

# Evolution of graphite phase morphology during graphitization process in hyper-eutectoid steels

*Graphite is one of the main phases in the structure of most cast irons whose shape, morphology and distribution have a significant effect on the mechanical properties of cast irons. In this respect we can mention the improvement in tensile strength and impact strength of ductile iron with spherical graphite in comparison with similar irons such as gray iron with lamellar graphite. In present research, the presence of graphite in the matrix of hypereutectoid steel is studied after performing the graphitization transformation from martensite structure using SEM (Scanning electron microscope) images and EDX (Energy Dispersive X-ray) qualitative analysis. In addition, the effect of casting process and the addition of graphitizing alloying elements on the morphology, size and distribution of graphite during the graphitization process in cast hypereutectoid steels is studied in comparison with commercial ones.*

Seyyed Amin Rounaghi, Payam Shayesteh and Ali Reza Kiani-Rashid, Mashhad, Iran

Manuscript received 6 May 2010;  
accepted 10 May 2010

S. A. Rounaghi, P. Shayesteh, A. R. Kiani-Rashid, Department of Materials Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

## 1 Introduction

Graphitization in steels is done during heat treatment from the solid structure. During this diffusion transformation, the semi-stable cementite phase is decomposed into stable graphite and ferrite phases [1-7]. Graphite is mainly formed in steels from martensitic or cooled-rolled structure at 600 to 700 °C [4-6, 8].

In nature, graphite is one of the best solid lubricants [9]. The presence of this stable carbon isotope in iron alloys – especially cast irons – results in the improvement of wear and machining properties of these materials [10, 11]. The above-mentioned properties – especially the mechanical properties of cast irons – are severely affected by morphology and the distribution type of graphite in their microstructures. In this respect, standards are defined by ASTM institute with which graphite in cast irons is classified according to its distribution and morphology [12].

A customary process for changing the morphology of graphite in cast irons is spheroidizing which causes the spheroidizing the graphite particles by adding spheroidizing elements such as magnesium and cesium to the melt of gray iron leading to the formation of ductile iron [13]. Based on relevant literature [12], mechanical properties – especially the strength and wear resistance of these cast irons – are considerably higher than gray irons.

According to the considerable effect of graphite's morphology on mechanical properties of cast irons, there is a similar expectation about graphitized steels in which the investigation of morphology and the distribution of graphite in them is less mentioned by researchers. For this reason attempts have been done to prepare steel by alloying the steel via casting using graphitizing alloying elements such as silicon.

So far, there are some reports that in this case, the graphite phase formed would be totally different from graphitized structures in common commercial steels during later heat treatment with respects to its morphology, distribution and size.

## 2 Experimental procedures

In this research, the graphite formed during heat treatment in commercial hyper-eutectoid steel (with the composition mentioned in **Table 1**) is compared to a hyper-eutectoid cast steel. In order to produce the steel by casting, 15 kg of CK45 steel was charged gradually into the induction furnace. The granular graphite was added to the melt along with Ferro-silicon (containing 75 wt % silicon) before pouring the melt. The addition of granular graphite was done in order to increase the carbon content of steel and therefore producing a hyper-eutectoid steel. In addition, Ferro-silicon was added in order to decrease the period of the graphitization transformation.

After the addition of the above-mentioned materials to the melt, pouring the melt was performed within wet sand molds. Then the solidified parts were rejected from the mold. The chemical composition of the cast steel was determined by quantometric analysis according to Table 1. Cast specimens were put inside a container full of cast iron's filings in order to prevent oxidation and decarburizing and then were held at 1100 °C for 18 hrs for homogenizing. After this period, they were cooled in air.

In order to form martensitic structure, the homogenized parts were austenitized at 900 °C for 20 min along with similar specimens prepared from CK100 commercial steel after being coated with anti-oxide/carburizing coating Carbostop. Then quenching was done immediately in water at ambient temperature.

For graphitization, specimens were put inside a container full of cast iron's filings after re-coating with Carbostop. Cast and CK100 specimens were held at 670 °C for 20 hrs and 60 hrs respectively.

In order to investigate the microstructure using metallographic technique, all of the parts were sectioned in order to prepare microscopic images from their central regions after surface preparation and etching with 2 % nital.

Some of SEM, EDX and mapping images were prepared in Razi Metallurgy Research Center, Tehran/Iran, using TESCAN machine and for preparing other images the Scanning Electron Microscope model 1450 VP made by Zeis Germany from the Central Laboratory of Ferdowsi University of Mashhad was used.

### 3 Results and discussion

Figure 1 indicates the graphitized structure of the mentioned steels. In order to confirm the presence of graphite, EDX analysis was performed from a graphite par-

ticle in the commercial and cast steels separately (Figures 2 and 3). For identifying the distribution of alloying elements, mapping and EDX line scan were carried out from a graphite nodule in the cast steel (Figures 3 and 4).

As seen, the carbon peak is identified by EDX in the place of the graphite phase (Figures 2b and 3b). The percent of other alloying elements such as chromium and manganese is low in these regions due to the presence of carbon in pure state in graphite. But according to mapping and EDX line scan images, a relative even distribution of these elements is observed in other areas. In addition, based on mapping analysis (Figure 4) and the findings of other researchers [14], the probability of the concentration of these elements in residual spherical carbides in the matrix is strengthened.

As seen in Figure 1, the graphite particles formed in the cast steel are more spherical than commercial ones. Also the size of these nodules is very bigger than the commer-

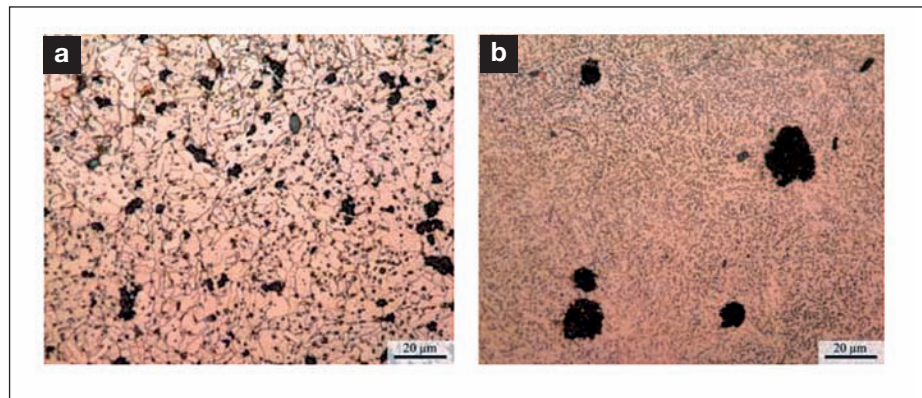


Figure 1: Microstructure of: a) commercial steel after annealing at 670 °C for 60 hrs; b) of cast steel after annealing at 670 °C for 20 hrs

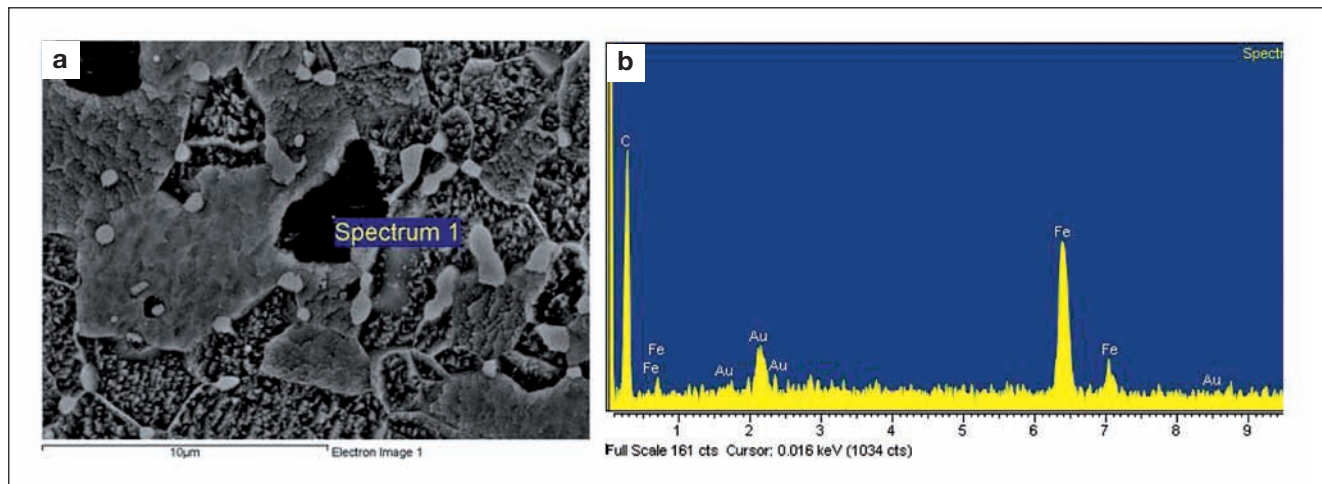
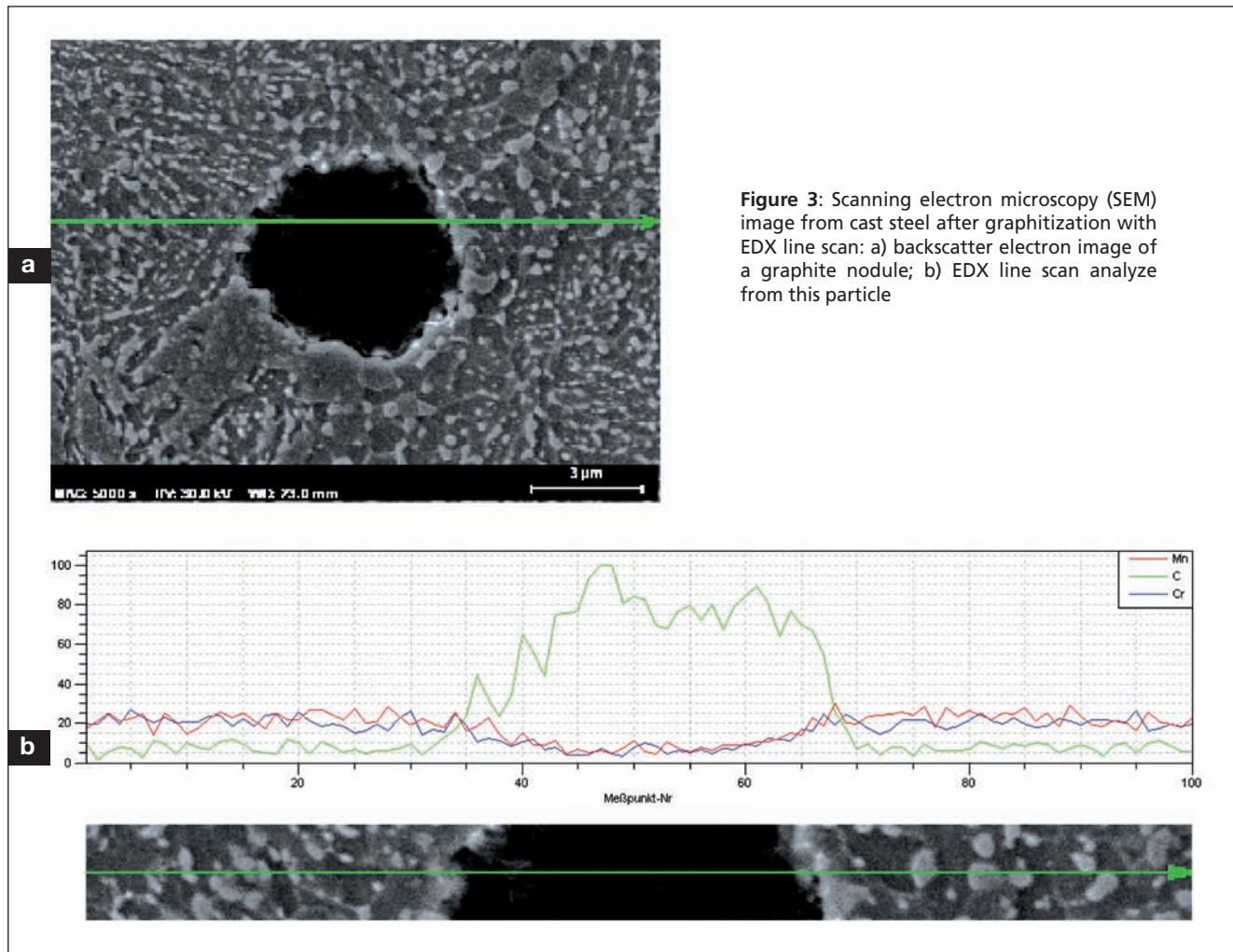


Figure 2: SEM image from commercial steel after graphitization with point scan: a) backscatter electron image of a graphite particle; b) point scan analyze from this particle

Table 1: Chemical composition of commercial and cast steels										
Steel	Chemical elements, wt %									
	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
As-cast	1.172	1.469	0.026	0.013	0.322	0.079	0.121	0.025	0.189	0.008



**Figure 3:** Scanning electron microscopy (SEM) image from cast steel after graphitization with EDX line scan: a) backscatter electron image of a graphite nodule; b) EDX line scan analyze from this particle

cial steel, but they have less and more limited distribution. It should be mentioned that the graphite formed in the cast steel are identical to the graphite of cast iron (about  $10\ \mu\text{m}$ ) [15, 16] forming a special structure in that steel. Based on the researches performed [14, 17, 18], the addition of aluminum and boron to the composition of the steel results in the formation of nitride precipitates which their structures are the same as graphite. Therefore, the presence of these nitride precipitates in the steel matrix increases the nucleation sites of graphite leading to their final fine structure.

Since graphitization periods are not considered identical in these two steels and the chromium content of the cast steel is higher than the cast one, according to the effect of this element on the stability of cementite and the decrease in the graphitization driving force [19], the decrease in the graphitization period in the cast steel may not be judged definitely (due to the addition of silicon in comparison with the commercial steel).

The surface area percent of graphite in the cast and commercial steels were calculated using optical microscopic image analysis as 2.2 % and 3.4 % respectively. **Figure 5** shows SEM images of graphite particles in both of these steels. By comparison these images with ASTM standards in relation to graphite's morphology in cast irons [12], the shape of graphite in the commercial steel may be considered similar to tempered graphite in malleable iron (type III). On the other hand, the shape of graphite in the cast iron is identical to the spherical graphite in ductile iron (type I). It has been

demonstrated lower Mn/S ratio in cast irons leads to formation of more spherical in tempered graphite particles [12]. So far, according to data listed in Table 1, Mn/S ratio for cast and commercial steels can be calculated 12.38 and 28.25 respectively. One can generalize the role of Mn/S ratio in cast iron for graphitic steels. In another word, the high difference in the morphology of graphite in these steels may be due in Mn/S ratio.

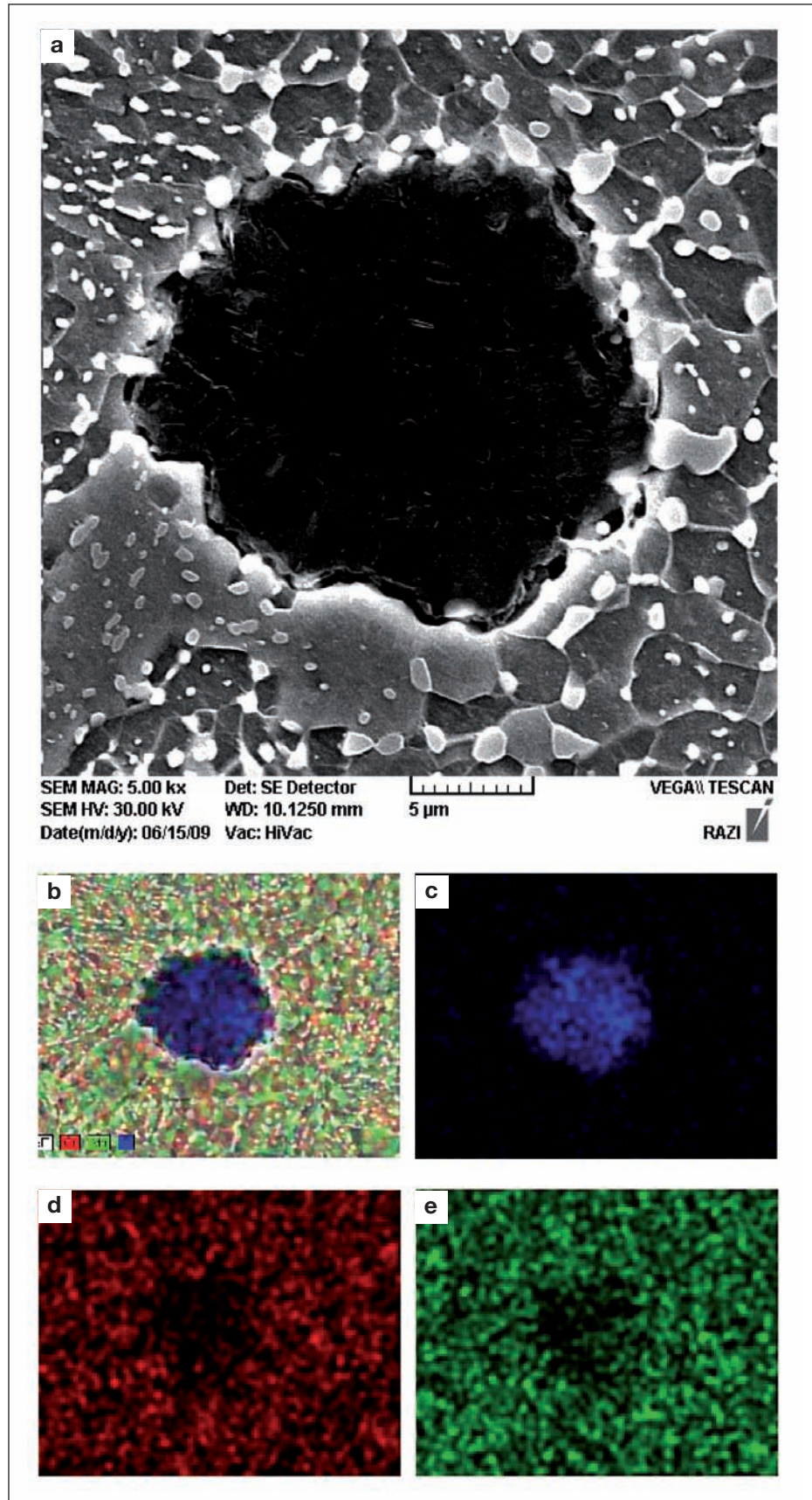
## 4 Conclusions

1. After graphitization, the shape of graphite particles in the cast and commercial steels are similar to their morphologies in ductile (type I) and malleable (type III) iron respectively.
2. Graphite particles in the commercial steel are very finer with more distribution in comparison with the same particles in the cast steel.
3. Graphite particles in the cast steel are identical to the particles in cast irons from size and distribution point of view.

*The authors of the paper appreciate Prof. Dr. Ahad Zabet and Part Sazan Co. for preparing some of the light optical microscopic images. In addition we thank Mr. Ghasem Isa-Abadi-Bozchelouie for performing some of the tests.*

## Literature

- [1] Andrew, J. H.; Lee, H.: Effect of cold-work on steel, section IV-effect of high-speed deformation on steel. *J. Iron Steel Inst.* 165 (1950), p. 145.
- [2] Smith, G. V.; Royle, B. W.: Compensated temperature parameters for correlating creep and creep rupture data. *Trans. ASME* 78 (1956), p. 1423.
- [3] Rosen, A.; Taub, A.: The kinetics of graphitization in steel at subcritical temperatures. *Acta Metall.* 10 (1962), p. 501.
- [4] Sueyoshi, H.; Suenaga, K.: Effects of pre-treatment on the graphitization behaviour in hypoeutectoid low alloy steel. *Rev. Soc. Jap. Met.* (1978) no. 42, p. 676.
- [5] Samuels L. E.: *Light optical microscopy of carbon steels.* ASM, Metals Park, 1980. Pp. 175-208.
- [6] He, K.; Brown, A.; Brydson, R.; Edmonds, D. V.: Analytical electron microscope study of the dissolution of the Fe<sub>3</sub>C iron carbide phase (cementite) during a graphitisation anneal of carbon steel. *Journal of Materials Science* 41 (2006) no. 16, pp. 5235-5241.
- [7] Bidash, V. I.; Prikhod'ko, A. I.: Graphitization of low-carbon steel during a spheroidizing anneal. *Met. Sci. Heat Treat.* 29 (1987), p. 116.
- [8] Neri, M. A.; Colás, R.; Valtierra, S.: Graphitization in high carbon commercial steels. *J. of Materials Eng. and Performance* (1998) no. 7, p. 467-473.
- [9] Pierson, H. O.: *Handbook of carbon, graphite, diamond and fullerenes properties, processing and applications.* Published by William Andrew Inc., 1993. P. 44-5.
- [10] Katayama, S.; Toda, M.: Machinability of medium carbon graphitic steel. *Journal of materials processing technology* 62 (1996) no. 4, pp. 358-362.
- [11] Klaus, H.: Comparative investigations into the machinability of graphite-containing cast iron-base materials. *Giesserei* 52 (1965), pp. 583-593.
- [12] ASM International, Handbook Committee. *Properties and selection: irons, steels, and high-performance alloy.* ASM International (1998), pp. 13-194.
- [13] ASM International, Handbook Committee. *Ductile iron, Casting.* ASM International, 1998.
- [14] He, K., e. a.: An electron microscopic study of spheroidal graphite nodules formed in a medium-carbon steel by annealing. *Acta Materialia* 55 (2007), pp. 2919-2927.
- [15] Lux, B.: On the theory of nodular graphite formation in cast iron. *AFS Cast Metals Research Journal* 8 (1972), p. 25-38.
- [16] Purdy, G. R.; Audier, M.: The physical metallurgy of cast iron. *Mater Res Soc Symp Proc*, 1986, 34. Pp. 13-23.
- [17] Banerjee, K.; Venugopalan, T.: Development of hypoeutectoid graphitic steel for wires. *Materials Science and Technology* 24 (2008), pp. 1174-8.



**Figure 4:** SEM image from graphitized cast steel with mapping: a) secondary electron image of a graphite nodule; b) mapping analyze from this particle; c) carbon K<sub>α</sub>; d) chrome K<sub>α</sub>; e) manganese K<sub>α</sub>

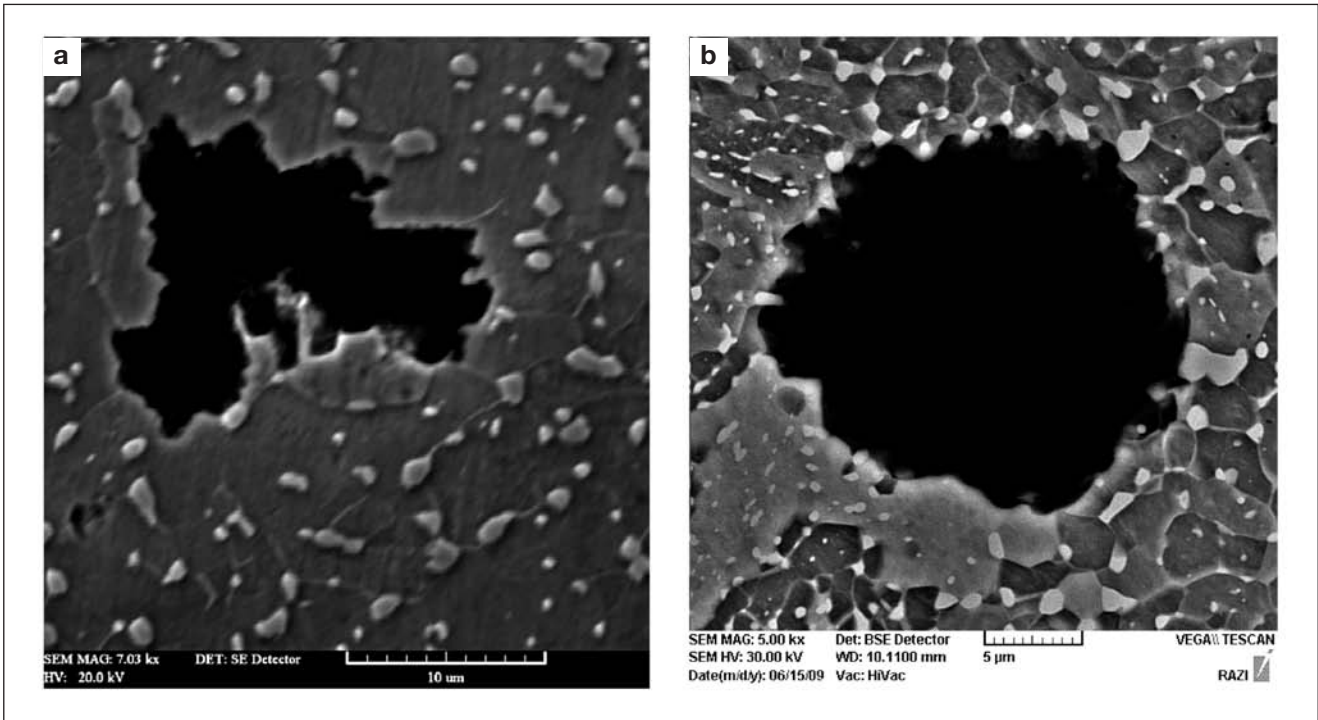


Figure 5: SEM image from graphitized steels: a) commercial steel; b) cast steel

[18]Iwamoto, T.; Murakami, T.: Bar and wire steels for gears and valves of automobiles-eco-friendly free cutting steel without lead addition. JFE GIHO (2004), no. 4, p. 64-9.

[19]Zhukov, A.: News in graphitization theory. Thermodynamics of graphitizing iron alloys. Metal Science and Heat Treatment 26 (1984), pp. 849-856.

