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USING CALCIUM-CONTAINING INJECTION WIRE FILLED WITH ELECTROLYTIC CALCIUM IN STEEL LADLE TREATMENT

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Abstract. Aluminum is one of the most common deoxidizers; when it is used in the melt, refractory inclusions of alumina are formed. The presence of these non-metallic inclusions negatively affects the purity of liquid steel, mechanical properties, makes casting difficult due to tightening of the steel-pouring fittings. The modification of alumina inclusions with calcium promotes the formation of liquid calcium aluminates, which leads to an acceleration of their removal from the metal due to a higher ascent rate. Having a high affinity for sulfur, calcium reduces its harmful effect by binding it with the formation of calcium sulfides, reducing the anisotropy of steel properties during further rolling. For steel treatment with calcium, injection wires with a calcium-containing filler are used. As a filler can be used: electrolytic calcium, silicocalcium, aluminum-tremic calcium, or ferrocalcium. The paper describes results of the tests carried out on a calcium-containing wire filled with electrolytic calcium and silicocalcium. It is shown that the consumption of calcium when using silicocalcium wire is on average 35 % higher in comparison with calcium injection wire filled with electrolytic calcium. The calcium recovery rate for different steel grades was evaluated using calcium-containing wires of different designs and filler. In this work, the steel pourability was analyzed. As a determining parameter, dependence of change in position of the tundish stopper rod on calcium content in the metal was considered in the sample from CCM. It was established that a wire filled with electrolytic calcium shows a more effective result in comparison with a silicocalcium wire.

Keywords: steel ladle treatment, calcium-containing injection wire calcium, electrolytic calcium, silicocalcium

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ОПЫТ ПРИМЕНЕНИЯ КАЛЬЦИЙСОДЕРЖАЩЕЙ ИНЖЕКЦИОННОЙ ПРОВОЛОКИ С НАПОЛНИТЕЛЕМ ИЗ ЭЛЕКТРОЛИТИЧЕСКОГО КАЛЬЦИЯ НА ЭТАПЕ ВНЕПЕЧНОЙ ОБРАБОТКИ СТАЛИ

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Аннотация. Алюминий является одним из наиболее распространенных раскислителей, при его использовании в расплаве образуются тугоплавкие включения глинозема. Присутствие данных неметаллических включений негативно влияет на чистоту жидкой стали, механические свойства, затрудняет разливку вследствие затягивания сталеразливочной фурнитуры. Модифицирование включений оксида алюминия кальцием способствует образованию жидких алюминатов кальция, что приводит к ускорению их удаления из металла ввиду более высокой скорости всплытия. Обладая высоким сродством к сере, кальций связывает ее, образуя сульфиды, тем самым уменьшая вредное влияние серы и снижая анизотропию свойств стали при дальнейшей прокатке. Для обработки стали кальцием используют инжекционные проволоки с кальцийсодержащим наполнителем. В качестве наполнителя могут быть использованы электролитический кальций, силикокальций, алюмотермический кальций, феррокальций. В данной работе описаны результаты проведенных испытаний кальцийсодержащей проволоки с наполнителем из электролитического кальция и силикокальция. Показано, что расход кальция при использовании силикокальциевой проволоки в среднем на 35 % выше в сравнении с кальциевой инжекционной проволокой с наполнителем из электролитического кальция. Проведена оценка коэффициента усвоения кальция для различных сортаментов сталей при использовании кальцийсодержащих проволок разных дизайнов и наполнителя. Выполнен анализ разливаемости стали, где в качестве определяющего параметра рассмотрена зависимость изменения положения штока стопора промежуточного ковша от содержания кальция в металле по пробе с установки непрерывной разливки стали. Установлено, что проволока с наполнителем из электролитического кальция показывает более эффективный результат в сравнении с силикокальциевой проволокой.

Ключевые слова: внепечная обработка стали, кальцийсодержащая инжекционная проволока, кальций, электролитический кальций, силикокальций

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INTRODUCTION

The properties of rolled steel products largely are significantly influenced by the presence of impurities such as sulfur, phosphorus, nitrogen, hydrogen, and others, as well as the content of non-metallic inclusions (NMI) that enter the metal during melting process. The chemical composition, quantity, distribution pattern, and morphology of MNIs have a profound impact on the quality and properties of steel.

In contemporary practice, aluminum is commonly added to steel for the purpose of final deoxidation. However, the deoxidation product (Al_2O_3), known as alumina, can form irregular shaped inclusions that tend to cluster together, as reported by Wasai K. et al. [1]. These inclusions have the potential to cause surface defects in rolled steel (Zaitsev A. et al. [2]) and adhere to casting equipment [3 – 5].

In order to mitigate these negative effects, the composition of NMI can be efficiently modified. Calcium is extensively employed as an additive through the use of calcium-containing cored wires [6 – 9]. The addition of calcium to steel enables control over the chemical and phase composition of NMI, making the steel more suitable for deep drawing operations and reducing the occurrence of hydrogen-induced cracking [10 – 13].

When calcium is added to the liquid metal, it dissolves throughout the entire volume. This leads to a reaction with Al_2O_3 inclusions [14; 15], resulting in their convertion to a liquid phase [16]. As a result, the refining rate is accelerated, with the liquid inclusions rising to the surface more rapidly. Lind M. [17] and Yang J. et al. [18] have documented the reaction responsible for the formation of calcium aluminates

$$\left(x+\frac{4}{3}y\right)\mathrm{Al_2O_3(s)}+y[\mathrm{Ca}]=\left(\mathrm{Al_2O_3}\right)_x\left(\mathrm{CaO}\right)_y+\frac{2}{3}y[\mathrm{Al}].$$

Calcium, known for its strong affinity for sulfur, forms sulfide and oxysulfide NMI (also at the crystallization front). Insufficient level of calcium accumulation along the centerline of the continuous casting billet can result in the elongated manganese sulfide inclusions. This centerline region may contain NMI and micro-discontinuities, leading to the rejection of rolled sheets during ultrasonic inspection or an increased susceptibility to hydrogen-induced cracking in corrosive environments [19].

The modification of NMI with calcium is a complex process. One key challenge involves maintaining the optimal range of calcium concentration within the melt, as well as ensuring the stable assimilation of calcium. Calcium has a high vapor pressure and its addition can induce intense boiling, which may cause liquid metal ejection from the ladle. Therefore, the method by which calcium is added to the liquid metal is crucial. Calcium should be introduced to the depth of the melt, where the ferrostatic pressure balances the pressure of the calcium vapor [20]. The effectiveness of a calcium-containing wire depends on multiple factors, including the steel and slag composition, steel temperature [21] weight, wire insertion rate, as well as wire design and a filler composition.

The filler is enclosed in a steel outer layer [22; 23], which serves the following functions:

– protecting the filler during shipping and storage by preventing contact with air and moisture;

– preventing the filler oxidation by acting as a barrier as the wire passes through the slag layer on the metal’s surface;

– providing rigidity to the wire, enabling it to pass the slag layer;

– facilitating controlled wire introduction depth by preventing direct contact between the core and liquid metal; this can be achieved by adjusting the wire feed rate and the thickness of the outer layer;

– the key design features of the wire include the outer diameter, calcium-containing filler diameter, steel outer layer thickness, outer layer joint type.

In current practice, calcium can be used as a filler material in both powdered and solid forms. The different types of calcium fillers include:

- electrolytic calcium;
- aluminothermic calcium;
- ferrocalcium;
- silicocalcium.

Each of these fillers possesses distinct characteristics, such as variations in the content of metallic calcium, impurity elements, and consequently, the assimilation rate. These differences in wire properties contribute to inconsistencies in the calcium addition process.

The objective of this study is to compare the performance of different calcium-containing wires using pure electrolytic calcium filler and silicocalcium filler.

Materials and Methods

We conducted tests on a ladle-furnace line using calcium-containing wires. The filler material used was pure electrolytic calcium. The wire designs were as follows:

- outer diameter: 10 mm; outer layer thickness: 0.8 mm (10×0.8);
- outer diameter: 11 mm; outer layer thickness: 0.8 mm (11×0.8);
- outer diameter: 10 mm; outer layer thickness: 1.0 mm (10×1.0).

For each wire design, the wire feed rate was adjusted accordingly, ranging from 120 to 180 m/min.

The composition of the wire filler is listed below (in %):

Ca	Al	Si	Mg	K + Na
99.300	<0.001	<0.010	0.010	<0.010

The table presents the physical characteristics of the calcium-containing wire.

Physical characteristics of the wire

Физические характеристики используемой проволоки

Property	Wire design, mm		
	10×0.8	11×0.8	10×1.0
Weight of the filler, kg	675	666	598
Fill factor, %	25	27	21
Rated filler content per 1 m of wire, g	74	94	67
Rated weight of 1 m of wire, g	295	342	323
Calcium consumption, g/ton	95	99	113

The wire was utilized in 43 melts, comprising 51 % medium-carbon (0.14 to 0.22 % carbon content), 37 % low-carbon (carbon content <0.14 %) and 12 % low-carbon, low-silicon steel products. A wire-feeding machine introduces the wire into the ladle with the molten metal. No instance of wire breakage were observed. We conducted a comparative analusis of the results obtained from this wire and the CK40 powder-cored wire.

Results and Discussion

Initially, we compared the average consumption per melt and the calcium consumption (Fig. 1, 2). It is evident that the CK40 wire demonstrate a higher average consumption compared to the calcium-containing wire with an electrolytic calcium filler, ranging from 30 to 45 %. The calcium consumption is higher by 30 to 40 %.

In addition, we conducted an analysis of the steel pourability to evaluate the impact of introducing calcium wire on pourability, while avoiding any obstruction to the casting equipment with with NMI). In order to achieve this, we recorded the positions of the intermediate tundish stopper rod during the steel casting process (Fig. 3). Positive values of this property may indicate the initiation of the NMI deposition, while negative values suggest erosion of refractory steel components. Our findings revealed that the stopper rod positions for calcium-containing wire sizes 10×1.0 and 11×0.8 are negative. This implies that the consumption of these wire sizes can be reduced in comparison to wires sizes 10×0.8 and CK40.

Fig. 4 illustrates the relationship between steel pourability and calcium content for the calcium-containing wire designs tested. It is evident that wire grades 10×1.0 and 11×0.8 exhibit the following trend: as the calcium content increases, the displacement of the intermediate tundish stopper rod shifts towards negative values. The obtained result aligns perfectly with Fig. 3. However, it is important to acknowledge that the variance in the displacement of the stopper rod is relatively high, indicating the presence of additional factors.

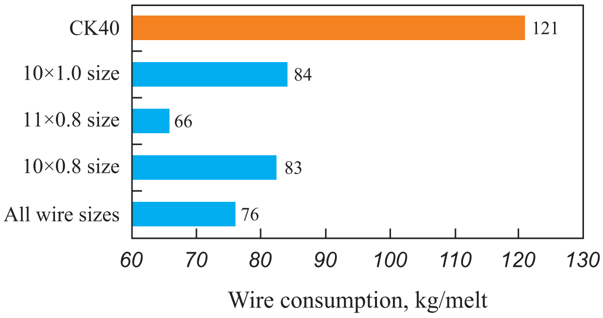

Fig. 1. Consumption of calcium-containing wire for melting

Рис. 1. Расход кальцийсодержащей проволоки на плавку

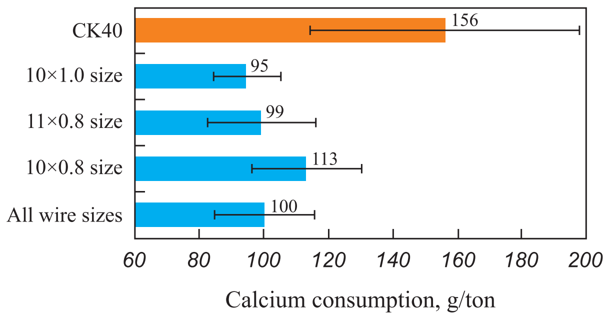

Fig. 2. Calcium consumption for melting

Рис. 2. Расход кальция на плавку

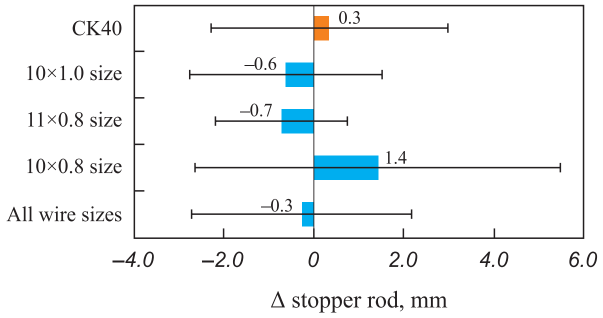

Fig. 3. Changing the tundish stopper position

Рис. 3. Изменение положения штока стопора промежуточного ковша

We thoroughly examined Fig. 3 and 4 and determined the optimal calcium content in the liquid metal that ensures consistent steel pourability for the tested wire grades. The results are depicted in Fig. 5.

Fig. 6 displays the estimated calcium assimilation factors for each wire size tested, categorized by steel grade. The findings indicate that the 11×0.8 wire exhibits the highest assimilation factor for low-carbon and carbon steel grades, whereas the 10×1.0 wire yields the best results for low-silicon steel grades. On average, wires with electrolytic calcium cores demonstrate assimilation factors that are 35 to 45 % higher compared to the CK40 wire.

Furthermore, it is important to emphasize that the primary objective of adding calcium to steel is to enhance the pourability and quality of rolled products. The calcium assimilation factor serves as a valuable tool for estimating the process variables required to achieve the desired calcium content in the melt under specific casting conditions.

CONCLUSIONS

We conducted a performance comparison between calcium injection wire filled with electrolytic calcium and the calcium-containing CK40 wire. Our findings reveal that, on average, the former wire exhibits a 30 to 45 % lower consumption (depending on the wire design) compared to the CK40 wire. To assess the steel pourability, we measured the position of the intermediate tundish stopper rod. Through our analysis, we determined that a minimum calcium content of 10 to 12 ppm in the metal guarantees consistent steel pourability. It is evident that expressing steel pourability in terms of the position of the interme-

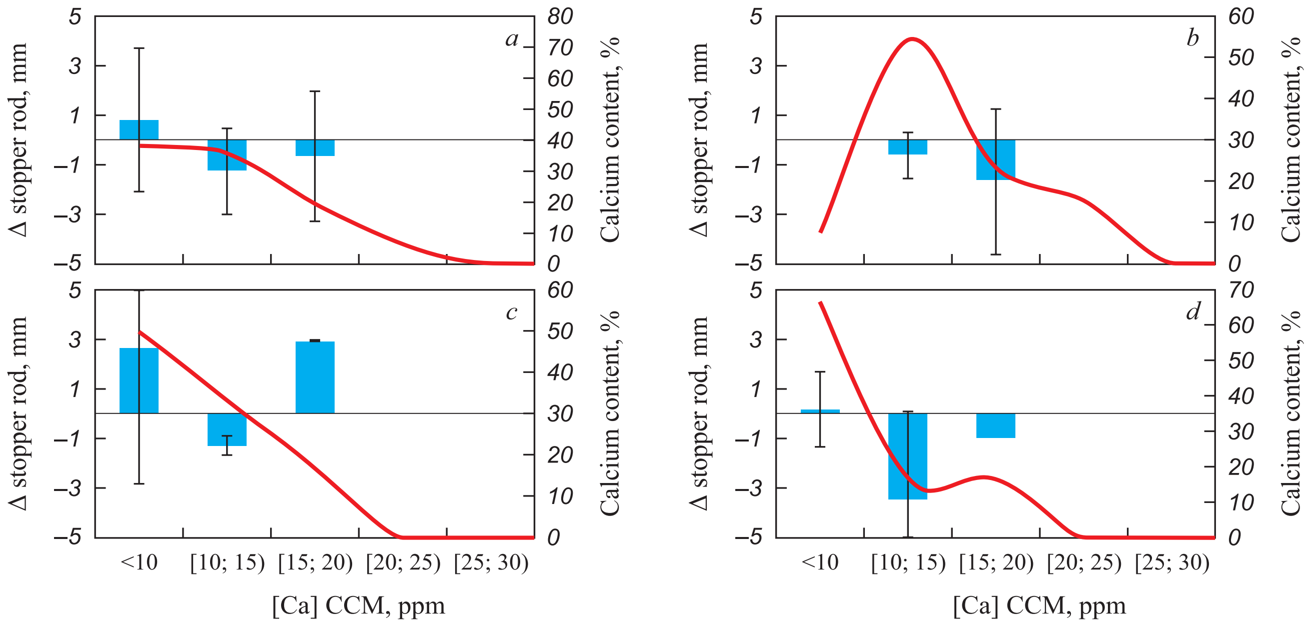

Fig. 4. Dependence of the tundish stopper rod from calcium according to the certification piece:
a – all calcium injection wires (CIW); *b* – 11.5×0.8; *c* – 10×0.8; *d* – 10×1.0; 🟦 – Δ ram, mm; ━ – data, %

Рис. 4. Зависимость положения штока стопора промежуточного ковша от содержания кальция по данным аттестационной пробы:
a – все КИП; *b* – 11,5×0,8; *c* – 10×0,8; *d* – 10×1,0; 🟦 – Δ штока, мм; ━ – данные, %

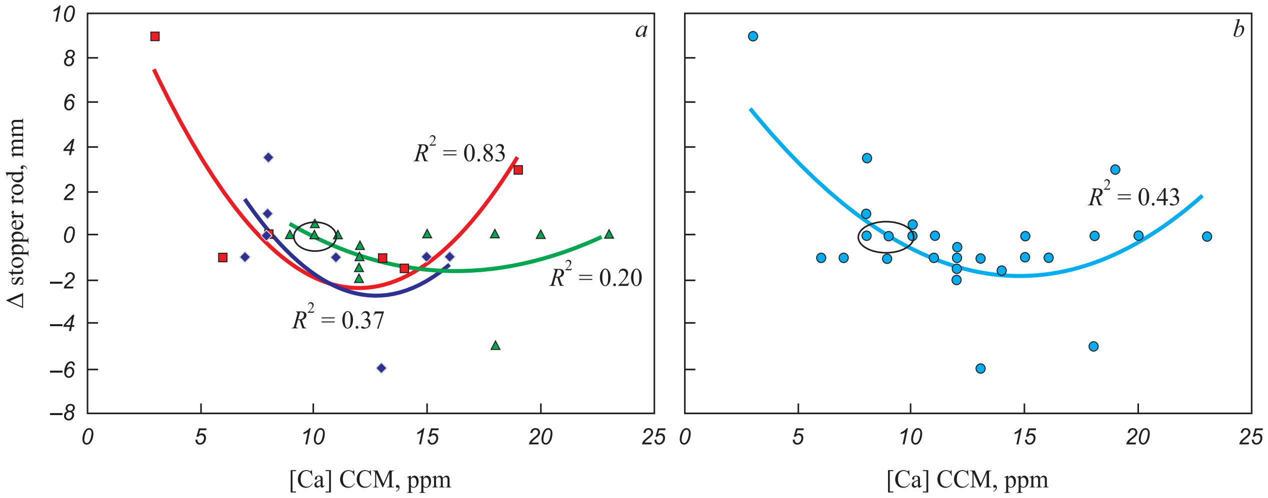

Fig. 5. Optimal calcium content in the metal:
🟥 – CIW 10×0.8, ◆ – CIW 10×1.0, ▲ – CIW 11×0.8 (*a*); ● – all CIWs (*b*)

Рис. 5. Оптимальное содержание кальция в металле:
🟥 – КИП 10×0,8, ◆ – КИП 10×1,0, ▲ – КИП 11×0,8 (*a*); ● – все КИП (*b*)

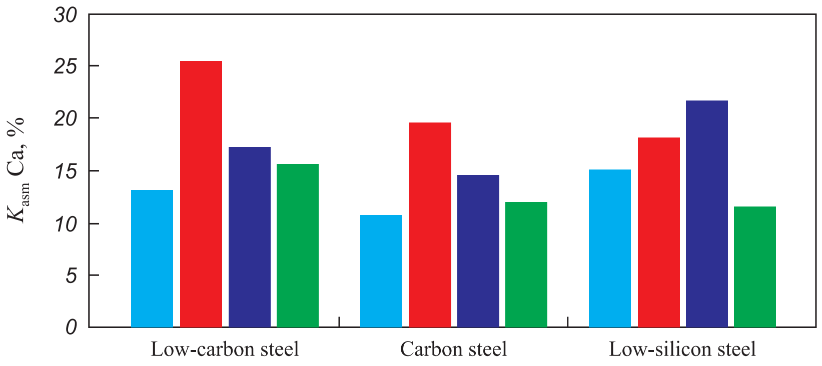

Fig. 6. Calcium recovery rate for various calcium-containing wires:
🟦 – 10×0.8; 🟥 – 11×0.8; ■ – 10×1.0; 🟩 – SK40

Рис. 6. Коэффициент усвоения кальция для различных кальцийсодержащих проволок:
🟦 – 10×0,8; 🟥 – 11×0,8; ■ – 10×1,0; 🟩 – СК40

diate tundish stopper rod serves as a convenient metric for evaluating the calcium-containing wire performance.

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