Article

Improving Shipbuilding Steel Grade Quality at Stages of Smelting, Secondary Refining, and Continuous Casting

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Abstract: This work studied the effect of the amount of additives and the composition of refining slags on the metallurgical of steel grades of the S355G10, S420G2, and S460G2 types. The objects of study were samples of industrial melts after out-of furnace refining of steel with different amounts and nature of additives. Based on the results obtained, the recommended amounts of additives and the composition of the refining slag have been developed, which makes it possible to reduce the metal contamination with non-metallic inclusions.

Keywords: continuous casting; alloying; deoxidation; structure; inclusions; shipbuilding steel

1. Introduction

The technological complexity of the process of obtaining high-quality shipbuilding steel is caused by the close interrelation of all technological conversions including the smelting of intermediate products, metal finishing and secondary, out-of-furnace refining, casting on continuous casting machines, roughing and finishing rolling of continuously cast billets (CCBs) by exactly following the specified thermo-mechanical treatment that completes the process of obtaining rolled products. Each conversion contributes to forming the structural heterogeneity observed in the finished rolled products [1–4].

In the production of low carbon micro-alloyed vanadium and niobium steels with manganese content of up to 1.5%, special attention should be paid to the metallurgical quality of continuously cast billets (CCBs). The metallurgical quality of CCBs is primarily determined by the level of steel contamination with nonmetallic inclusions of the endogenous and exogenous nature of formation. Inclusions of the endogenous nature of formation remaining in steel after secondary refining contribute to the overgrowth of immersion cups during steel casting, lead to forming clusters of nonmetallic inclusions in the finished product, and form a spot heterogeneity zone in CCBs. The inclusions of the exogenous nature of formation, the source of which are worn-out bucket lining particles, entangled slag particles, as well as casting node particles also contribute to forming clusters of nonmetallic inclusions that have a negative effect on continuity, mechanical properties, and performance characteristics of the finished product. The increased gas saturation of steel, including increased content of nitrogen and hydrogen, leads to forming gas bubbles, flocs in steel, internal laminations, as well as disruption of the metal continuity [5–8].

In the process of secondary refining and subsequent casting of steel, nonmetallic inclusions are formed and distributed over the volume of the metal in accordance with their temperature-time nature

and surface properties at all the boundaries of coexisting phases, taking into account hydrodynamics of the melt behavior. During the billet solidification in continuous casting machines, dendritic and zonal chemical heterogeneities develop in CCBs, different structural zones are formed in accordance with the gradient that arose before the crystallization front, nonmetallic inclusions continue forming not only because of decreasing the temperature, but mainly due to the melt enrichment with liquation impurities. Thus, in the cast state, macro- and micro-structural heterogeneity is formed over the CCB section, due to the above-mentioned physical and chemical processes. This heterogeneity is superimposed by a highly inhomogeneous thermal-deformation effect with the following plastic deformation caused by the specificity of the plate-rolling process that occurs under conditions of extremely uneven distribution of temperatures, stresses, strain degrees, and rates across the thickness of the rolled strip. Thus, chemically and structurally inhomogeneous CCBs undergo uneven thermal mechanical processing, during which microstructural banding is formed inherited from dendritic heterogeneity, and a segregation band inherited from axial point and/or zonal segregation. In the areas poorly developed during hot rolling, there will remain structural components morphologically inherited from the structure of the cast metal, such as Widmanstätten ferrite, coarse austenite grains inherited from uncrushed cast crystals [9,10].

It is known from metallurgical practice that increasing the metallurgical quality of a metal can be performed at the stage of metal producing from a steelmaking unit, secondary refining steel by optimizing the deoxidation technology and modifying liquid steel, as well as during continuous casting by protecting the metal mirror in the crystallizer and affecting the crystallizing ingot [11–13].

Such characteristics as the quantity, the morphology, and the distribution pattern of nonmetallic inclusions in the metal matrix are mainly laid at the stage of metal producing from a steel-smelting unit, as well as in the process of deoxidation and steel modification during its secondary refining. The technology of deoxidizing and modifying steel, including their introduction into steel, the sequence and method of their introduction into the steel melt, should ensure the most complete removal of deoxidation products from the liquid metal, as well as the minimum content of nonmetallic inclusions in the finished metal [14–16].

The objective of this study is developing measures to improve the quality of shipbuilding steel grades such as S355G10, S420G2, and S460G2 by adjusting the additives of aluminum and silicocalcium and adjusting the composition of the refining slags.

2. Materials and Methods

In the framework of this work, for analyzing shipbuilding steel grades (S355G10, S420G2, and S460G2) contamination with nonmetallic inclusions, samples of cast metal from three pilot melts were selected in the amount of 10 pieces from each melt. At the steel vacuuming stage, samples were taken before and after modification with calcium-containing reagents directly from the casting ladle. At the stage of steel continuous casting, samples were taken from the tundish ladle in the course of metal discharging from the casting ladle. Samples were taken using vacuum samplers, the liquid metal solidified in quartz molds, and the sample sizes were no more than 30 mm in diameter and 10 mm in height.

To carry out metallographic studies of metal contamination with nonmetallic inclusions, the samples underwent several grinding stages that included cutting samples on a cutting machine using abrasive wheels, hot pressing in phenolic resin in an automatic press, multistage grinding and polishing on an automated grinding and polishing machine. By combining the materials, the rotational speeds of the polishing wheel, pressure on the samples, and duration of the polishing stages, an optimal quality of the section was achieved that consisted in the absence of scratches, surface relief, crumbled inclusions adhering to the polishing suspension. Evaluation of metal contamination with oxide and sulfide nonmetallic inclusions was carried out in 100 fields of view on non-etched sections in accordance with the ASTM E 1245 standard.

To determine the chemical and phase composition of the detected non-metallic inclusions, X-ray microanalysis capabilities were used. X-ray microscopic studies of the chemical composition of the nonmetallic inclusions found were performed using a ZEISS SUPRA 55VP (Carl Zeiss AG, Germany) scanning electron microscope. This microscope is equipped with an electron beam computer control scanning system and digital signal and image recording, as well as an INCA WAVE (Oxford instrument, Oxfordshire, UK) and INCA X-MAX (Oxford instrument, Oxfordshire, UK) X-ray micro-analyzer.

3. Results

In the present work, in order to develop technological recommendations aimed at improving the quality of shipbuilding steel grades of the S355G10, S420G2, and S460G2 types, we took part in the technological support of the production of three pilot melts under the conditions of oxygen-converter production. From these melts for the analysis of metal contamination by nonmetallic inclusions we took samples of the cast metal at the steel vacuuming stage after modification with calcium-containing reagents (ferrocalcium), as well as at the continuous steel casting stage.

Figure 1 shows the flow chart of the secondary refining of shipbuilding steel, the melt mass is 360 t. The chart is a graph of the melt temperature changing in the course of processing against the background of the material additives being applied at various stages. Vertical columns indicate the quantities, type, and time of the analysis of the process of adding materials: aluminum was used as a deoxidizing agent (secondary when discharged, then in the form of chaff) and ferrosilicon; alloying agents were metallic manganese (Mn = 95%), ferromolybdenum (Mo = 60%), metallic nickel, and ferroniobium, slag-forming lime.

Figure 1. Flow chart of the secondary refining of shipbuilding steel, 2017.

As the analysis of the producing technology of the three pilot melts of shipbuilding steel showed, for all the melts there were no significant deviations in the carbon content at the metal discharge from the converter ($[C]_{av} = 0.039\%$). Accordingly, the metal oxidation at that stage should also be at the same level ($[O]_{calc} = 0.073\%$). At the same time, the total amount of aluminum added during the secondary refining stage for melt No. 1 has the maximum value compared to melts No. 2 and No. 3 (1014 kg versus 869 kg and 968 kg). This leads to increasing the concentration of aluminum in steel before casting (0.046% versus 0.029% and 0.032%) and increasing the Al/Ca value (the ratio of the total weight of aluminum to the total weight of added calcium) to 10.24 (versus 7.49 and 7.39). Despite the

fact that this value is satisfactory, this leads to increasing the proportion of Al_2O_3 in the composition of nonmetallic inclusions of this melt compared to the others.

The difference between the total time elapsed from the moment of discharging from the converter to the start of casting, and the total time of metal processing at different stages of secondary refining, conditionally the “idle time”, does not exceed 100 min for all three melts. However, the maximum value is observed in melt No. 2 and makes 76 min. Since this parameter represents the time within which the lining of the ladle and slag interacted without an active parallel mixing of the melt due to purging with an inert gas, an increased amount of the $\text{MgO-Al}_2\text{O}_3\text{-CaO}$ system with MgO content up to 30% in that melt was recorded (Figure 2). The calculation of the oxide and sulfide components content in the composition of each inclusion was carried out on the basis of X-ray microanalysis data and the corresponding stoichiometric ratios between the elements. Verifying the phase composition was carried out using isothermal sections of triple state diagrams. For example, for inclusion having, according to X-ray microanalysis, composition $\text{Ca} = 32.04\%$; $\text{Al} = 14.81\%$; $\text{Mg} = 1.17\%$; O —the rest, the mass content of oxides (CaO) = 60%; (Al_2O_3) = 37%; (MgO) = 3%. The phase composition corresponds to $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ with an insignificant content of MgO .

Figure 2. Nonmetallic inclusion of the $\text{Al}_2\text{O}_3\text{-MgO-CaO}$ system with 30% MgO revealed in melt No. 2, 2017.

In one of the experimental melts, the presence of melt processing was twice recorded at the ladle-furnace set (before steel was vacuumed and before casting); in addition, the interval between introducing the main mass of aluminum and calcium was 41 min. This leads to forming large inclusions in the form of calcium aluminate compounds of the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ type, with the CaS content up to 4%, being completely in the liquid state at modifying temperatures, reach in this case the size of $15\text{ }\mu\text{m}$ (Figure 3). The presence of such sufficiently large calcium aluminates in the metal is associated with a large time interval between introducing the last portion of aluminum and calcium-containing reagents. This leads to an insufficient degree of modification of nonmetallic inclusions and their incomplete removal from the melt [14].

Figure 3. Nonmetallic inclusion of the Al_2O_3 -CaO-CaS system revealed in melt No. 3, 2018.

Thus, based on analysis of the production process of the three pilot melts of shipbuilding steel, as well as the results of the metallographic analysis of metal contamination and X-ray microanalysis of nonmetallic inclusions, the following optimal flow chart for the production of shipbuilding steel grades was determined. For smelting steel in an oxygen converter, it is necessary to use liquid pig iron that has been desulfurized and metal scrap with the lowest possible level of contamination with non-ferrous metal impurities in the ratio of 75–85% pig iron and 15–25% metal scrap.

On the metal discharge from the oxygen converter after the primary slag has been cut off with a cone, lime in the amount of 2000–2500 kg is added as 10% of the discharge duration, silicon-manganese-containing materials are introduced as 20% in an amount necessary to provide the specified content of [C], [Mn], [Si]. If necessary, micro-alloying additives are added. A proportion of 30% pig iron is introduced in the amount of 400–800 kg. If possible, the time of steel discharging from the converter should be minimized (5–6 min). To minimize as possible the time of discharging steel from the converter for prevention of oxidation and decreasing the temperature of discharging. The production experience shows that the optimal time is 5–6 min. To reduce the time is technically impossible.

As soon as possible, steel is purged with argon after the metal is discharged from the converter. In this case, the faster the steel begins to be purged with argon after the metal is discharged, the more favorable conditions are formed for the removal of nonmetallic inclusions.

The amount of aluminum introduced at the discharging from the converter should not exceed the critical value determined by the steel oxidation. The option of using only Mn and SiMn for preliminary deoxidation is also not excluded, the introduction of aluminum is carried out at later stages. The final aluminum deoxidation should be performed shortly before introducing the modifier into the metal. In addition, a more uniform introduction of alloying materials (FeNb, FeMo, Cu) should be ensured in the course of secondary refining with a single injected portion not exceeding 350 kg.

During subsequent secondary refining it is necessary to ensure that the aluminum content in steel is 0.01–0.02% higher than the upper limit of the steel grade composition by introducing aluminum no more than 10 min before introducing calcium-containing materials. When vacuuming steel, the amount of aluminum and silicocalcium should be in the range of 0.89–0.91 kg of aluminum per 1 kg of silicocalcium. For effective assimilation of inclusions, it is recommended to strive to direct refining slags close to the following composition: 50.00–55.00% CaO; 5.50–6.50% SiO_2 ; 2.00–2.40% FeO; 6.60–7.00% MgO; and 31.00–33.00% Al_2O_3 . It should be noted that liquid calcium aluminates, similar in composition to $\text{CaO} \cdot \text{Al}_2\text{O}_3$, are formed at relatively low aluminum contents in steel $[\text{Al}] < 0.01\%$ that do not fall within the specified grade interval. Therefore, it is recommended for the entire working range for calcium ($[\text{Ca}] = 0.0005\text{--}0.0050\%$) to be at the lower limit for aluminum $[\text{Al}] \rightarrow 0.015\%$.

To minimize the effect of the metal secondary oxidation, it is recommended to increase the tightness of the casting elements stages of casting ladle–tundish ladle, as well as tundish ladle–mold. The following intensities of purging with argon during continuous casting are recommended: 140 L/min for the steel ladle–the tundish ladle interval and 14 L/min for the tundish ladle–the crystallizer interval. These values have been obtained from the empirical observations when developing the technology of smelting the steel grades mentioned above. To ensure a uniform fine-grained structure of continuously cast billets and to minimize segregation processes during crystallization, it is necessary to use a system of soft reduction of an ingot in the solid-liquid state.

4. Conclusions

Based on the comprehensive studies carried out, it was established that in order to improve the quality of shipbuilding steel grades of the S355G10, S420G2, and S460G2 types in the course of its vacuuming, the amount of aluminum and silicocalcium added should be in the range 0.89–0.91 kg of aluminum per 1 kg of silicocalcium. For effective assimilation of inclusions it is recommended to strive to use refining slags close to the following composition: 50.00–55.00% CaO; 5.50–6.50% SiO₂; 6.60–7.00% MgO; 31.00–33.00% Al₂O₃; and <1% FeO.

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