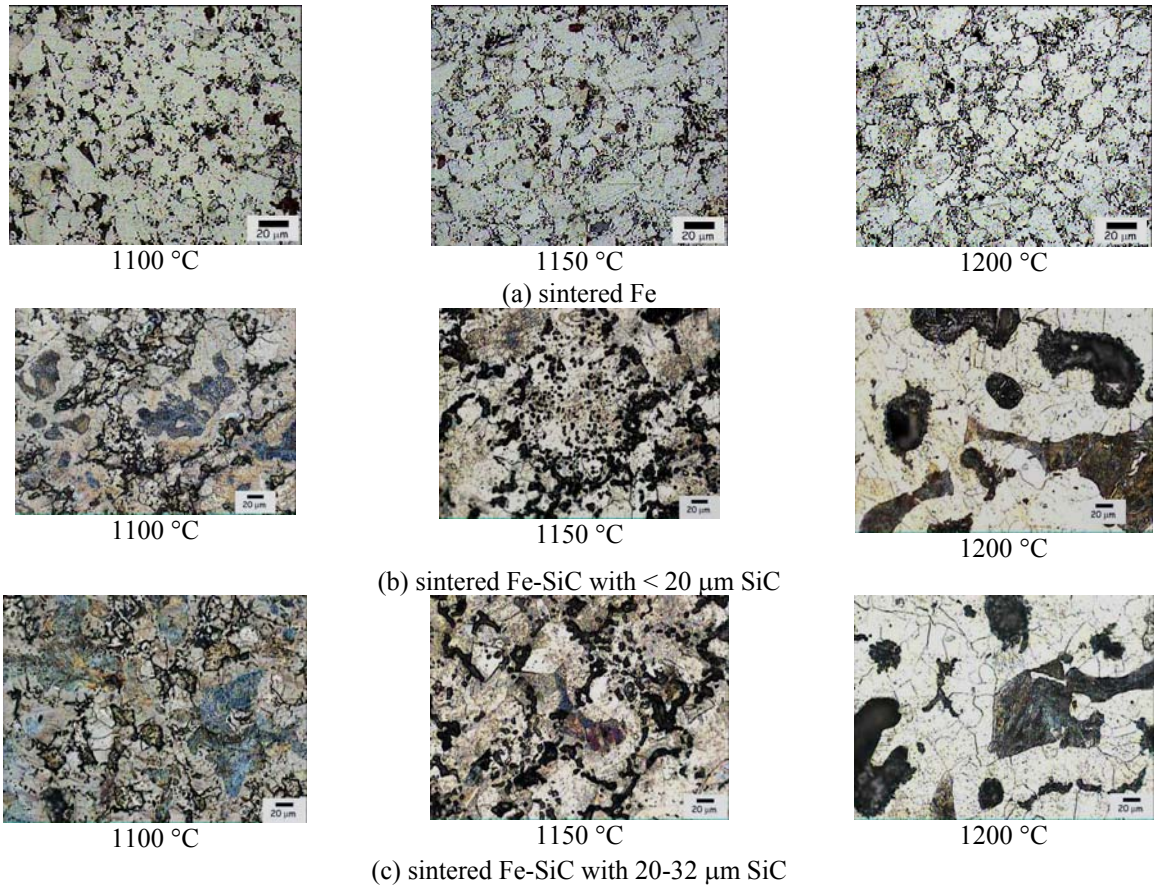

Figure 4. Microstructures of the sintered materials[5, 8]

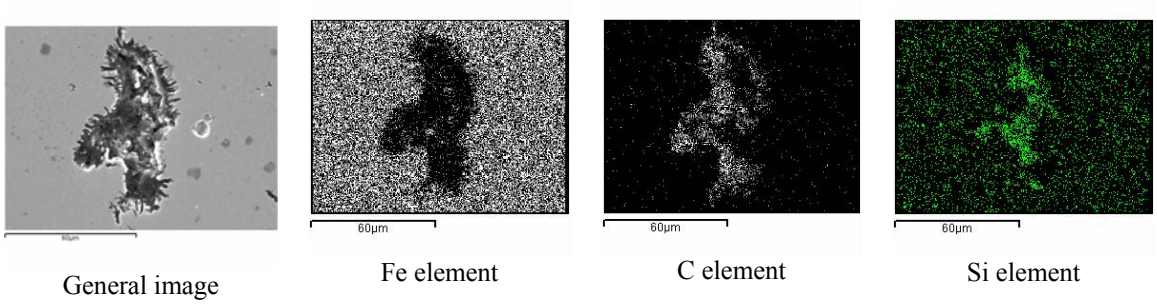

Figure 5. Mapping image of the sintered Fe-SiC material (with <20 μm SiC) sintered at 1200 ºC[5, 8]

Conclusions

During heating of the Fe-C mixture, the changes observed included (i) magnetic Fe to non-magnetic Fe, (ii) pure α-Fe to pure γ-Fe, and (3) pure γ-Fe to pure δ-Fe. Thermal analyses of Fe-TiC, Fe-VC and Fe-WC mixtures showed the same changes as for the Fe-C mixture. DTA curves of the Fe-TiC, Fe-WC and Fe-VC mixtures did not show peaks corresponding to melting. This indicates that TiC, WC and VC were stable when they were contacted with iron at elevated temperatures. For the Fe-SiC mixture, melting of eutectic Fe-C was indicated by the strong endothermic peak at 1227°C. The eutectic composition could be formed because of SiC particle decomposition and elemental diffusion into Fe powder particles.

Acknowledgements

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