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## The effect of quenching media and annealing temperature on graphitization transformation kinetic of CK100 tool steel

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### Abstract

In this research, graphitization transformation of a commercial hypereutectoid steel called CK100 was studied by the dilatometric experiments at the range of 600 – 700 °C from prior martensitic structure. Also the effect of quenching media on the initial graphitization time and completion of transformation has been discussed. Also, graphitization transition from the different prior microstructures was studied using microscopic observations. Analyzing dilatometric data acquisitions confirmed good following results from Johnson–Mehl–Avrami equation. By calculating Avrami exponent, following of transformation kinetic from diffusion controlled nucleation and growth was resulted. Also, the minimum time for completion graphitization transformation was concluded about 45 hrs relative to the water quenched specimen after annealing at 670 °C.

**Keywords:** Graphitization, CK100, Microstructure, Martensite.

### 1. Introduction

In recent decades there have been done many different attempts by researchers to producing steels with unique properties and special applications. In order satisfy the requirements, graphitic steels (GS) were developed to improve wear resistance <sup>1)</sup>, Machine-ability <sup>1,2)</sup> and cold workability <sup>3)</sup> of steel parts due to the presence of graphite particles instead of intermetallic compounds such as cementite in a ferritic matrix. Previous studies have shown that an increase about 3-7 times in tool life more than lead free steels and exceeding two times more than leaded ones <sup>1)</sup>. However prolonged graphitization annealing time related to steel parts has limited industrial applications. In order to overcome this problem, some researchers increased graphitization tendency in the steel during the subsequent heat treatment by the addition of some alloying elements such as silicon and aluminum to the melt. In the same manner, He et al. could decrease cementite dissociation time down to 4 hrs by alloying hypereutectoid steels containing silicon and aluminum <sup>4)</sup>. Also, some investigations evidenced intermetallic compounds such as AlN and BN, while the crystallographic structure similar to graphite, can play a useful

role as graphite particles nucleation sites and accelerate graphitization process consequently <sup>4,5)</sup>.

On the other hand, it has been attempted to decrease graphitization time kinetically by a number of researchers. For instance, it has been cleared that the graphitization can be accelerated from cold worked structures <sup>6)</sup>. Also martensitic and bainitic structures have been known as most effective phases for formation graphite particles during subsequent annealing process <sup>4,7)</sup>. Although, the dominant studies on graphitic steels have been conducted on medium carbon and highly alloyed steels but it seems increasing carbon content of steel as the best alloying element to use for graphitization <sup>8)</sup> can reduce the phase transition time. So, it has been tried to accelerate graphitization time in unalloyed high carbon steels. In order to achieve this aim, it has been studied the effect of kinetic parameters such as the prior microstructure, annealing temperature and quenching media on this phase transition.

### 2. Experimental procedures

All experiments were carried out on unalloyed hypereutectoid steel known as CK100. The composition of this steel is given in Table 1. This kind of steel was chosen in order to reduce the effect of alloying elements on graphitization thermodynamics and proposing a modified heat treatment cycles in order to graphitization in conventional commercial steels. Also it has been tried to avoid the production of highly alloyed steels with special compositions and consequently limited applications.

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Spheroidizing steels is a heat treatment in which specimens are heated to 770 °C and held at this temperature for 4 hrs, cooled to 660 °C at the rate of 6 °C/h, and held for 4hrs at this temperature before air cooling stage. All other structures were prepared from spheroidized specimens. In other words, martensitic and normalized specimens were produced by austenitizing spheroidized parts at 900 °C for 20 min and subsequently cooling to ambient temperature in different three types of media: air, oil and water. In order to study graphitization transition from spheroidized and normalized structures, the samples were annealed at 670 °C for 110 hrs with the heating rate of 100 °C/min and air cooled subsequently. Linseis 2171 dilatometric machine was used to measure length changes of martensite cylindrical test samples with 4mm in diameter and 18 mm in height. Afterwards, they were heated isothermally at the range of 600 - 700 °C. Finally extracted dilatometric data was analyzed by Origin data analysis and graphing software.

Before each heat treatment cycle, the surface of all specimens were coated by an anti-carburizing layer called Carbo-stop to avoid surface oxidation and decarburization during the process. Optical microscopy investigations were performed on the cross section of all specimens after conventional grinding, polishing and etching (2% Nital) stages. In order to view the images with higher resolution it was used, the scanning electron microscope model 1450 VP made in Carl Zeiss (Jena, Germany) from the Central Laboratory of Ferdowsi University of Mashhad (Mashhad, Iran).

### 3. Results and discussion

Analyzing dilatometric graphs using the Origin software results a mathematical equation for each dilatometric specimen as be given in Table 2. The Figs. 1 and 2 were also obtained from plotting and extrapolating the derived equations using the Origin software. The details of this procedure have been published elsewhere <sup>9</sup>. As can be seen, all equations follow Johnson-Mehl-Avrami equation in general follow format which can be explained as <sup>10</sup>:

$$X = 1 - \exp(-Kt^n) \quad (1)$$

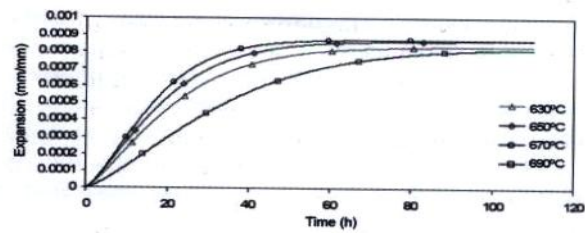


Fig. 1. Extrapolating dilatometric graphs related to water quenched specimens at the range of 600- 700 °C according to equations listed in Table 2.

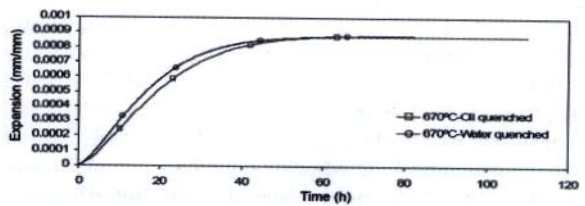


Fig. 2. Plotting graphitization graphs for water quenched and oil quenched specimens at 670 °C according to equations listed in Table 2.

Table 1. Chemical composition of CK100 steel (weight percent)

| 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 |

Table 2. Mathematical equations and graphitization time for each dilatometric specimen that were elicited by origin software

| Quenching media | Temperature | Equation                            | $t_{0.05}$ (h) | $t_{0.5}$ (h) | $t_{0.95}$ (h) |
|-----------------|-------------|-------------------------------------|----------------|---------------|----------------|
| water           | 630 °C      | $X = 1 - \exp(-(0.00071t)^{1.319})$ | 8.3            | 26.1          | 63.3           |
| water           | 650 °C      | $X = 1 - \exp(-(0.00080t)^{1.331})$ | 6.7            | 22.5          | 54.2           |
| water           | 670 °C      | $X = 1 - \exp(-(0.00090t)^{1.404})$ | 4.8            | 18.9          | 45.1           |
| water           | 690 °C      | $X = 1 - \exp(-(0.00046t)^{1.379})$ | 11.1           | 38.9          | 91.4           |
| oil             | 670 °C      | $X = 1 - \exp(-(0.00070t)^{1.459})$ | 5.1            | 21.6          | 50.8           |



Where  $X$  is the volume fraction of phase transition,  $t$  is Transformation time,  $K$  is temperature-dependent coefficient, and  $n$  is Avrami exponent. It is obvious that  $n$  values for all equations are about 1.4. According to the literature, Avrami exponent value indicates that the kinetics of nucleation and growth is controlled by diffusion which grain boundaries and dislocations can be considered as nucleation sites of graphite particles<sup>11,12</sup>. Another outcome from Figs. 1 and 2 is the effect of temperature and quenching media on graphitization time. So the devoted time for each transition volume fraction ( $t_{0.05}$ ,  $t_{0.5}$ ,  $t_{0.95}$ ) is extracted from dilatometric results and given in Table 2. As can be seen, the transformation occurs very slowly at 690 °C. This is due to decrease in graphitization driving force caused by approach annealing temperature to spheroidizing treatment zone in Fe-C phase diagram. Since the spheroidized microstructure considers as one of the most stable structures in steels, annealing the steel over this temperature range postpones cementite dissociation. It must be mentioned that such competition between decomposing and spheroidizing cementite particles has also been reported previously<sup>13</sup>. Minimum graphitization time is 45.1 hrs which is related to the water quenched specimen and annealed one at 670 °C. In other words, there is a reasonable balance between increasing diffusion coefficient and decreasing graphitization driving force due to temperature enhancement and decrement respectively. comparing water and oil quenched specimens which were annealed at 670 °C as optimized temperature, it is obvious that the graphitization has been took place more rapidly in water quenched specimen. This can be justified by higher cooling rate of water. As discussed previously, Avrami exponent obviously represents a function of dislocations as graphite nucleation sites in conducted experiments, so water quenching increases the cooling rate of the specimen and enhances crystallographic defects density such as dislocations and furthermore promotes carbon diffusion. Therefore, the higher dislocation density in water quenched specimen can promote the transformation of graphitization compared to oil quenched sample.

In Fig. 3 it has been illustrated the microstructure of martensitic, normalized and spheroidized specimens before graphitization annealing heat treatment. In Fig. 4, it has been presented the microstructure of graphitic steel after annealing treatment at 670 °C for 60 hrs from prior water quenched structure (Fig. 3 c). As can be seen, this structure consists of graphite particles in ferritic matrix and some fine carbide spheres which retain after graphitization annealing treatment. Incomplete cementite decomposition can be due to increased amounts of carbide stabilizer elements such as chromium and manganese in

steel composition which dissolve preferentially in carbide particles. During graphitization annealing treatment, cementite particles are dissociated so it is increased the concentration of these elements in remained carbides and graphitization driving force decreases which impedes eventually more phase transformation<sup>14</sup>. The concentration of carbide stabilizing elements has been confirmed by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis<sup>15</sup>.

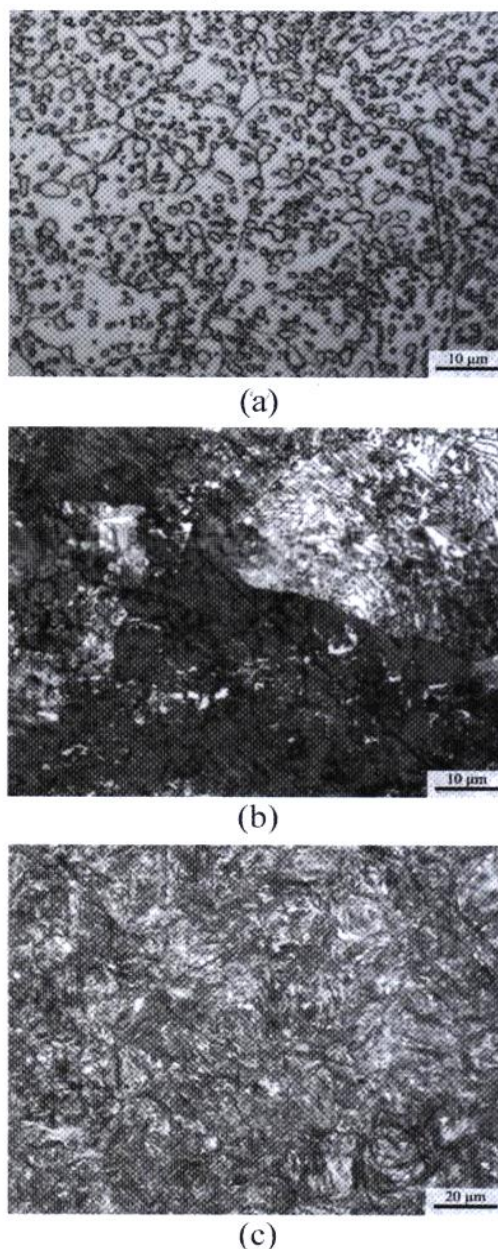


Fig. 3. Optical micrographs of Prior steel microstructures a) spheroidized, b) normalized and c) martensitic structure.



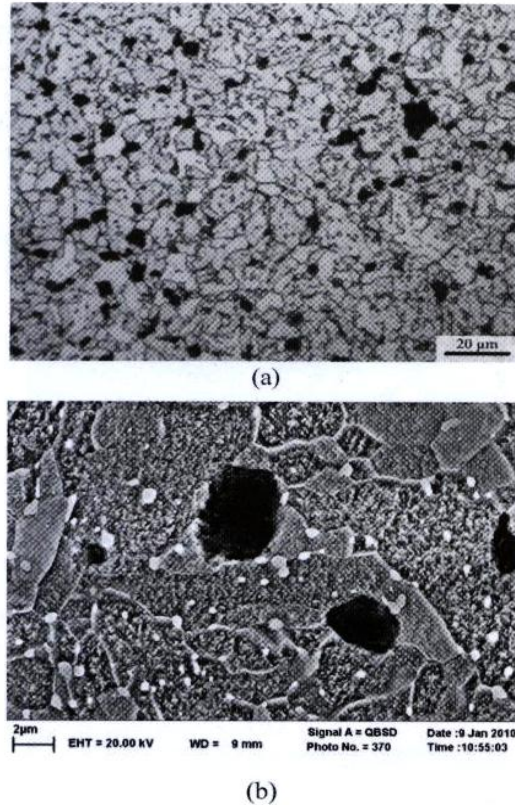


Fig. 4. (a) Graphitized steel microstructure annealed at 670 °C for 60 h from prior martensitic structure, (b) SEM micrograph from the same microstructure.

In Fig. 4, it is presented the formation of graphite particles at grain boundaries of the ferrite. This particle confirm that boundaries act preferred site as graphite. It was also concluded from Avrami exponent as discussed above. On the other hand, optical microscopy observations performed on graphitization behavior of primary normalized and spheroidized structures confirm the inexistence of graphite particles during annealing the structures at 670 °C even for 75 hrs. Just after annealing treatment for 110 hrs, a few amount of large and sporadic graphite particles can be observed in these specimens (Figs. 5 a and b). Also, using image analyzing software, graphite phase fraction after anneal of water quenched (martensitic), normalized and spheroidized specimens were measured 3.4, 0.1 and 0.1 respectively; so it can be easily concluded that higher amounts of graphite have been formed after anneal of martensitic specimens even at shorter time (60 hrs) than two other specimens. This severe difference in transformation time and graphite amounts evidences the function of martensitic structure on graphitization transition acceleration.

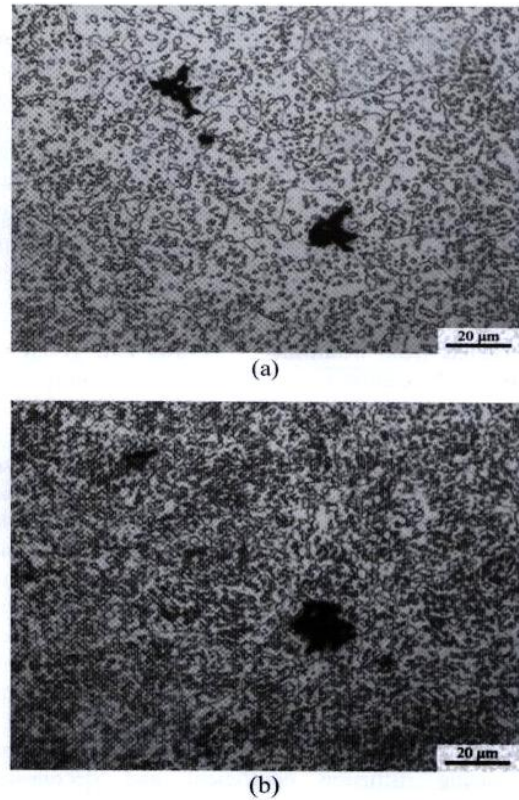


Fig. 5. Partial graphitized microstructure of prior non-martensitic structures (a) spheroidized and (b) normalized steels after annealing at 670 °C for 110 hrs.

#### 4. Conclusions

The graphitization transformation in the hypereutectoid steel was investigated using dilatometric experiments and microscopic observations. Dilatometric aids confirm the control of diffusion phase transformation kinetics and it was supposed that graphite particles nucleate on dislocations and ferrite grain boundaries. By investigating the effect of annealing temperature on graphitization transition, water quenched specimen with martensitic structure was potentially proposed as the best prior microstructure for graphitization which transformation completion takes place at 670 °C for 45.1 hrs in this specimen. This time can be considered as the shortest time even from oil quenched specimen that it occurs probably due to higher cooling rate of water compared the oil. Additionally, in similar annealing conditions, graphitization takes place very slowly from other microstructures such as normalized and spheroidized ones which is not more favorable from economic viewpoint.

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