PROCESSES AT THE INETRFACE MOLTEN METAL-SAND MOLD

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The processes that take place at the liquid metal-sand mold interface during the casting and crystallization of metal were studied in this paper. The mold was made using the C O_2 – method, with the addition of ac tive components, such as: MgO, TiO₂, AlK(SO₄)₂ and Na₂SO₄. At the liquid steel pouring temperature, these active components undergo decomposition in the mold, caused by heat release during pouring, crystallization and cooling of castings. Silicates, which have an important influence on casting surface quality, are formed as a result of the interaction between the mould material and liquid steel.

Key words: molten steel, sand mold, interface

INTRODUCTION

The forming of a casting usually is monitored at the liquid metal-mold interface, i.e., during the cooling period, in the temperature range from the pouring temperature to room temperature. In this interval a remarkable interchange of heat occurs between the liquid metal and the mold. The forming of a casting is followed by many processes which have substantial influence on the casting quality.

At the liquid metal-mold interface, a lot of chemical and/or metallur gical reactions occur. The products of those reactions are set on both sides, it means at the side of casting as well as at the side of the mold.

During consideration of interactions at the interface between the mold and the liquid metal, the following variables must be included: primary metal (M), alloying elements ($M_1, M_2, ..., M_i$), oxygen (O), oxides of mold material (RO), and temperature. Three types of chemical reactions can occur between the participants in the process at the mould surface [1]:

$$M_{1}M_{i} + 1/2O_{2} = M_{1}O_{i}M_{i}O$$
(1)

$$M_{1},M_{i} + RO = M_{1}O,M_{i}O + R$$
 (2)

$$M_1O,M_1O + RO = M_1O \cdot RO,M_1O \cdot RO$$
 (3)

The equilibrium of these reactions is determined by behavior of the interface between mold and liquid metal.

The reaction between metal and oxygen can be shown by general equation (3).

The composition of an oxide which forms on the metal surface depends on the properties of the casting material. For a carbon steel, among the oxides iron ox-ides prevail, primarily iron (II)-oxide (FeO) with a melt-

ing temperature of 1 370 °C. These oxides, highly superheated at the steel casting temperature, are very active and liquid, and react with the mould material, forming silicates. Formed silicates have certain physical and chemical properties: high surface tension, low viscosity (5-10 Pa·s), optimal melting temperature (800-900 °C), and high oxidation potential [2].

Similar problems were studied, for example by Zhang et al [3], who presented an oxidation mechanism of CaOFeO_xSiO₂ slag with high iron content in a pure oxygen atmosphere. The phase equilibria for slag systems containing iron oxides were studied byTurkdogan, Bodsworth and Bell [4], and Kongoli and Yazawa [5]. Muan and Osborn [6] reported the phase diagrams for the FeOMnO system in a low oxygen pressure, as well as for the FeOMnO-SiO₂ system in CO₂/H₂ and air atmospheres. Structural models for binary silicate systems, including MnO-SiO₂ and CaO-SiO₂, as well as thermodynamics of Fe₃O₄–Mn₃O₄ spinels, are presented in the work of Pelton et al. [7, 8]. Semykina and a few other authors worked on the oxidizing kinetics of liquid FeO-MnO-CaO-SiO₂ slags [9-11].

EXPERIMENTAL

The experiments were conducted in laboratory and industrial conditions, on steels from the manufacturing program of the Foundry of Steel Casts.

The moulds were made according to the CO₂ procedure. The mould mixture consisted of about 90 % quartz sand; 6 % casting water glass, density 1,55 g/cm³; 0,1 % sodium-sulfate; and the remainder of active components.

As active components the oxides of titanium and magnesium, TiO_2 and MgO, were used. They transfer the binary Na₂O - SiO₂ system, into the ternary Na₂O SiO₂ M_xO_y system with higher viscosity and surface tension. We also used sulfates of aluminum, sodium, and potas-

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sium, where sodium sulfate was a constantly present component in the mould mixture, and aluminum sulfate and aluminum potassium sulfate were added as active components. Due to thermal effects in the mould during processes of casting, solidification and cooling down of the ingot, these active components dissociate, releasing gaseous reaction products and steam from chemically bonded moisture, which additionally affects oxidation of metal fi brils, and thereby the formation of new compounds in the contact zone of metal and mould.

Experimental ingots had a cylindrical shape, with dimensions of $0,038 \times 0,060$ m. The casting was used steel cast taken directly from manufacturing process of the foundry, with the chemical composition shown in Table 1.

Table 1 Chemical composition of the steel / %

C	Si	Mn Cr		Мо	S	Р
0,79	0,53	0,85	1,60	0,32	0,025	0,033

Casting temperature was in the range 1 580-1 600 °C, with initial temperature of the mold, and its external surface temperature equal to environment temperature (~ 20 °C).

The studies of behavior at the metal-mold interface, during the production of castings were done using the following methods: visual inspection, measuring the surface roughness, optical microscopy , quantitative chemical analyses, powder dif fraction, and electronmicro probe analysis. The other characteristics of the mold material, including mechanical, thermo-physical, and thermodynamic characteristics, were monitored, as well as the appearance and thickness of newly formed zones at the metal-mold interface.

For better understanding of the processes at the contact surface, the temperatures were measured at distances of 0, 1, 2, 3, 5, 10, 15, 20 and 25 mm from the surface. The interface region was studied using optical microscopy, scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS).

RESULTS AND DISCUSSION

A section of the mould with visible changes in the mould mixture caused by reaction with the metal and the non-reacted part of the mould mixture is given in Figure 1, [12].

By observing the section of the mold in Figure 1, four layers-zones are visible. Changes occurred in the first three zones depending on temperature, and the fourth layer remained unchanged, as shown in the Figure 1.

The first zone is dark in color and is a zone of penetration of a liquid metal into the mold pores.

The second zone is light in color due to allotropic changes of quartz.

The third grey zone is the area in which only small changes have occurred.



Figure 1 Section of the mold with visible zones

The fourth zone is a layer of unchanged mould mixture with unchanged compounds and properties.

Major changes, the subject of interest, occurred in the first zone. In this zone, the liquid metal penetrated into the mold material immediately after pouring into the mold, causing intensive reactions of liquid phase with the mould surface. The contact of such intensity, which causes reaction on entire mold surface, results in maximal speed of reaction layer growth at the beginning of the casting solidification.

Since the process on metal-mould contact surface directly depends on temperature to which the mold is subjected, it comes out that penetration of liquid phase into the mold will be more intense with the temperature increase. Consequently, the process of chemical interaction with participation of liquid phase will be shifted towards the mold depth.

Temperature measuring of the contact zone in solidification period of liquid metal showed that contact zone warms up to high temperatures, 1 400 to 1 500 °C, Figure 2.

These temperatures cause dehydration, oxidation, and formation of new compounds (for instance, silicates). The formation of interaction products in the contact zone is significantly determined by kinetics and temperature. Consequence of both, oxidation of elements and formation of silicates is determined by their concentration and change of thermodynamic potential of oxides and silicates which characterize ener getic potential, reaction course and stability of product formation.

Photographs of microscopic structure in the transmitted polarized light taken from the first contact layer, Figure 3a, show that the shape of quartz grains is changed in the vicinity of the castings surface. Those grains are deformed, cracked, embedded in reactive melt, and partially transformed into crystobalite. Frequently , those quartz grains are impregnated by metallic minerals, Figure 3b, or they are pasted together with hematite, Figure 3c, but they rarely grew together, Figure 3d.



Figure 2 The temperature vs. time over the mold cross-section for different additives

For correct interpretation of some reactions which were carried out, the use of energy dispersive spectroscopy (EDS) became necessary . The SEM-EDS results are shown in Figure 4.

CONCLUSIONS

The following conclusions may be withdrawn from this investigation:



Figure 3 Microscopic photographs of the Ārst contact zone in transmitted light



Figure 4 a-h SEM – EDS images

- Products of interaction between the melt and the mold are generally oxides whose physical and physicochemical properties essentially depend on the type of a defect in the structure and on their concentration. Interaction between the liquid steel and the mold takes place under the thermal shock, causing the formation of non-stoichiometric oxide composition, thus determining the course of subsequent reactions in the contact zone.
- Chemical changes are visible in a more intensified reaction zone of penetrating metal fi brils with quartz and active components, with formation of a glassy phase.
- Penetrating compounds into the mold from liquid steel are: iron, manganese and chrome.
- Considering components that the mold mixture consists of, the major reaction significance has the silicon and partially the potassium, while the sodium leaves the system.

- The composition of the reaction melt is rather complex, based on silicon, iron, manganese and potassium. It is predominantly presented by glassy phase with occurrence of the fayalite, the wustite, the spinel and a smaller share of other minerals.

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REFERENCES

- A. N. Tsibrik, Fiziko-khimicheskie protsessy v kontaktnoi zone metal-forma, Naukova dumka, Kiev , 1977, pp 12-45.
- [2] B. Kočovski, Founding Theory, BIGZ, Belgrade, 1972, pp. 38-56.
- [3] L.-N. Zhang, L. Zhang, M.-Y. Wang, and Z.T. Sui, Trans. Nonferr. Metals Soc. China, 15 (2005), 938–943.
- [4] C. Bodsworth and H. B. Bell, Physical Chemistry of Iron and Steel Manufacture, Longman, London, 1972, pp. 343– 345.
- [5] F. Kongoli and A. Yazawa: Metall. Mater. Trans. B, 32B (2001), 583–592.
- [6] A. Muan and E. F. Osborn, Phase Equilibria Among Oxides in Steelmaking, Addison-Wesley, Reading, MA, 1965, pp. 33–86.
- [7] A. D. Pelton, H. Schmalzried, and J. Sticher, Berichte Bunsengesellschaft f
 ür Phys. Chemie, 83 (1979) 3, 241–252.
- [8] A. R. Serrano and A. D. Pelton, Metall.MaterTrans.B, 26B (1995), 305–315.
- [9] A. Semykina, V. Shatokha, M. Iwase, and S.Seetharaman: Metall. Mater. Trans. B, 41B (2010), 1230–1239.
- [10] A. Semykina, J. Nakano, S. Sridhar, V.Shatokha, and S. Seetharaman, Metall.Mater .Trans.B, 42B (201 1), 471–476.
- [11] A. Semykina, J. Nakano, S. Sridhar, V.Shatokha, and S. Seetharaman, Metall.Mater .Trans.B, 41B (2010), 940–945.
- [12] Z. Janjušević, Contact surface Metal-Mould, Fondation Andrejević, Belgrade, 2008, pp 48.
- [13] S.I. Filipov, Teorya metallurgicheskih procesov, Metallurgiya, Moskva, 1985, pp. 23-89.
- [14] Yu. P. Vasin, A. Y. Rasulov, Okisliteli novye protivprigarnye materialy, Chelyabinsk, 1969, pp. 6.
- [15] O. Kubichevski, B. Gopkins, Okiselenie metalov i splavoy Metallurgiya, Moskva, 1985, pp. 12-35.
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