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Preventing liquid aluminium adhesion to surface of copper crystallizer by creation protective oxide film

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Abstract. In order to achieve prevention of molten aluminium adhesion to the surface of a copper crystallizer, an oxide film producing the needed thickness is suggested. Potassium permanganate $\text{KMnO}_4$ in the form of an aqueous solution can be used as an oxidizing agent with the positive result of its usage being proved experimentally. The thickness of a $\text{KMnO}_4$ layer estimated by a computational-experimental way is about (~0.3 µm), inter-reaction with molten aluminium leads to oxide film formation, which is thick enough to prevent aluminium sticking to the copper surface. The needed solution $G_{sol}$ consumption, fed for atomizing inside the crystallizer in order to achieve the layer of $\text{KMnO}_4$ formation of the indicated thickness, is defined by the chosen solution concentration, perimeter $P$ of a crystallizer groove and linear velocity $V$ of surface moving during casting wheel rotation. For instance, the solution consumption might equal $G_{sol}=23$ l/h with the concentration equal to 0.3% with the characteristic of the crystallizer of $P=0.5$ m, $V=0.38$ m/s.

1. Introduction
One of the factors, decreasing dramatically the operation life of copper crystallizers of a casting machine of a continuous casting unit and aluminium wire rod rolling, is molten aluminium adhesion to the crystallizer groove surface [1] with formation of aluminium outgrowths there after solidifying the melt, which deteriorates the workpiece surface quality. The outgrowths removal at production sites tends to be accomplished by mechanical abrasive cleaning. During this process alongside with aluminium, the crystallizer surface coating is removed as well, which leads to walls thinning. When the walls are thinned till the certain gauge, the crystallizer is rejected.

For the prevention of the above-mentioned adhesion to the groove surface at the domestic production, sites are usually tallowed with animal grease. For this purpose one uses lubrication with oils, emulsions, cooling liquids, lubricants including chloride-containing ones [2,3]; the use of all those either fails to achieve optimum effect or is limited due to the adverse environmental impact.

In this regard, the development of an effective and relatively cheap way of crystallizer protection from molten aluminium adhesion seems to be a relevant objective. The work in question proposes one of the possible solutions to this problem.

2. Reasons of the technical solution
In accordance with the unit for a rod production technical scheme, molten aluminium with the temperature of 700-720 °C comes from the mixer into the casting bath (1 Fig.1). Through the spout it is...
moved to the shroud groove (2) of the water-cooled crystallizer casting wheel (4) with the walls temperature about 120-150 °C where it is covered with a steel tape (5) [4]. Accomplishing 3/4 of rotations simultaneously with the crystallizer, the melt inside the groove crystallizes, and in the form of a continuously cast ingot (6) is moved to the rolling mill [5]. The aluminium-free surface of the groove is lubricated with animal grease by means of the shoe (7), and until it reaches the place of melt feeding it is exposed to air oxidation.

Figure 1. Scheme of casting machine crystallizer: 1 - casting bath, 2 - crystallizer shroud, 3 - atomizers, 4 - casting wheel, 5 - steel tape, 6 - aluminum ingot, 7 - shoe with oil rags, 8 - shaft of the driving unit.

When reasoned about the technical solution, we relied on the data that having perfect contact of fine (i.e. with oxide-free surface) solid metals with liquid ones; their inter-reaction leads to forming an adhesive bond between them (as a result of metallic characteristics) even in spite of the possible dissolution absence between these metals [6]. The presence of an oxide film on the solid metal surface reduces intermetallic inter-reacting in case of one group of metals, while in case of another one it keeps it at a high level [7]. As a rule, the latter is found in case of a liquid metal, which has strong affinity to oxygen [6]; in our situation it is aluminium. At the same time, its adhesion to solid metal oxide increases along with a thermodynamic stability decrease, i.e. with a decrease of its affinity to metal oxygen forming this oxide. Considering the fact that copper oxides (CuO, Cu2O) forming on the crystallizer surface have low thermodynamic stability [8], strong liquid aluminium adhesion is to be expected not only to the pure copper surface but also to the oxidized one, as it happens in the process of crystallizer exploitation where the melt sticks to the oxidized copper surface.

It is a well-known fact that upon the molten aluminium contact with oxygen and oxygen-containing agents on the surface of the melt, oxide film Al2O3 is instantly formed. It has high strength and protective properties [9]. In this regard, it could be supposed that to prevent liquid aluminium adhesion to the crystallizer surface, an oxide film thick enough to avoid adhesive bond between the melt and copper substrate is needed to be formed on the melt before its contact with the copper surface. For such purpose, the usage of ambient oxygen as an oxidizing agent, delivered between the spout of the casting
bath and the groove surface, turned out to be technically unrealizable due to the possibility of space plugging with oxidation products. After the analysis of chemical agents, capable of instant inter-reacting with liquid aluminium without negative impact on the process of the melt crystallization, as such oxidizing agent, the authors chose potassium permanganate KMnO₄ in the form of aqueous solution and interreacting with molten aluminium according to the reaction [10]:

\[ 2\text{Al} + 2\text{KMnO}_4 = \text{Al}_2\text{O}_3 + \text{K}_2\text{O} + 2\text{MnO}_2 \]  

with an oxide film formation consisting of aluminium oxides, potassium and manganese.

3. Experimental test of the technical solution and evaluation of the needed amount of the oxidizing agent.

The samples cut out of the copper wire (d = 1 mm) with pointing ends were maintained at the temperature of around 150 °C, as the temperature of the crystallizer groove surface at the moment of its contact with the melt for the time of about 1 minute needed for their complete preheating and surface oxidation. The aluminium sample was inserted (about 10g) into the other thermostat heated to 700 °C (the temperature of the melt in the casting bath), and it was soaked in a graphite crucible till its total meltdown and heating till the temperature of thermostat. The pointing ends of the samples were immersed to the melt with the subsequent inspection for the presence of the stuck aluminium remains to their surfaces. The other part of the heated samples was immersed to the water or in to the solution of different concentrations, and they were again heated to 150 °C, dipped in the melt and observed. The appearance of the ends of the samples after the tests is presented in figure 2.

![Figure 2](image)

**Figure 2** - The appearance of the samples after the contact with the molten aluminium: untouched (*a*), with preliminary immersion into the water (*b*), the same into the 1-2% solution KMnO₄ (*c*), the same into its 3% solution (*d*).

It was discovered that immersing heated copper samples into the melt leads to the aluminium films formation on the surface (Fig.2, *a*). The films are firmly tied to the copper substrate and it is possible to remove only with the coating surface. Preliminary samples immersed into the water and solution KMnO₄ of the concentration 1-2% do not change the results of the process (Fig.1, *a, b*). At the moment of immersing, water is boiling in the local amount of the liquid around. At the same time, starting with the concentration of 3%, the subsequent immersion of the samples to the melt does not lead to the liquid metal adhesion to them (Fig.2, *d*), which can be an experimental proof of the positive impact of the potassium permanganate, left in the samples, to the copper property to prevent the surface from molten aluminium sticking. Observation of the place of the melt contact with the copper substrate processed with 3% solution failed to detect any specific particularities in the form of the solid melt and substrate surfaces.

The layer thickness δK₄MnO₄, remaining on the sample after the immersing it into the solution of the indicated concentration, was established due to the assumption that all the heat Q evolved in sample cooling from T₁=150 °C to T₂=100 °C as the temperatures of water boiling termination is expended
for the water evaporation from the solution with all the amount of KMnO₄ in the volume of the evaporated water staying on the surface ($S_{smp}=35\,\text{mm}^2$) of the immersed part of the sample.

Then the mass of the boiled over water:

$$M_{H_2O} = \frac{C_{Cu} \cdot M_{Cu} \cdot (T_1 - T_2)}{L} = 1 \cdot 10^{-6} \, \text{kg}$$

where $C_{Cu}$ - copper heat capacity (385 J/(kg K)); $M_{Cu}$ - mass of the immersed part of the sample (0.142 $\cdot 10^{-3}$ kg); $L$ - heat of water evaporation (2,260 $\cdot 10^6$ J/kg).

Accordingly, the mass of KMnO₄ left on the copper surface after the water boiling over 3% solution is 0,03 $\cdot 10^{-6}$ kg, and the layer thickness:

$$\delta_{KMnO_4} = \frac{M_{KMnO_4}}{S_{smp} \cdot \rho_{KMnO_4}} = 3,2 \cdot 10^{-7} \, \text{m (0,32 µm)},$$

where $\rho_{KMnO_4}$ - density of KMnO₄ (2700 kg/m³).

In accordance with (1) such layer thickness of KMnO₄ corresponds to the thickness of the layer of Al₂O₃:

$$\delta_{Al_2O_3} = \delta_{KMnO_4} \cdot \frac{M_{Al_2O_3}}{2 \cdot M_{KMnO_4}} \cdot \frac{\rho_{KMnO_4}}{\rho_{Al_2O_3}} = 0,07 \cdot 10^{-6} \, \text{m (0,07 µm)},$$

where $M_{Al_2O_3}$, $M_{KMnO_4}$ - molecular weight Al₂O₃ (0.102 kg/kmol) and KMnO₄ (0.158 kg/kmol); $\rho_{Al_2O_3}$ - density Al₂O₃ (3990 kg/m³).

It can be noted that the thickness of the oxide film is close to the maximum thickness that is forming on the surface of the aluminium in the air of about 0.2 µm.

4. Technological design of the technical solution

Aqueous solution of KMnO₄ of the indicated concentration is suggested to atomize continuously with the necessary solution discharge $G_{sol}$ to the crystallizer groove surface before liquid metal feeding. Entering the heated (with T being around 150 °C) surface of a massive crystallizer, the water from the solution evaporates instantly, and till the moment of contact with the melt on the groove surface a layer of permanganate is left designed to be thicker ($= 0.32 \, \mu\text{m}$).

$G_{sol}$ is estimated by the chosen concentration of KMnO₄ (% KMnO₄), groove geometrics and linear velocity of its surface moving V while casting wheel rotation:

$$G_{sol} = (\delta_{KMnO_4} \cdot \rho_{KMnO_4} \cdot \frac{\Pi \cdot V}{1000\%});$$

with $\Pi$ - groove perimeter.

Choosing the concentration of KMnO₄ equal to, for instance, 0.3%, the needed solution discharge for the crystallizer with characteristics $P=0.5$ m, $V=0.38$ m/s would be 23 l/h. Solution feeding and atomizing with such discharge could be provided by the electric pump TMZ, model NDG 1,0 RE 25/40 ($G_{max}=25$ l/h; $P_{max}=40$ bar; N=0.25 kW) [11] and an atomizer of the firm VKT, model CU 7622-110 08 ($G_{max}=0.36$ l/h; spray angle - 110, bore diameter - 0.8 mm) [12].

The technical solution presented protects the surface of crystallizers from aluminium adhesion and also is available and reasonably priced. As the oxide film will be applied to the surface of the melt.
without any dynamic effect, its impingement to the melt itself is excluded as it could have adversely affected the quality of the solid ingot.

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