EFFECT OF POWDER MODIFIERS ON STRUCTURE FORMATION OF IRON-CARBON ALLOYS

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Abstract: *Effective modification not by expensive nano-powders but by relatively large ones (up to several microns) and capable to dissolve when entering into the melt and become additional crystallization centers at its start point was shown. That provides a metal structure refinement and, consequently, increases the whole complex of mechanical properties. The optimal process parameters of refractory compounds disperse powders modification were proposed.*

Keywords: DISPERSION POWDERS, CRYSTALLIZATION, MODIFICATION, STRUCTURE, MATHEMATICAL MODELING.

1. Introduction

One of the main tasks of modern materials science is increase in both strength and plastic properties [1]. An effective method of solving it is grain metal structure refinement [2] by dispersible powders modifying to obtain fine cast structure [3]. This allows not only improvement of the structure and mechanical properties characteristics in a cast state, but also to strengthen this action in subsequent thermomechanical processing [4]. One of the ways to the structure formation process control is usage of crystallization modifiers – dispersed solid particles injected into the melt before solidification [3, 5]. It's known that a significant effect could be achieved by using nano-sized powders [6], but their production, storage and input into the melt technology are difficult and expensive.

Thus, research aimed at efficiency improving of the usage as modifiers disperse powders of larger fractions capable of when entering into the melt being dissolved to nano-sized substrates at the time of the crystallization begining [7 – 11] looks promising. The use of computer and mathematical modeling allows you to quickly and cost-effectively identify the optimal parameters modification.

The **purpose** of this work is to study using mathematical modeling the structure formation and crystallization of iron-carbon alloys in the case of modification by disperse powders of refractory compounds and optimal technological parameters of their entry into the melt determination.

2. Results and discussion

One of the main characteristics of the material used as the modifier, it is stability of the particles suspension in the melt. This characteristic is related to the equilibrium concentration of the constituent chemical elements in the melt with the solid particles which has influences on the diffusion processes. Figure 1 shows plots obtained on the basis of physico-chemical calculations [9] which represent equilibrium with the corresponding nitrides and carbides content of carbide- and nitride-forming elements at 1530 ºC depending on carbon content. The nitrogen content in the steel was set on the level of 0.006 %.

The concept of the proposed modification means that the melt concentration of carbide and nitride forming elements should lie in the area below the respective curves [9]. Otherwise, there may be suspension of dissolution and activation of the particles coagulation processes. On the other hand, since the concentration of carbide- or nitride on the surface of the particles is close to the equilibrium value, too much difference between a current concentration (occurred due to dissolution of the modifier) and an equilibrium one (near-surface) leads to too rapid dissolution of the particles and reduce their effectiveness as a substrate [9].

To evaluate the options of introduced modifier particles behavior in a melt, the probabilistic model [9, 10] has been developed and the corresponding computer program was written for the calculations execution. The program allows to determine the proportion of the particles, which will be effective crystallization centers, how many particles dissolve completely (in this case, there may be the effect of microscopic inhomogeneities, as well as the effect of micro-alloying), and how much, being captured by the solidification front and become relatively large carbide and nitride inclusions. The calculation results showed that restriction of the variation around the optimum size range and reduced the melt temperature when the powder input to the values close to the liquidus. This substantially (up to 5.0 fold) increases the effective part (capable of becoming crystallization centers) of the particles. This effect in the case of input TiN powder shown in table 1.

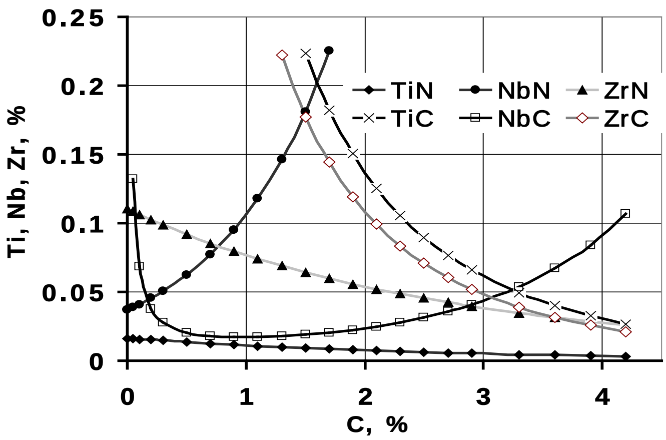

Fig. 1. *The dependence of equilibrium with the nitride or carbide content of Ti, Nb, Zr and carbon in Fe-base melt*

Table 1

The effect of input temperature and the size of the TiN particles on the proportion of ones that can become crystallization centers

The melt temperature when the modifier entering, ºC	The particle sizes, μm	The proportion of effective particles, %
1550	1,0 – 5,0	0,096 – 0,102
	2,1 – 3,9	0,178 – 0,189
1535	1,0 – 3,0	0,183 – 0,246
	1,0 – 2,0	0,481 – 0,543

Process of particles dissolution in the melt before and during the crystallization (taking into account powder size distribution) we described using our computer model [11]. There was considered an input of dispersed TiN powder into a low-carbon steel melt. The simulation results showed that in this case, effective as a modifier is a fraction ~ 1...3 μm. when injection the melt temperature should be close to the liquidus temperature, that for such steels is about 1530 ºC. It was shown that by introducing of a larger mass of the modifier there can lead to increase of the proportion of the effective particles and significantly prolong its lifetime. In addition, by varying the type of the original particle size distribution (normal, log-normal or rectangle) we can affect the dynamics of the particles dissolve.

The dissolution time of the powder in the case of normal and rectangle particle size distribution are similar but there is a difference in the process way. After 10 seconds, in the case of rectangle initial distribution the melt contains stored $8{,}18 \cdot 10^{11}$ particles per 1 t, while in the original normal distribution case, their amount will be 1.87×10^{11} per t, that is 4,4 times less. Thus, a uniform distribution of particles within the input fraction of the modifier can significantly increase the number of particles in the melt which can become additional crystallization centers, compared to the case of the normal distribution. The simulation results showed that at the beginning the number of particles in the case of the original normal distribution will be more, but in about 8 seconds, the amount of particles in the melt will be equivalent. During the rest period, the number of particles in the melt in the case of initial rectangle distribution will be larger, and as the course of the process, this advantage will grow over, after ~ 12 seconds will be more than 5 times.

The results of theoretical research on the modification of cast iron and steel have been confirmed in a series pilot scale experiments on iron and steel.

Cast iron for the molds of K13 type manufacture (transverse ones, with height 2600 mm, weight 9.5 t) and C8 type (muffled bottom ones, with height 2060 mm, weight 8.0 t) were treated with powdered modifier:

modifier expense: 0.5 kg / t;

composition: 40% TiC and 60% SiC;

particle size: TiC 1...3 μm and SiC 2...4 μm;

For preventing of white cast iron parts formation in addition to the mixing chamber modifier loaded fine powder of ferrosilicon FS65.

The modification leads to a significant refinement of graphite inclusions and increases the proportion of pearlite in structure, which provides a significant improvement in the mechanical and operational characteristics (Table 2).

Table 2

*Effect of modification on the mechanical properties of cast iron and operational stability of molds**

Metal state	$\sigma_в$, MPa	Hardness, HB	The number of uses before wear
Without treatment	$\frac{150…160}{154}$	$\frac{95…110}{102}$	$\frac{56 – 82}{71}$
TiC + SiC	$\frac{170…180}{176}$	$\frac{130…135}{132}$	$\frac{85 – 108}{97}$
TiC + SiC + FS65	$\frac{175…190}{180}$	$\frac{135…145}{139}$	$\frac{115 – 144}{127}$

* - averaged data 18 by ladles; numerator represents the minimum and maximum values, the denominator is the average.

A trial approbation of “Steel 20” modification by dispersed refractory modifiers (TiN fraction of 1 ... 3 mm at a rate of 0.12 kg / t, injected in an argon stream) for siphon casting into ingots weighing 2 tons [9] was successfully carried out. Deformed metal of conventional production has a fairly uniform ferrite-pearlite structure with 3 – 4 score of the grain size. In the modified metal observed ferrite-pearlite structure was up to 5 - 6 score.

In the process of steels modifying by carbides and nitrides dispersed powders in addition to effects on structure formation during solidification occurs microalloying with titanium, niobium, zirconium and nitrogen (if used nitride), due to the transition of significant portion of modifier material into the melt, and then (during solidification) into solid solution. This secondary effect may be useful in increasing of steels thermomechanical treatment processes efficiency because of carbonitride hardening. To optimize the conditions it is necessary to know the phases formation and composition data. It was found that the most effective modifiers in the aspect of precipitation of dispersed carbonitrides in the solid state are niobium compounds. Carbide and nitride forming elements (titanium, and to a lesser extent vanadium), carbon and nitrogen present in the steel, are adsorbed by grain boundaries, followed by decomposition of the supersaturated solid solution and the formation of film type precipitates Ti (CN), V (CN), Ti, V (CN) , thus weakening the intergranular bond and causing metal embrittlement. The enrichment of the grain boundaries and Nb, respectively, the formation of these carbide and nitride precipitates practically not observed, indicating a preference for the use of niobium carbonitride hardening carbon steels compared to the titanium or vanadium.

3. Conclusions

1. Mathematical models and computer programs to describe the behavior of dispersed refractory particles in the melt, allowing to determine the optimal modification parameters were developed. Identified equilibrium conditions near the liquidus temperature for the various carbide and nitride phases, depending on the carbon content in the melt.

2. The concept of effective metal melts modification by refractory powders dispersed of relatively large fraction (up to several micrometers) that can be dissolved down to the nano-sizes at the beginning of solidification and become additional centers forced bulk crystallization.

3. It is found that a rectangle distribution of particles by their sizes within the input fraction can increase their number in the melt during latter stages of dissolution and capable to form additional crystallization centers up to 2,0...5,0 times compared with the initial normal distribution. The possibility of increasing to 2.0...4.0 times of the proportion of effective particles by reducing the range of variation of their initial sizes and reduce the input temperature to values close to the liquidus was shown.

4. The optimum process parameters for various steels and cast irons modifying (particle size and fractional composition, amount of modifiers, melt temperature when entering), providing a significant refinement of the metal structure and the increase of the complex mechanical properties were offered.

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