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TECHNOLOGIES OF REFINING AND RECYCLING OF COPPER AND COPPER ALLOYS

TECHNOLOGIE RAFINACJI I RECYKLINGU MIEDZI I JEJ STOPÓW

It is proposed the complex of technologies for refinement and recycling of Copper and Copper alloys – technologies of deoxidizing, degassing, filtration, impurities oxidizing, fluxing and intermetallic compounding refinements, and also technology of thermal reduction. Their application is actual both to provide the high quality of production, and to decrease the expenses for their manufacture by involving the maximum quantity of scrap materials in charge, including slag waste received from slag.
Keywords: Refining and recycling of copper and copper alloys, filtration, thermal reduction

Zaproponowano kompleksowe technologie rafinacji i recyklingu miedzi i jej stopów. Technologie obejmują odtlenianie, usunięcie zanieczyszczeń gazowych, filtrację, usunięcie wtrąceń metodą ich utlenienia, rafinację żużlową i rafinację wtrąceń międzymetalicznych, a także technologię redukcji termicznej. Ich zastosowanie zarówno istotnie umożliwia uzyskanie produktów o wysokiej jakości i zmniejsza koszty wytwarzania przez stosowanie maksymalnej ilości złomu we wsadzie, jak też umożliwia odzysk użytecznych składników z żużla.

It is proposed the complex of technologies for refinement and recycling of Copper and Copper alloys – technologies of deoxidizing, degassing, filtration, oxidizing, fluxing and intermetallic compounding refinements, and also technology of thermal reduction. Their application is actual both to provide the high quality of production, and to decrease the expenses for their manufacture by involving the maximum quantity of scrap materials in charge, including slag waste received from slag.

The technology of deoxidizing refinements involves removing of the excessive dissolved Oxygen from liquid Copper or Bronze.

The effective technology of Copper deoxidation by Carbon is proposed. Carbon is low dissolved in liquid Copper and forms a deoxidation product in a gas phase form which can be easily removed from melt. However, the reaction of Copper deoxidation by Carbon [C] + [O] = CO proceeds very slowly because it is realised on a kinetic regime. Consequently the rate of all deoxidation process is limited by the rate of chemical reaction. Therefore for the intensification of the Copper deoxidation process it is necessary for liquid Copper to provide: a) an increase of the reactionary surface (boundary surface of Copper-Carbon) and b) activation of the removing process of reaction product – monoxide of Carbon (CO). For this purpose: a) a special reactor provides repeated increase of a reactionary surface, and b) melt flushing by inert gas are applied [1].

Such technology is especially important at Oxygen-free Copper manufacture. So, by using this technology of deoxidizing refinement allows Copper receiving with Oxygen content no more than 5-10 ppm %.

The technology of degassing processings provides melt refinement from extra dissolved Hydrogen and a decrease of casting and ingots defectiveness on gas holes and porosity. To increase the process efficiency the technology of melt flushing by thin high-speed streams of inert gas is proposed. For reception of thin streams apply nozzles with extremely small sections into the gas channel, and for the providing of the high-speed outflow of the gas stream the pressure of injected gas P_{inj} must be maintain as for a critical level, at which Mach number M = 1.

The combination of stream thinness and high speed of its extrusion the stream dispersion of injected gas on greater number of small gas bub-

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bles is provided. Thus the interface ≪metal-gas≫ wherethrough the Hydrogen extraction increase accordingly. Small gas bubbles also emerge more slowly, therefore duration of their contact to liquid metal increases, which provides fuller course of Hydrogen extraction process. It is also conducted that the high-speed stream has the big distance of action and consequently the emerging course of bubbles becomes longer.

Using the technology of degassing processings at the liquid Cast Iron by flushing of Nitrogen causes to significant increase of the melt quality and castings. It was obtained improving the casting properties, raising of the structure uniformity, reduction of the structural components size, perlitizing of metallic matrix, stabilization or increasing of the mechanical properties dates, decreasing of the casting defectiveness by slag and sand inclusions, gas holes, porosity and cracks [2].

The technology of filtration refinement provides melt clearing from nonmetallic particles by the realization of a grid, adhesive and seed mechanisms. Thus the resultant effect of filtration refinement is equal to sum of its partial effects: $\eta_{sum} = \eta_{grid} + \eta_{adh} + \eta_{seed}$.

At the grid mechanism the particle of the foreign phases, with size greater than size of filter channels, hold on the entering side of the filter. Therefore the grid effect $\eta_{grid} = P$, where P – a quota of the particles with size greater than size of filter channels.

At the adhesive mechanism nonmetallic particles settle on inner walls of filter channels. Thus the adhesive effect is numerically equal to quantity of the particles delivered to walls of filter channels on various mechanisms:

$$\eta_{adh} = 1 - (1 - \eta_{capt}) \cdot (1 - \eta_{seed}) \cdot (1 - \eta_{ctf}) \cdot (1 - \eta_{grad}),$$

where η_{capt}, η_{seed}, η_{ctf} and η_{grad} – quotas of the nonmetallic particles are delivered to a surface of the filter at the expense of effects of direct capture (contact), sedimentation, centrifugal forces and a gradient of velocity of the melt flow on section of filter channel accordingly.

At the seed mechanism the above equilibrium dissolve impurity elements R (O, S, etc.) are removed from melt. They are removed from a solution by linkage to the chemically combined condition – nonmetallic phase (R_mO_n, R_mS_n and others). Thus reaction of formation of a nonmetallic phase is realised directly on the filter surface as on the ready substrate.

Efficiency of the seed mechanism η_{seed} depends on initial and equilibrium concentration of impurity removal, and also its diffusion coefficient and a thickness of diffusion layer in filter channels. Besides, value η_{seed}, as well as η_{adh} (η_{capt}, η_{sed}, η_{ctf} and η_{grad}) are defined by filter parametres (thickness, size curvature and tortuosity of channels), conditions of filtering (velocity), properties of filtered melt (viscosity and density) and parameters of nonmetallic particles (density and the sizes).

On the basis of the developed conceptions about the mechanism and laws of filtration refinement of liquid metals the new type of the filter – **gradient-porous**- is developed [3]. It differs from known filters, because the pore channels are executed in it consistently narrowing in a filtering direction. Such filters have the best combination of high efficiency of filtrational refinement owing to involvement of all filter layers in the refining process, the maximum throughput (absence of channels blinding) and low hydraulic resistance.

The technology of oxidising refinement provides clearing of Copper and Copper alloys from impurity elements [R] dissolved in them which have greater affinity to the dissolved Oxygen [O], than base elements of the alloy. The process is based on the realisation of the reaction: m [R] + n [O] = (R_mO_n).

For the effective realisation of this reaction and achievement of the maximum effect of refinement it is necessary to provide the high content of the dissolved oxygen in melt and to reduce activity of the reaction product (R_mO_n).

The first problem is solved by the selective input of Oxygen in melt in the form of O_2, CuO or ZnO. The second problem is solved by selective application of flux or slag which is able to dissolve the products of oxidation R_mO_n.

An example of this technology using is the deep refinement of brass melts from impurities of Aluminium and Silicon by mixes based on oxides of Zinc and Copper. Achieved effect essentially depends on many technological factors: content and quantity of the refining composition, duration and processing temperature, and also intensity of melt mixing during the refining treatment. At using the recommended processing parameteres the refinement effect of 70-90% can be reached [4, 5].

The technology of flux processing provides clearing of Copper melt from nonmetallic inclusions. Besides fluxes are used to protect the melt against oxidation, and also to ease the input of nonmetallic reagents in refined liquid metal. Therefore specified requirements are many-sided also. Fluxes for treatment of Copper alloys has to be low-melting and less dense (concerning Copper), with low viscosity and a surface tension, well moisten the nonmetallic inclusions and etc. On the basis of availability, ecological compatibility and efficiency the choice of flux components is limited enough and include NaCl, Na_2CO_3, $Na_2B_4O_7$, Na_3AlF_6, Cu_2O, ZnO, etc.

As the nature of nonmetallic inclusions (Al_2O_3, SiO_2, Ca_2Pb, etc.) in Copper alloys is different and depends on the presence of those or others impurity elements (Al, Si, Pb, etc.), and also the applied refining reagent (P, C, Li, B) so the fluxes for carrying out of refining processes use selectively.

The technology of intermetallic compounding refinements provides removal of impurities in Copper melt which fail to be extracted by Oxidising refinement methods. Such impurity is Lead in Brass. Lead is widely used as alloying element, but is hazardous to health. And consequently in recent years the Lead content has been limited in Brasses under the factors of life safety.

For removal of lead from Brass melt by the method of Intermetallic compounding refinements is proposed. This method is based on compounding of Lead to a stable chemical (intermetallic) connection by treating of Lead-containing melt by Rare-Earth or Alkaline- earth metals (Ce, La, Y, Ca).In this case the reaction of Lead intermetallic compound forming is realized: $[Me] + n\ [Pb] = Me_mPb_n$.

Realisation of this reaction, first of all, provides the neutralization of Lead by transforming it from active metallic condition to non-active intermetallic condition. Moreover, the part of Lead as Intermetallic compound, which formed at Liquid Brass, may be removed from Melt by various methods – Filtering, Fluxing, Gas-Injection and Sedimentation [6, 7].

The technology of thermal reducing is using for recycling of Copper from Slag or from the waste of mechanical utilization, where the largest quantity of Copper is presented as oxides. The refining process is based on the realization of Copper reducing reaction: $2(CuO) + 2C + CaCO_3 = 2[Cu] + (CaO) + 2\{CO_2\}$.

Carbon is used as the reducer, and limestone as the activator for the reducing process. To increase the Effectiveness of this reaction it is necessary to realize the reducing process in the presence of Flux and Seeder. The Flux provides the decreasing of CaO activity, and Seeder forms the centers for reaction realization [8].

Advantages of this technology consist in possibility of additional copper extraction from slag waste and decrease of irrevocable losses during melting and casting of Copper and Copper alloys.

Relatively high extraction ratio of Copper and Zinc from pulverized waste of brass slag at reducing melting (~ 90-100%) creates possibilities of complex non-waste processing of Copper production waste.

Summary

The proposed Complex of Technologies for Refinement and Recycling of Copper and Copper alloys provides:

1. Production of the refined Copper, including Oxygen-free Copper with the content of Oxygen less than 5 ppm, refined from the harmful impurities, the dissolved Hydrogen and nonmetallic inclusions.
2. Recycling of Copper scraps for manufacture of electrotechnical production;
3. Recycling of Brass scrap to its maximum by using the selective refinement of melt from various impurities;
4. Recycling of Bronze scrap to its maximum by using the effective refinement from various impurities and qualitative deoxidation of melt;
5. Recycling of Copper and alloying elements by reducing them from the slag formed during the melting of Copper and Copper alloys;
6. Refinement of Brass from Lead by its compounding in intermetallic compounds and the subsequent removal from melt.

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