V. L. Naidek, A. M. Verkhovliuk

Physico-Technological Institute of Metals and Alloys, National Academy of Sciences of Ukraine, Kyiv, Ukraine

Some considerations of the mechanism of nodular graphite formation in cast iron

The influence of alkaline-earth, rare-earth and impurity elements on the interfacial properties of iron-carbon melts and also on the process of graphite nodules formation was studied. It was represented a likely mechanism of the graphite formation in cast iron.

Keywords: *alkaline-earth, rare-earth metals, nodular graphite, interfacial properties, iron carbide, dissolution enthalpy*

Introduction. Investigation of nodular graphite formation is important for elaboration of technologies of high-quality cast iron manufacture. Despite intensive development of practical techniques of the cast iron production, many principal moments are still unclear. In this way, an effect of interfacial properties on the shape of graphite inclusions have been studied in great number of works [1-12], however unambiguous conclusions on the mechanism of the inclusions growth are not available, i.e. it is assumed an existence of several mechanisms of graphite nodules formation.

Results and Discussion. It can be concluded on results of work [2] that graphite-melt surface energy increases as a result of inoculation. Treatment of the iron-base melts by addition of magnesium or cerium results in the binding of sulfur in the stable sulfides, and hence the surface tension rises up to 1790 mJ m^{-2}, which approaches to σ_{lg} of pure iron. Excess of magnesium and cerium in the cast iron promotes their adsorption at the interphase boundary, and the surface tension of these elements is relatively low (σ_{lg} of Mg and Ce are 588 mJ m^{-2} and 707 mJ m^{-2}, respectively) [13, 14], for this reason the melt surface tension decreases. Thus increasing of σ_{lg} and σsl by the addition of spheroidizing elements is related to their interaction with oxygen and sulfur, which are always present in an industrial iron-base melts. The surface tension of σ_{lg} decreases upon soaking of the modified melt in a vacuum. This probably is due to decomposition of the magnesium or cerium sulphides and subsequent adsorption of sulfur at the interphase boundaries15. The maximal surface tension is peculiar to the cast iron with 0.010-0.020 wt. % of Mg [16-17]. In this case there are several modifications of graphite in the solid sample, namely, the spotted, fine-flaky and interdendritic graphite. Magnesium content diminishes due to evaporation on long standing of the melt and an inflection point occurs on curve (the surface tension vs. the content) at magnesium content of 0.010-0.015 wt. % for the melt of Fe-3.60%C-1.80%Si-0.50Mn-0.11%P-0.027%S. The inflection point is probably connected with partial increase of the free sulfur and oxygen concentration. It should be concluded from the analysis of the data that the absolute value of surface tension is not the sole condition of graphite nodulation, but alteration of graphite inclusions growth conditions as a result of surface-active elements adsorption at the melt-gas and melt-graphite boundaries is also important.

It has been suggested [9, 10] that surface-active elements form impermeable to carbon atoms compact adsorption layers on graphite nuclei, and it promotes kinetic regime of the inclusions growth and leads to formation of flaky graphite. More weak surface-active elements (spheroidizators) are adsorbed on the graphite nuclei less tightly in the case of their optimal concentration. It allows penetration of carbon atoms through the adsorption layers, which decrease insignificantly the rate of carbon delivery to the nuclei, and the growth of graphite inclusions takes place by diffusion mode, and that is the condition of nodular graphite formation. In Sidorenko's opinion [10], the unsaturated adsorption layers are formed in the case of optimal concentration of magnesium and cerium in iron-carbon melt. With further increases in concentration of these elements, the adsorption layers become saturated and impermeable to carbon atoms, i.e. de-nodular effect occurs. Such explanation of the nodular graphite formation mechanism doesn›t answer to some questions, for example, about the duration of the modification effect and so on.

Milman and co-authors [3, 11] have studied an influence of magnesium, cerium, aluminum, bismuth and antimony on surface properties of cast iron. The investigations have been carried out by a sessile drop method on pyrolytic carbon substrates. The measurements were conducted on both basal and prismatic planes. It has been shown that magnesium content increases from 0 to 0.09 wt. % results in the σ_{lg} enhancement from 1380 to 1620 mJ m^{-2}. A contact angle (θ) changes simultaneously for the basal plane from 121 to 140° and for the prismatic plane – from 119 to 149°. The cast iron melt with cerium content of 0.18 wt. % has surface tension of 1590 mJ m^{-2} and contact angle of 141 and 148° on the basal and the prismatic plane, respectively. The σ_{lg} is reduced to 1110 mJ m^{-2}, but

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Note: σ_{lg} – liquid-gas surface tension; σ_{sl} - solid-gas surface tension; σ_{00l} – surface tension between the basal plane of graphite and the melt; σ_{hk0} - surface tension between the prismatic plane of graphite and the melt.

the contact angle remains the same with increase in cerium content from 0.18 to 0.70 at. %. Additions of antimony and bismuth affect the surface tension of the cast iron melt as well as to the large cerium content.

It has been established that surface tension between the basal plane of pyrolitic graphite and the cast iron melt is larger than between the prismatic plane and the melt ($\sigma_{00l} > \sigma_{hk0}$), and additions of magnesium and cerium reverse this inequation. This effect can be related to predominant desorption of impurity elements on the prismatic planes of graphite inclusions by magnesium and cerium adding into the melt.

Takita and Ueda [8] noted that the increase of magnesium content in the cast iron changes insignificantly the σ_{lg}. The surface tension alters from 1320 to 1390 mJ m^2 with increase in magnesium content from 0.02 to 0.06 wt. % and the inequation become like that $\sigma_{00l} < \sigma_{hk0}$.

In opinion of Bunin and co-authors [18], the flaky graphite and the nodular graphite belong to the same type of graphite crystallite and differ in degree of noncrystallographic branching and relation of longitudinal and transversal growth rates. The hypothesis of the graphite inclusions formation is based on a splitting of screw dislocations. For example, when the splitting occurs rarely, the longitudinal growth prevails. But when the splitting becomes more frequent it is accompanied by a radial turn of the plates, the nodular graphite faceted by the basal planes is formed at the early stages of splitting. The modifying elements are adsorbed on the graphite crystallite surface, and the growth rates in different directions are equalized [19, 20]. Besides, oxygen, sulfur and other surface-active elements are adsorbed predominantly on the prismatic planes of the graphite, reducing their surface energy and, consequently, reducing ratio between surface energies on the prismatic and the basal planes [18]. In this case the flaky graphite inclusions become stable. A similar effect is observed at an excess of the modifying agents that substitute surface-active elements of the oxygen group and the agents modifying are adsorbed on the graphite prismatic planes. It is assumed that the nodular shape is not the result of the presence of modifying agents in the melt, but represents a natural graphite form in pure Fe-Si-C alloys, due to the energy characteristics of growth of such graphite forms.

It is determined [21-24] that difference in chemical potentials of components in the solid and liquid phases makes a negative contribution to the interfacial tension in the non-equilibrium systems, and the interfacial energy at the graphite boundary with the iron-carbon melt is significantly lower than at equilibrium. In this regard, crystals with flat faces grow from the melt under conditions close to equilibrium, which is determined by the high interfacial energy and by the intention to form a crystal with a minimum surface energy. On dissolving of such crystal in a saturated melt, its faces are covered with etch figures [25]. It is assumed that the surface energy of the solid is somewhat less during dissolving than in the course of growing and equilibrium.

The results of the interfacial interaction can be conveniently represented in a form of correlation dependence between the difference in wetting angles of the prismatic and the basal faces of pyrolytic graphite substrate and the respective value of adhesion work (Fig. 1). The presented data have revealed the correlation concerning the elements influence on the form of graphite inclusions. One can conclude that the adhesion work on the basal plane should be greater than on the prismatic plane to form graphite nodules. The above condition is necessary but not sufficient.
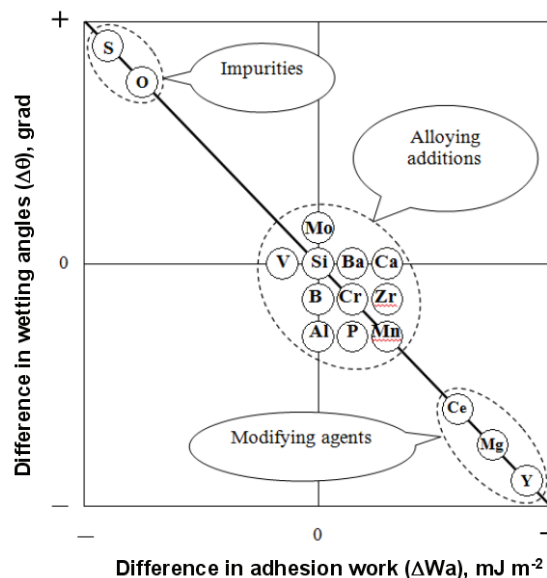
Regarding the cooling rate effect on the nodular graphite formation, it can be in general formulated like that «the cooling rate increase facilitates the formation of graphite nodules». It was established experimentally that the preferential growth of graphite occurs on the basal plane at an accelerated cooling rate of 10 K s^{-1}.

The experimental results on interfacial properties and influence of cooling rate on the growth of graphite inclusions suggests that the inhibition of growth on the prismatic crystallographic faces of polycrystalline graphite is essential for the formation of compact graphite inclusions. Moreover, this condition can be satisfied by formation of a certain composition of adsorbed layers on the growing faces, as well as by adjusting the rate of carbon atoms delivery from the melt, i.e. by changing of the polycrystal growth mode from the kinetic to diffusive with increasing of the cooling rate, alteration of chemical composition and other factors.

The last statement requires a special consideration. It is well known from the practice of amorphous metallic materials production that cooling rates of 106-107 K s^{-1} are required for significant suppress of the diffusion mobility of atoms in molten metal alloys [26, 27]. But a marked effect of cooling rates (from 0.9 to 10 K s^{-1}) on the nodular cast iron formation is observed in the range where the suppression of the diffusion mobility of atoms is practically impossible. One has paid attention to investigations of the structure and physical properties of liquid cast iron in order to elucidate the above effect. Numerous studies on a liquid state of metals and alloys, including cast iron, indicate that the molten cast iron is a complex system having a dynamic micro-inhomogeneity.

Detailed X-ray diffraction studies of the liquid iron-carbon alloys show that the equilibrium state of the melt assumes the existence of two types of ordering. The one type corresponds to a carbon solution in iron, the other does to carbon-containing clusters like carbides. It was studied that graphite-like clusters are unstable and decompose with increasing of temperature and soaking time of the liquid metal [28-33].

Thus part of the carbon atoms is bound with the metal atoms of iron solvent and carbon atoms are necessary for the graphite inclusions growth. For their release during the cooling it is necessary to overcome an energy barrier, it means to transit from a metastable state to a stable one. The rate of the transition depends significantly on the energy barrier height (activation energy) and the temperature. It can occur slowly enough and if the characteristic time of the heat sink is less than the same magnitude for the decay of carbon-containing groups in the melt, they are retained in the solid state after crystallization, as observed in practice. We can confidently say that the cause of rate reducing of carbon atoms delivery to the interface graphite – melt at accelerated cooling is the limited rate of decay of metal-carbon clusters rather than a decrease in the diffusion mobility of carbon atoms. The clusters serve in this process as internal sources of carbon with a limited rate of release.

Chemical composition and stability of such clusters differ significantly by the presence of these or other elements in the melt. Free energy of expected compounds formation in the iron-carbon melts is presented in Table [34]. The data show that only the magnesium carbides are characterized by a positive free energy, i. e. these compounds are unstable. The clusters of carbon and magnesium atoms are the closest to entities that are called «energetic structures». Formation and destruction of chemical bonds between carbon and magnesium occur simultaneously. Thus, we can conclude that magnesium mainly refines the melt and protects carbon atoms from interaction with impurity elements.

Impurity, alloying and modifying elements in the melt can both increase and decrease the height of the energy barrier, thereby determining the rate of the microgroups decay, that finally affects significantly the shape of graphite inclusions. The mechanism of this phenomenon has dual character. Elements that exhibit surface-active properties, do not participate in the formation of stable chemical bonds in the clusters. These elements are located at the clusters borders and can have a significant impact on the growth of graphite inclusions at low concentrations.

Surface-inactive alloying elements (silicon, chromium, manganese, vanadium, etc.) can stabilize or destabilize microgroups, participating in chemical bonds within them. For example, carbide-forming ability of chromium can be explained so that chromium binds carbon more strongly, than iron does, thus raising the energy barrier of the carbon-containing groups destruction [35]. On the contrary, silicon forms more strong bonds with iron than carbon, thus contributing to a reduction of the potential barrier and reinforcing the cast iron graphitization [36] (Fig. 2).

From this point of view the known fact can be explained, that minimal cooling rate required for the

Free energy of expected compounds formation in the iron-graphite melts

Compound	Temperature, K	Free energy of formation, ΔZ, kJ mol^{-1}
CaC_2	1600	- 5,81
	1700	- 5,93
	1800	-5,91
Mg_2C_3	1600	7,27
	1700	8,44
	1800	9,62
MgC_2	1600	6,51
	1700	7,11
	1800	7,68
Mn_7C_3	1600	- 9,11
	1700	- 9,45
	1800	- 10,10
$Cr_{23}C_6$	1600	- 27,06
	1700	- 27,27
	1800	- 27,49
Cr_7C_3	1600	- 12,34
	1700	- 12,49
	1800	- 12,63
Cr_2C_3	1600	- 6,70
	1700	- 6,82
	1800	- 6,91
Fe_3C	1600	- 0,35
	1700	- 0,41
	1800	- 0,46
SiC	1600	- 2,42
	1700	- 2,34
	1800	- 2,15
$FeSi$	1800	- 3,47
$FeSi_2$	1800	- 4,11

nodule graphite formation, ceteris paribus, increases in the following sequence: iron-carbon, nickel-carbon, cobalt-carbon [37]. Incidentally, this sequence does not correspond to the elements order in the Periodic table. Fig. 3 represents the correlation between the partial enthalpy of dissolution of graphite in the liquid metal at infinity dilution [38-40] and the minimal rate of solidification, which is sufficient for graphite nodules formation [37]. The graph shows the high level of correlation of the quantities. Increase in the first partial dissolution enthalpy of graphite can be interpreted as a metal-carbon bond weakening in the mentioned sequence, which reduces the stability of the carbon-containing microgroups and increases their rate of decomposition. The increasing of solidification rate promotes maintenance of the desired ratio between the rate of the carbon atoms deposition at the surface of growing inclusions and the rate of its evolution from the carbide clusters, which gives rise to graphite nodules growth.
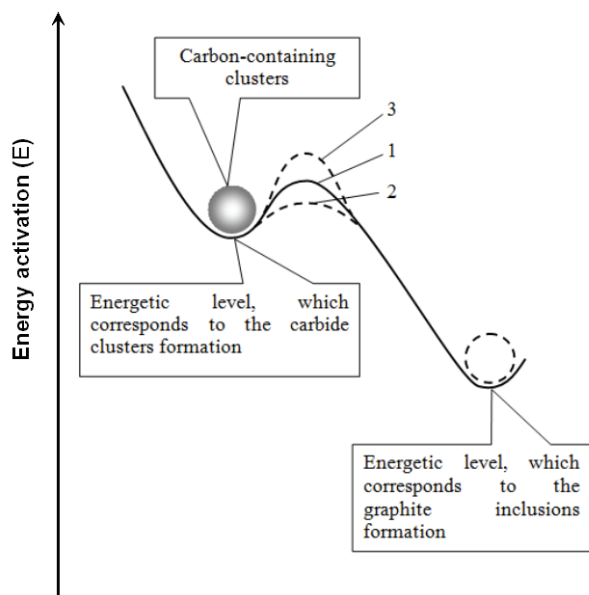
Fig. 2. Influence of silicon and chromium on the stability of the carbon-containing clusters: *1* – Fe-C melt; *2* – Fe-C melt, doped by Si; *3* – Fe-C melt, doped by Cr

Fig. 3. Relationship between the solidification rate and the partial enthalpy of dissolution of graphite in the liquid metal infinity dilution

Conclusions. The main condition for the graphite nodules formation is to provide the preferential growth of the basal faces of graphite, which is achieved by refining of the melt from the oxygen, sulfur and other surface-active elements and by adsorption of modifiers on the prismatic faces of the graphite inclusions. The difference between the values of adhesion work at the basal 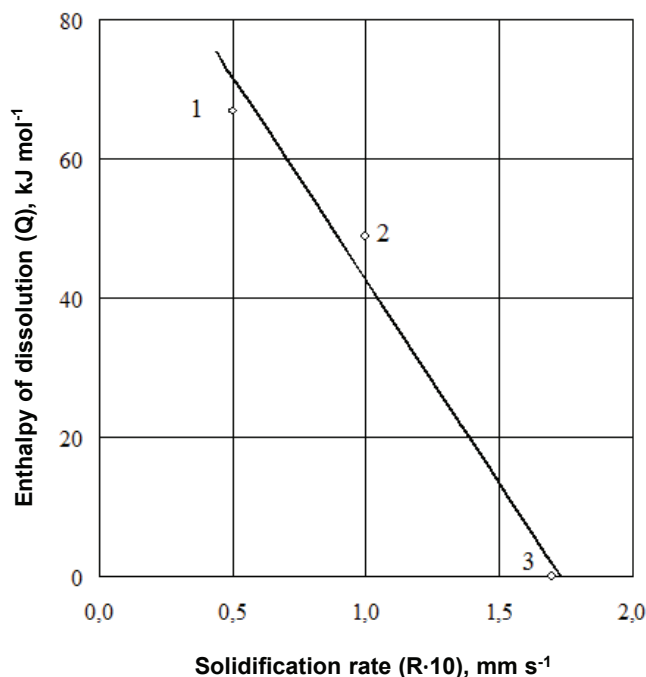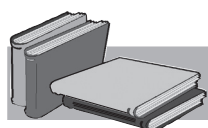and the prismatic planes of graphite becomes in this case positive, and the growth of inclusions is carried out in the diffusion mode. Acceleration of the cooling rate leads to changes in the ratio of growth rates on the basal and the prismatic faces of graphite, and generally promotes a quasi-diffusion growth mode.

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Анотация

Найдек В. Л., Верховлюк А. М.

О механизме образования шаровидного графита в чугуне

Изучено влияние щелочноземельных и редкоземельных элементов и примесей на межфазные свойства железоуглеродистых сплавов, а также на процесс формирования шаровидного графита. Представлен вероятный механизм образования графита в чугуне.

Ключевые слова

щелочноземельные, редкоземельные металлы, шаровидный графит, межфазные свой-ства карбид железа, энтальпия растворения

Анотація

Найдек В. Л., Верховлюк А. М.

Про механізм формування шароподібного графіту в чавуні

Досліджено вплив лужноземельних та рідкісноземельних елементів та домішків на міжфазні властивості залізовуглецевих сплавів, а також на процес формування шароподібного графіту. Представлено ймовірний механізм утворення графіту в чавуні.

Ключові слова

лужноземельні, рідкісноземельні метали; шароподібній графіт, міжфазні властивості, карбід залізу, ентальпія розчинення.