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Microstructure evolution in hypereutectoid graphitic steel

In spite of the excellent machinability and wear resistance of graphitic steels, they exhibit low hardness and mechanical properties due to the presence of a ferritic matrix, soft graphite phase and need for prolonged annealing time. So the matrix evolution of graphitic steel from ferritic to pearlitic, bainitic, martensitic and tempered martensite can overcome to this shortcoming. To achieve this purpose, reaustenitizing graphitic steel has been done at two temperatures (820 °C and 850 °C) and followed by different cooling rates. During this treatment, the ferritic matrix in graphitic steel was replaced by other phases such as pearlitic, bainitic etc. which also contain graphite particles. These transformed microstructures can improve the hardness and mechanical properties of graphitic steel.

Keywords: Graphitic steel; Microstructure; Ferrite; Phase transformation

1. Introduction

Hypereutectoid tool steels belong to a large group of steels which exhibit high strength, high hardness and high wear resistance relative to other steel types [1]. These kinds of steels are usually spheroidized to improve cold formability and machinability [2]. The aim of spheroidizing annealing is to produce a soft structure by changing all hard constituents such as pearlite, bainite and martensite into a structure of spheroidized carbides in a ferritic matrix [3]. However, for completion of the process, it is necessary to hold the steel for a long time, in some cases more than 100 hr, at temperatures close to A_{c1} [2]. To overcome this problem, graphitic steels are considered as an impressive substitution for conventional free cutting and spheroidized steels, due to their very good wear resistance, cold forgability and machinability [4–6].

Graphitization in steels is accomplished during the dissociation of the cementite phase to ferrite and graphite [7–12], which mainly occurs from a martensitic structure at 600–700 °C [9]. The main disadvantage of graphitization is prolonged annealing time. In common commercial steels, alloying elements such as Cr and Mn aggregate in carbide phases, decreasing the cementite free energy [13, 14] and therefore they decrease the graphitization driving force, so graphitization from steels containing these elements entails annealing for a long period of time which is not appreciated from an economical viewpoint [15–17]. Nevertheless it has been confirmed that graphitization from a prior martensitic structure can reduce the annealing time remarkably [10, 11, 18]. Some authors, [19], have succeeded in reducing the graphitization time to less than 4 hr by addition of graphite stabilizer elements such as Al and Si to the steel melt. Therefore, lower annealing temperature (below A_{c1}) and relatively short annealing time for graphitizing steels make them comparable to spheroidized steels.

The only structure reported after graphitization in carbon steels is ferritic-graphitic. This structure may be considered as an intermediate or final product. In both cases, shaping and forming processes should be carried out in this step because of excellent machinability and cold forgability of graphitized structure as mentioned above but when higher strength and properties are required the final product can be obtained by subsequent quenching and tempering [6]. In this case graphite particles dissolve in the matrix during reaustenitizing and there are no graphite particles in the final product to compromise mechanical properties [20]. In another case, there are indications from the literature on graphitized steel and evidence from other systems that graphite particles can enhance certain types of wear resistance through a self lubrication action [4, 21–23]. In spite of the positive effect of graphite on the wearing properties of steel and other materials, in the latter case the microstructure displays low level of strength and hardness due to the ferritic matrix and soft graphite particles. This matter causes a decrease in the mechanical properties of graphitized steel. Therefore, the authors of this work have tried to replace the ferritic matrix with hard constituents and protect graphite particles by precise and controlled heat treatment cycles. In order to achieve this aim, austenitization is applied at low temperatures and controlled by time. Samples are then cooled under various conditions or immersed in a molten lead bath to produce a bainitic matrix. Thus, new structures with distinct properties are produced from graphitized steel. These kinds of steels exhibit higher hardness than common graphitic steel.

2. Experimental

2.1. Materials

The steel used was a low alloyed hypereutectoid steel, with the commercial name CK100, whose chemical composition is listed in Table 1. The primary steel structure (as received) consists of ferrite with spheroidized carbides. Although the authors of this work have some experience with graphitization of high silicon as-cast steels [24, 25], increasing the silicon content higher than 0.4 wt.% makes the steel prone to brittle fracture [26, 27]. The authors therefore tried to modify the microstructure of conventional tool steel instead of focusing on a specific steel with a special composition which can cause to some application limitations.

Table 1. Chemical composition of CK100 steel in wt.% (balance Fe).

Steel	C	Si	S	P	Mn	Ni	Cr	Mo	Cu	Al
CK100	0.949	0.213	0.012	0.017	0.339	0.047	0.061	0.008	0.076	0.017

2.2. Dilatometric testing

The dilatometric test was conducted on cylindrical samples with 4 mm diameter and 18 mm length using a 2 171 Linseis instrument. For dilatometric study of the phase transformation, many specimens were produced. Dilatometric samples and other samples were prepared from steel (as received) and austenitized at 900 °C for 20 min and immediately water quenched to produce the martensitic structure. Graphitization was achieved isothermally by annealing the martensitic structure at 670 °C. A heating rate of about 100 K min^{-1} was used to reach the final temperature (670 °C). All dilatometric samples were coated with an anti-carburizing coating called "Carbostop" to avoid decarburizing.

2.3. Heat treatment

Table 2 details the heat treatment cycles applied to the specimens. The time required for graphitization in steel specimens was about 60 hr at 670 °C. To avoid decarburization of specimens during graphitization, they were covered with a Carbostop coating and then placed in containers with cast iron chips. After graphitization, austenitizing was carried out at two temperatures, 820 °C and 850 °C. Austenitizing temperature and required time for producing martensitic-graphitic, tempered martensite-graphitic and pearlitic-graphitic structures were at 820 °C for 30 min. Martensitic-graphitic specimens were water quenched immediately after austenitizing. Tempered martensitic-graphitic specimens were annealed at temperatures of 300 °C and 600 °C separately for 2 hr after quenching. After austenitizing, pearlitic-graphitic specimen was cooled in air.

Table 2. Heat treatment cycles applied to hypereutectoid steel.

Speci-men	Heat treatment cycle	Micro-structure
1	As received	F + C
2	900 °C, 20 min → W.Q. (water quenched)	M + A
3	Specimen 2 → 670 °C, 60 hr → air cooled	F + G + C
4	Specimen 3 → 820 °C, 30 min → W.Q.	M + G
5	Specimen 3 → 820 °C, 30 min → air cooled	P + G + F
6	Specimen 3 → 820 °C, 30 min → W.Q. → 300 °C, 2 hr → air cooled	F + G + C
7	Specimen 3 → 820 °C, 30 min → W.Q. → 600 °C, 2 hr → air cooled	F + G + C
8	Specimen 3 → 850 °C, 15 min → 250 °C, 1 hr → air cooled	B + G

F: Ferrite, C: Cementite, G: Graphite, A: Austenite, P: Pearlite, B: Bainite, M: Martensite

To produce a bainitic-graphitic structure, austenitizing was done at 850 °C for 15 min then the specimen was immersed in molten lead bath at a temperature of 250 °C, and after being held at this temperature for 1 hr it is cooled in air.

2.4. Metallography

In order to perform metallographic investigation of the microstructures, all samples were sectioned and light microscopic micrographs were prepared from their central regions after conventional surface grinding and polishing followed by etching in 2 % Nital.

For preparing scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) analysis, an SEM model 1450 VP made by Zeiss Germany from the Central Laboratory of Ferdowsi University of Mashhad was used.

2.5. Mechanical properties (hardness measurements)

The hardness testing was conducted on a Koopa instrument according to the Rockwell A scale. Several hardness tests were made on each specimen and the reported data are the average of the tests (Table 3).

3. Results and discussion

According to dilatometric experimental data (Fig. 1), the shortest period of time for graphitization in steel specimens from a primary martensitic matrix structure was 60 hr at 670 °C. Figure 2a and b illustrate the structure of as-received and graphitized steels respectively. As can be seen in Figs. 2b and 3a, the graphitized structure mainly consists of ferritic matrix and graphite particles at grain boundaries with a small amount of retained carbide in the microstructure. Also EDX analysis confirms the presence of graphite particles in this specimen (Fig. 3b).

Table 3. Hardness of heat treated specimens according to Rockwell A scale.

Specimen	Microstructure	Hardness (HR$_A$)
1	F + C	38.6
2	M + A	83.9
3	F + G + C	33.4
4	M + G	81
5	P + G + F	60.5
6	F + G + C	73.7
7	F + G + C	59.8
8	B + G	68

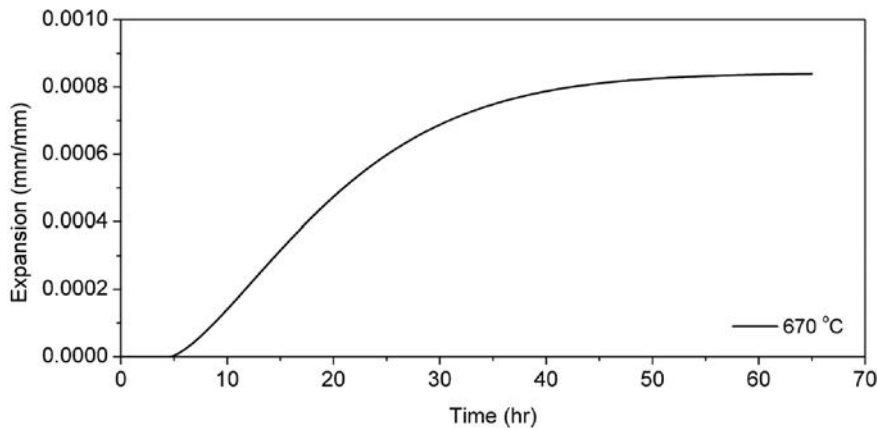F: Ferrite, C: Cementite, G: Graphite, A: Austenite, P: Pearlite, B: Bainite, M: Martensite

Fig. 1. Dilatometric diagram related to graphitization transformation from martensitic structure at 670 °C.
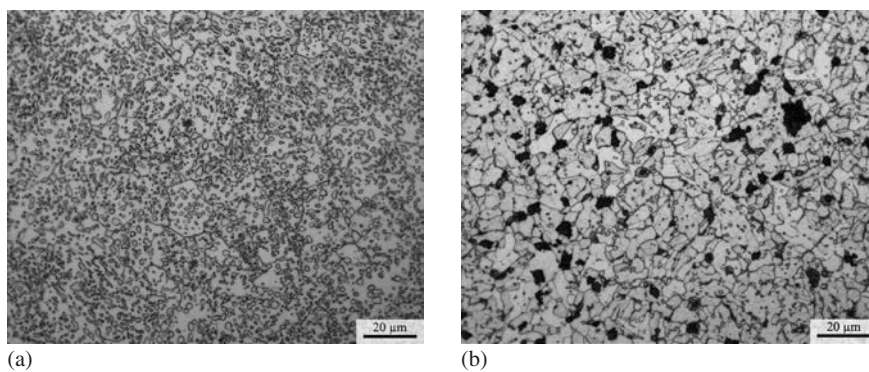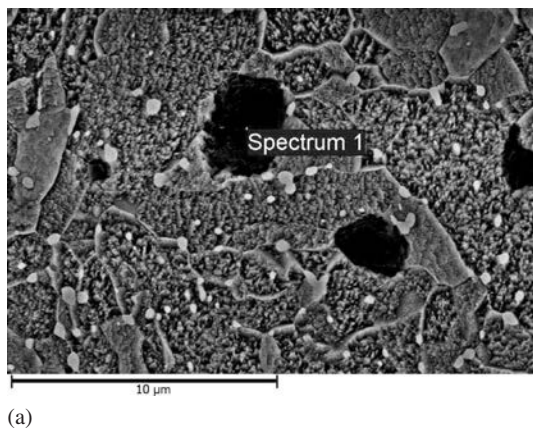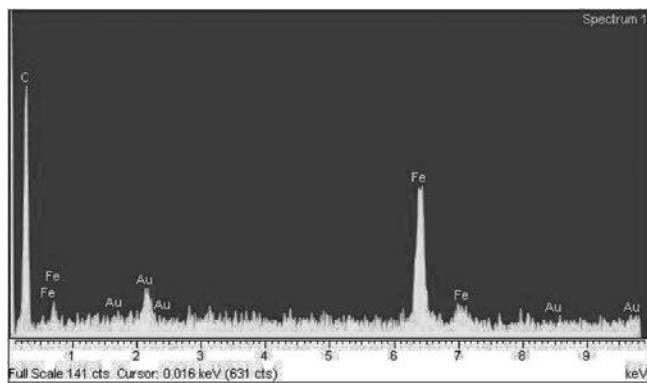

(a)

(b)

Fig. 2. (a) Primary steel structure (as received) consists of ferrite with spheroidized carbides. (b) Graphitized structure consists of graphite particles and retained carbides in ferritic matrix (specimen 3).


(a)

(b)

Fig. 3. (a) SEM image from graphitized structure (specimen 3). (b) EDX analysis of a graphite particle. Carbon peak confirms the presence of graphite.

Some graphitized specimens were reaustenitized at temperature just between A_{cm} lines in Fe–C and Fe–FeC$_3$ diagrams (i.e. at 820 °C). It must be noted by soaking the specimens at 820 °C, actually we expose the steel at higher temperature than A_{cm} line in Fe–FeC$_3$ diagram witch cause to cementite particles be more unstable and dissolve in the matrix. In contrast, this temperature is lower than A_{cm} line in Fe–C diagram and keeps graphite particles away to dissolve completely [28, 29]. Equation (1) illustrates our statement that all cementite with only partial graphite particles can react with ferritic matrix to form austenite:

$$Fe(\alpha) + C(Graphite) + Fe_3C \rightarrow Fe(\gamma) \tag{1}$$
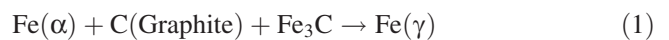
Graphite particles are larger and thermodynamically more stable than retained carbides in graphitized structure [30, 31], therefore it can be assumed that at a low austenitizing temperature (820 °C) the carbide phase is dissolved more rapidly than graphite in austenite and so some graphite particles remain in the microstructure. Therefore, if specimens are immediately quenched in water, the austenitic matrix will be transformed to martensite. If specimens are cooled in air from 820 °C, austenite will be transformed to pearlite (Fig. 4). It is necessary to explain that as carbon will diffuse into austenite due to the carbide dissolution and a modicum of carbon transfers from the graphite surface, phases with a higher percentage of carbon are produced after the cooling stages. These phases significantly affect hardness and other mechanical properties in the final structure.

Martensite is transformed to ferrite with small carbide particles by tempering the martensitic-graphitic structure at two different temperatures (300 °C and 600 °C) for 2 hr (Fig. 5).
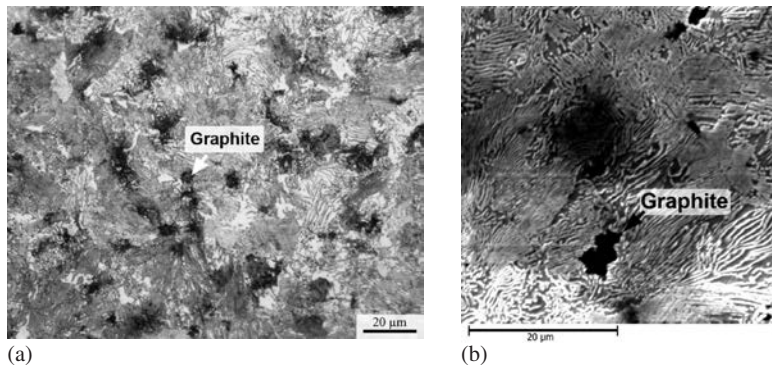
(a)

(b)

Fig. 4. (a) Pearlitic-graphitic structure, specimen 5. (b) SEM image from the same structure. Pearlite colonies are clearly considered around graphite particles.
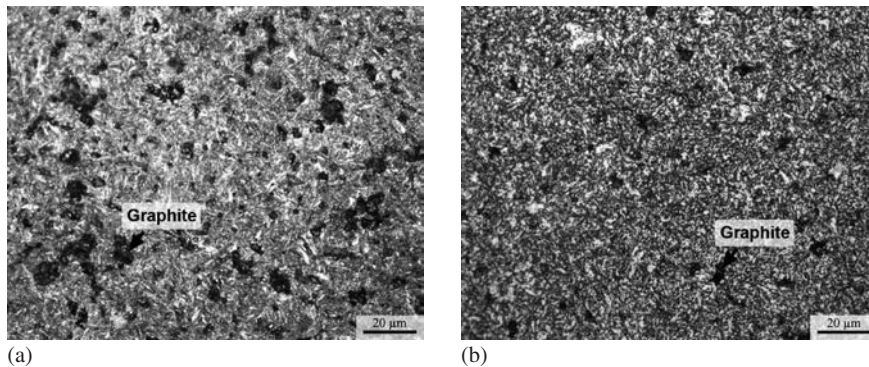

(a)

(b)

Fig. 5. Tempered martensite structures have been heated: (a) at 300 °C for 2 hr. (b) at 600 °C for 2 hr.
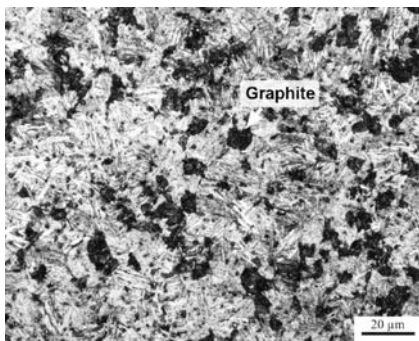

Fig. 6. Lower bainitic-graphitic structure, specimen 8.

According to the experiments, an austenitizing temperature of 820 °C is not adequate for producing bainitic structures; therefore austenitizing at 850 °C were applied to achieve appropriate conditions. By using a suitable dissolution treatment, i.e. by choosing an austenitizing temperature above the A_{cm} line for 15 min, the graphite particles become unstable so the authours attempted to control the austenitizing process by time. After austenitizing, the specimen was immersed in a molten lead bath. Figure 6 illustrates graphite particles in a needle like bainitic structure. It is evident that lower bainite is a mixture of ferrite (α-phase) and carbide particles which are found inside the α-phase. ε-carbide is the carbide phase in lower bainite that can turn into cementite when the holding time is increased [3, 32]. So by using LOM micrographs, it is difficult to establish precisely which kind of carbide formed in the microstructure.

Table 3 shows hardness variants in graphitized steel influenced by heat treatment cycles. The highest hardness is related to the martensitic structure before graphitization. The lowest hardness is related to the ferritic–graphitic structure (specimen 3) because of growing ferrite grains and annihilating lattice defects after prolonged annealing

time and also the presence of graphite as a soft phase in the microstructure. Other structures produced have hardness values between these two limits. The results show that the hardnesses of all of the graphitized specimens that were heat treated after graphitization (specimens 4–8) are higher than for the ferritic–graphitic structure (specimen 3) and even the as-received steel (specimen 1). Moreover, these structures have a wide range of hardness which can be applied as a replacement for conventional graphitic steels according to different conditions and requirements. Probably evolution in other properties such as mechanical strength and wear resistance can be expected by increasing hardness in newly produced structures with graphite particles but it still needs further experiments to confirm. Also another interesting point is that these heat treatment cycles can be carried out on each type of graphitic steel especially with higher silicon contents when a significant reduction in graphitization time is desirable.

4. Conclusions

Graphitized steel exhibits good wear properties due to the presence of a graphite phase. However, graphitized steel with a ferritic matrix phase has low hardness and strength. In this work attempts were made to replace the ferritic matrix phase with other metallic matrixes with superior mechanical properties. To avoid the dissolution of graphite particles during austenitizing heat treatment of the specimens, this process was carried out at a lower temperature being controlled over a short period of time.

The results show that all of the new structures produced from graphitized steel exhibit higher hardness than the primary graphitized steel and these structures can be applied according to different conditions and requirements.

Experiments show that by increasing isothermal heat treatment time in the bainitic formation range, the volume

fractions of these phases have been significantly changed which is explained by diffusional transformation in this range.

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