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THE INFLUENCE OF CALCIUM ON TECHNOLOGICAL PROPERTIES AND MICROPURITY OF STEEL CASTINGS

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The paper analyzes the technological parameters, micro-purity and mechanical properties of castings of steel alloyed with calcium. The effect of calcium on the steel was analyzed on samples taken in the process of casting heavy castings and ingots of the weight of ranging from 40 000 to 60 000 kg. Samples for the determination of the liquidus temperature and the solidus temperature of cast steels were analysed using differential thermal analysis (DTA). The production of low alloyed steel grades was performed on the EAF - ASEA-SKF facilities and the production of high-alloyed steels on the EAF - ASEA-SKF - SS-VOD facilities. The purity calcium was added into the steel by the injection of a stuffed profile.

Key words: steel, calcium, technological procesings, inclusions, crystalization

INTRODUCTION

Calcium is added into the steel which is deoxided by aluminium with the purpose of the removal of small aluminate inclusions. Verma et al. [1], Lind and Holappa [2], Potter, Lind and Story [3, 4] state that the basic idea of this technology is the conversion of alumina inclusions to the CA (C = CaO, A = Al_2O_3) type, which are fluid in the given temperatures, they quickly coalesce and quickly leave from the melt to the slag. In the steel there also occurs sulfur forming sulfide, therefore, it is possible to also make modifications to the MnS inclusions to the transformation of the time. Kepka in his monograph [5] describes solubility tests carried out by the calcium in the steel under the atmosphere of argon, when the pressure of 1,36 MPa prevents its evaporation and the iron solubility of Ca 0,032 % was found at the temperature of 1 600 °C. It was further shown that carbon, silicon, aluminum and nickel increase the solubility and that the chromium decreases it. The Ca solubility values are listed in Table 1.

Fruehan [6,7], Kepka[5] and Mitura, Landova [8] point out to the advantages of the steel processing by calcium:

- improvement of fluidity, changing the morphology of nonmetallic inclusions and increasing the liquid phase [6,7]
- improvement of the inclusion content of the rapid departure of the inclusions from the melt to the slag [6,7]
- minimalization of the surface defects [6,7]

Table 1 **Elements that enhance solubility of calcium in the iron**

The alloying element in the Fe	The solubility of calcium / %
Fe	0,032
Fe – 1 % C	0,061
Fe – 1 % Si	0,049
Fe – 1 % Al	0,038
Fe – 1 % Ni	0,035

- improvement of the machinability of steel at high cutting speeds [6-8]
- minimize the risk of cracking when re-heating near the heat affected zone of welded joints [5]
- preventing lamellar tearing [8]
- minimizing the sensitivity of the micro-pipe with high strength (HSLA) due to hydrogen cracking (HIC), e.g. steel for acid gases or oil pipe [6,7]
- reduction of the differences of mechanical properties after cross-section [5]

The above mentioned advantages of steel with adition of calcium which was used to modify the shape of inclusions can be further increased for the effect of Ca on the liquidus temperature and the solidus temperature. The influence of Ca on the liquidus temperature is stated in equation (1) by Liu, Zhang, Wang and Wang [9].

$$T_L = 1\,538 - (31{,}15\cdot(\%\,C)^2 + 62{,}645\cdot(\%\,C) + 0{,}609\cdot(\%\,Si)^2 + 2{,}0678\cdot(\%\,Si) - 0{,}0674\cdot(\%\,Mn)^2 + 5{,}3464\cdot(\%\,Mn) + 20\cdot(\%\,P)^2 + 9\cdot(\%\,P) - 1{,}7724\cdot(\%\,S)^2 + 24{,}775\cdot(\%\,S) + 1{,}159\cdot(\%\,Nb)^2 + 5{,}3326\cdot(\%\,Nb) - 0{,}0758\cdot(\%\,Ca)^2 + 3{,}1313\cdot(\%\,Ca) + 0{,}0379\cdot(\%\,Ni)^2 + 5{,}2917\cdot(\%\,Ni) + 0{,}6818\cdot(\%\,Cu)^2 + 2{,}5955\cdot(\%\,Cu) + 0{,}0214\cdot(\%\,Mo)^2 + 3{,}2214\cdot(\%\,Mo) + 0{,}0359\cdot(\%\,Cr)^2 + 1{,}1402\cdot(\%\,Cr) + 10{,}797)\ °C \quad (1)$$

The information gathered on the influence of Ca on the liquidus temperatures is very brief and no author mentions the influence on the solidus temperature.

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Therefore, for the addition of the missing information on the effect of Ca on the liquidus temperature and particularly on the solidus measurements, there were performed measurements on the samples that were taken during melt smelting operation, which were evaluated by measuring on the DTA.

EXPERIMENTAL PROCEDURES

The samples of melt steel were collected during the operation melts in the weight from 40 000 to 60 000 kg of the following quality: G17CrMoV5-10 according to EN 10213:2007, G20Mn5 according to EN 10293:2005 produced by the duplex EAF - ASEA-SFK method, followed by quality GX4CrNi13-4 according to EN 10283:2010, X46Cr13 according to EN 10088:2005 produced by the triplex EAF - ASEA-SKF - SS-VOD procedure. The crude steel for prime quality was made from molten alloy scrap for electric arc furnace (EAF) type RBT (Round Bottom Tapping) with a nominal capacity of 70 000 kg of liquid steel and with the input transformer of 40 MVA. After the completion of all metallurgical operations and after the acquisition of the required temperature of the bath, there was performed the tap of the melt to a refining ladle. The cylindrical refining ladle was equipped with two Hibrid Plugs for Argon and two nozzle controlled by a slide closure. The ladle has an inner diameter of 2 855 mm and a maximum capacity of 70 000 kg of melt. The average size of the basin is useful in order to create excellent conditions for all the necessary metallurgical processes occurring in the melt during the refining.

The crude steel was deoxidized at the process of tapping by the addition of Al and FeSi or only Al. It was partially desulfurized and pre-alloyed. In the case of steel production by the triplex procedure on the ASEA-SKF device, heating and precision steel alloying were performed. Refining ladle with melt was transported to a secondary metallurgy SS-VOD (Strong Stirring-Vacuum Oxygen Decarburisation) facility, which is a type of the keson. In the production of steel by the duplex procedure, the transportation of the refining ladle to a facility of secondary metallurgy ASEA-SKF was performed, where the following operations took place:

- steel heating (thermal and chemical homogenization with the help of mixing Ar and EMS (Electromagnetic Stirring))
- alloying and deoxidation of steel
- reduction of non-metallic inclusions and their modification
- vacuum treatment with the help to reduce the content of the (H), (N) and the deep desulfurization of steel
- final stirring or inclusions, or another ingredient of Ca into the steel
- cast steel into the sand casting (a cast), or into the mold (ingot)

Steel samples for analysis of the effect of calcium on the liquidus and solidus temperatures were taken by an immersion sampler in the course of melting after alloying, homogenizing with argon and EMS in vacuo.

1. Before the pre-injection of pure Ca by the feeder of filled profiles.
2. After the injection of pure Ca.

This procedure was chosen due to the minimum dispersion of the steel chemical composition and therefore for the same conditions for measuring the liquidus temperature and the solidus temperature before and after adding Calcium into the steel. After sampling was performed chemical analysis on a spectral analyzer.DTA analysis was carried out with samples taken from the above mentioned heats. Samples of cylinders ø 3,5 mm and hight 2,5 mm were cut, sanded and then cleaned in acetone. Samples were analysed in corundum crucibles in an inert atmosphere (Ar, 6N). Setaram SETSYS 18_{TM} thermal analyser equipped with graphite furnace was used for performing DTA. Samples were analysed at heating process. The heating rate of samples was 10 °C/min. DTA curves from heating process were evaluated nad solidus and liquidus temperatures were obtained.

RESULTS AND DISCUSSION

Measurements of the solidus and liquidus temperatures were performed on samples taken in seven operating heats:

4 heats of the G17CrMoV5-10 (24 886, 25 118, 25 307, 25 351) quality.
1 heat of the G20Mn5 (24 603) quality.
1 heat of the GX4CrNi13 - 4 (25 243) quality.
1 heat of the X46Cr13 (24 724) quality.

Each melt had a different final Ca content (Table 2). The results of measuring the liquidus temperatures are shown in Table 3. The results of measuring the solidus temperature are shown in Table 4.

Table 2 **The calcium content in the selected heats**

The calcium content in the melt / ppm			
Heat No.:	before alloing Ca	after 1. alloing Ca	after 2. alloing Ca
24 886	5	29	-
25 118	7	51	-
25 307	5	21	32
25 351	10	35	-
24 603	12	48	-
25 243	5	30	-
24 724	12	26	-

Table 3 **Changes of liquidus temperature of analysed heats**

Change of liquidus temperature T / °C				
Heat No.:	before alloing Ca	after 1. alloing Ca	after 2. alloing Ca	ΔT
24 886	1 508	1 507	-	- 1
25 118	1 507	1 505	-	- 2
25 307	1 506	1 505	1 503	- 3
25 351	1 506	1 504	-	- 2
24 603	1 506	1 506	-	0
25 243	1 490	1 491	-	+1
24 724	1 463	1 463	-	0

Table 4 **Changes of solidus temperature of analysed heats**

Change solidus temperature T / °C				
Heat No.:	before alloing Ca	after 1. alloing Ca	after 2. alloing Ca	ΔT
24 886	1 429	1 433	-	+ 4
25 118	1 470	1 455	-	- 15
25 307	1 469	1 469	1 469	0
25 351	1 464	1 462	-	- 2
24 603	1 470	1 471	-	+ 1
25 243	1 473	1 474	-	+ 1
24724	1 424	1429	-	+ 5

With the steel grade of G17CrMoV5-10, a decrease of the liquidus temperature after putting the Ca ingredient was found - by 1 and by 3 °C. The solidus temperature was increased by 4 °C. With No. 25 118 heats, the solidus temperature was decreased by 15 °C and with the melt No. 25 351 by 2 °C.

With the G20Mn5 steel, after adding of Ca, there was a decrease of the liquidus temperature by 0 °C and the solidus temperature increased by 1 °C. With the steel grade of GX4CrNi13-4, there was an increase of the liquidus temperature after adding Calcium by 1 °C and there was the solidus temperature increase of 1 °C. The steel grade X46Cr13 liquidus temperatures increased by the calcium ingredient by 0 °C and the solidus temperature increased by 5 °C.

Rating of micropurity of steel after vacuum treatment and after doping Ca into the melt was performed according to the ISO 4967:1998 method B on the area of 200 mm^2. During the rating of micropurity of steel after vacuum treatment globular oxides of the grade from 0,5 to 1 were found. During the rating of micropurity of steel after doping Ca only globular oxides of the grade from 0,5 to 1 were found.

For the verification of the calcium effect on the mechanical properties of steel castings, there were evaluated impact strength tests.

Figure 1 presents a comparison of the energy impact of two castings of cast steel of the same weight and of the G17CrMoV5-10 quality according to EN 10213:2007 and by the same heat treatment. The first casting was cast from the melt No. 25 102 containing 5 ppm of calcium and the other casting was cast from the melt No. 25 118 containing 51 ppm of calcium.

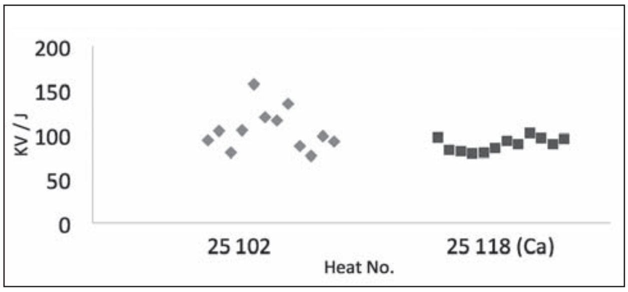

Figure 1 Comparison of the values of impact energy for heat with 5 ppm Ca with heat with 51 ppm Ca

APPLICATION OF RESULTS IN A STEEL AND FOUNDRY PLANT

The temperatures obtained from DTA were used to control the metallurgical treatment of steel in the process of casting of ingots and castings. From the evaluated fusions it follows that a sufficiently high content of Ca in the melt enables lowering temperature of 5 °C in the steel processed by the machine ASEA-SKF and SS-VOD. The reduction of melt overheat above the liquidus temperature also reduces the power consumption required for the production of steel.

CONCLUSIONS

From the measured liquidus and solidus temperatures using DTA follows that the Ca content of the melt to 32 ppm lowers the liquidus temperature by 1 - 3 °C and the solidus temperature is on increase by 0 - 4 °C. As a result of this restricted interval of solidification, the internal quality and surface quality of castings improves. In the casting of high-alloy steels with a content of 30 ppm Ca, there increases the liquidus temperature by 0 - 1 °C and solidus temperature by 1 - 5 °C. The Ca content in the steel over 35 ppm, by contrast, the liquidus temerature decreases by 2 °C and the solidus temperature decreases by 2 - 15 °C. Thus the fluidity of steel is improved.

The evaluated operating melts show a high level of purity and the homogenity of the cast microstructures of samples. Even distribution of mechanical properties over the entire cross section of the casting is documented by minimum variance values of toughness of steel containing Ca = 51 ppm compared with the steel with Ca = 5 ppm (Figure 1).

The above mentioned findings can be used to control the metallurgical quality of casting of complex shaped steel castings, ingots or more ingots from one cast.

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