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AN ATTEMPT TO USE VARIOUS METALLURGICAL SLAGS IN THE MODIFICATION PROCESSES OF CASTING ALLOYS

The paper presents preliminary results of research on the use of certain smelting slags in the process of modification of casting alloys, leading to a change in the structure of these alloys and improvement of their mechanical and operational properties. The positive effect of ground copper slag with a fraction below 0.1 mm on the effect of modifying the hypoeutectic silumin AlSi7Mg towards changing the morphology of coarse-grained eutectic to fine-dispersive was demonstrated. The modifying effect also applies to the pre-eutectic α phase and results in the formation of additional crystallization sites (nucleation process), which was demonstrated by the thermal ATD solidification analysis, showing an increase in the temperature T_{liq} and $T_{E\max}$. The positive and noticeable influence of the mixture of copper and steel slag on the surface modifying effect of fragmentation of the structure was demonstrated in casting nickel superalloy IN-713C. Based on the results of research conducted so far on the modifying effect of cobalt aluminate, a hypothetical model of the impact of reduced metallic components of the applied metallurgical slags on the nucleation process and shaping of the microstructure of nickel alloys was developed.

Keywords: Surface modification, metallurgical slags, cobalt aluminate, nickel and aluminium alloys, free enthalpy, microstructure

1. Introduction

Metallurgical slag is the largest group among the total amount of industrial waste. The processes of smelting pig iron and steel produce large amounts of blast furnace and steel-converter slag. A significant amount of slags is produced in the metallurgical processes of smelting copper (copper slag) as well as nickel and zinc. Process dust (zinc production) and electrolysis sludge (copper anode electrolysis) have a significant share in metallurgical waste.

The availability, chemical composition and physicochemical properties of some metallurgical slags as well as economic and ecological considerations constitute the basis for research on the possibility of their use in various industries. Thus, slags can be regarded, on the one hand, as waste from various metallurgical processes, and as an important raw material and output product in other processes, on the other hand. Metallurgical slags are more and more often the object of interest in terms of the possibility of their development, especially as materials used in construction (structural foundations, buildings and other engineering structures), road construction (roads, highways, bridges), in foundry for refining and purification of liquid alloys, production of abrasives for surface treatment of regenerated machine parts, also as mine backing materials, in the production of cement and many other applications [1-4]. In turn, electrolytic sludge and process dust are used to recover some heavy metals (Zn, Cu and Pb) and noble metals (Ag, Au, Pt and others) [5-7].

The analysis of the chemical composition of some metallurgical slags (copper slag and steel slag) shows that they contain many valuable components. These slags, after appropriate mechanical and chemical treatment, can be components of refining and modifying preparations used in the foundry of metal alloys. In this case, it is about improving the metallurgical purity of the liquid alloys and ensuring certain solidification conditions (ability to nucleate), and thus the formation of a favourable structure, for given operating conditions of the device element.

2. Research problem

The chemical composition of most metallurgical slags has been found to contain a number of valuable components that may show refining and modifying properties. After appropriate preparation and introduction into the liquid alloy at a specific

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melting stage, casting, or introduced to the surface of a casting mould, they can affect the nucleation and solidification processes of a specific casting alloy. In this way, they can improve the metallurgical purity and structure, and thus the operational properties of the products.

The presence of Si, Al, Cu, Mn, and Fe was confirmed in the copper granular slag, i.e. the main components of casting alloys and components with modifying properties: Na, Mg, Ca, Ti and P. These components are most often in the form of oxides and in the metallic form. Most of the abovementioned components are present in steelmaking dusts, and additionally in larger amounts of Zn, Fe and Pb and NaCl compounds, KCl and CaF_2, which is important from the point of view of refining and modifying properties. There are studies on the operation of some metallurgical slags in the refining processes of casting alloys, especially steel and aluminum alloys [8-10].

So far, there is no data in the literature on the research on the use of certain slags and dusts in the processes of volume and surface modification of casting alloys.

The paper presents preliminary results of research on the use of suitably prepared slag mixtures and preparations in the processes of modifying the structure of the AlSi7Mg aluminium alloy and the IN-713C nickel alloy.

3. Author's research

3.1. Material preparation

To check the modifying properties, steel slag from the processing of steel dust (known as EAFD from the English "Electric Arc Furnace Dust") obtained from the company BOL REC Sp. z o.o. (Bolesław Recykling) and granulated copper slag obtained from the Głogów Copper Smelter.

A typical chemical composition of dusts in terms of metal content can be presented as a mixture of iron compounds (approx. 40-50%) and zinc (15-25%) with mineralogical compounds. The dust also includes: PbO, MnO, CaO, MgO, Cr_2O_3, Al_2O_3, SiO_2, NaCl, KCl, CaF_2 [11, 12]. In the copper slag, in addition to the main oxide components (SiO_2, Al_2O_3, Fe_2O_3 and CaO), the presence of modifying elements for liquid aluminium alloys, such as Na, Mg, Ca, Ti and P, was found.

Both materials were ground in a Melino Bals ML005 laboratory ball mill and then sieved (1.0, 0.5, 0.25, 0.1, 0.071 sieves). The obtained product was calcined in an electric chamber furnace at the temperature of 800-850°C for 1.5 hours. Slag powders with granulation below 0.071 mm were used for the tests.

3.2. AlSi7Mg hypoeutectic silumin modification

Hypoeutectic silumin is used in many industries, including automotive, aerospace, precision and electromechanical industries, which is the result of low density, good electrical and thermal conductivity, good chemical and corrosion resistance and good mechanical properties [13,14]. The main disadvantage of these alloys is the presence of a coarse-grained eutectic (α + Si solution) in the structure, which reduces the mechanical properties. Therefore, these alloys are modified in the liquid state, which changes the form of coarse-grained eutectic into fibrous eutectic. Proven modifiers in this state are $AlSr_{10}$ in the amount of 0.15% and AlB_4 in the amount of 0.2% [15].

The charge, weighing about 1 kg, was melted in a silicon carbide crucible, in an electric PSK-4 chamber furnace, under a protective slag with NaF and KCl (in a ratio of 20% to 80%).

After reaching the temperature of about 850°C, the specified slag in the amount of 30 g (in two doses of 15 g) was applied to the surface of the bath. The alloy was held at this temperature for about 5 minutes, periodically being vigorously stirred. After this time, the alloy was poured into the QC40-80 probe (40×40×80 mm – registration of the solidification process), pictured in Fig. 1.

Fig. 1. Alloy cast into the QC40-80 probe

Chemical composition of investigated alloy before and after the modification is presented in Table 1.

TABLE 1

Chemical composition of AlSi7 alloy

Stan	Zawartość, % mas.							
	Si	Cu	Mg	Mn	Fe	Ti	Ni	Al
Wyjściowy	7,24	0,56	0,72	0,14	0,38	0,01	0,14	reszta
Po odlaniu	7,14	0,58	0,69	0,12	0,41	0,01	0,15	reszta

The samples for structural testing were taken from the ATD ingot from the temperature measurement area. The specimens were prepared on the Knuth-Rotor machine, using water-based abrasive papers of grain size: 320, 600, 800 and 1000 and dia-

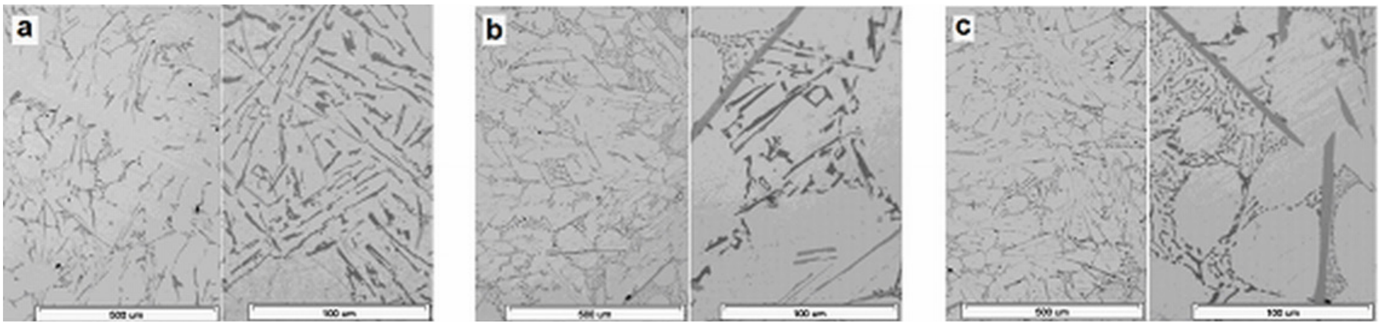

Fig. 2. Microstructure of the AlSi7Mg alloy: initial state (a), modification – steel slag (b), modification – copper slag (c)

mond pastes of 1-3 μm. The metallographic observations and photos taken using the Reichert MeF-2 light microscope by are shown in Fig. 2.

The obtained microstructure images indicate a beneficial effect of modifying with slags on changing the morphology of eutectics from granular to fibrous, especially after modifying with copper slag. The fragmentation of the pre-eutectic α dendrites can also be observed.

In addition, long plate precipitates are observed in the structure, which can be identified as the β-AL$_5$FeSi intermetallic phase, rich in iron, increasing the brittleness of the castings. In some cases, such as machining, the presence of a small amount of this phase improves chip breakage.

The results of the ATD thermal analysis (the whole study is presented in [16]) indicate an increase in T_{liq} temperature by 4°C, after modification with copper slag. This may indicate a slight but observable effect of heterogeneous nucleation. Probably, the finely dispersive compounds present in the copper slag, based on silicon, copper and calcium, may constitute "foreign" (heterogeneous) bodies, acting as supports for the pre-eutectic crystallization of α dendrites and then eutectics.

Thus, on the basis of the conducted research, it can be stated with caution that a properly prepared granulated copper slag (grinding, screening and drying) introduced in a small amount into the alloy shows satisfactory modifying properties. The obtained results should be an incentive to conduct further research in this direction, using a wider range of slags, e.g. nickel slag and any other slag containing chlorides (NaCl and KCl) and compounds of phosphorus, sodium and potassium.

3.3. Surface modification of IN-713C nickel alloy castings

Nickel-based casting alloys called superalloys are among the most popular materials used for high temperature and mechanical stress operation. They are used in particular for the production of gas turbine components, used in many industries for energy production, including land, sea and air transport [17].

One of the most important structural parameters in superalloys is the grain size. As the grain size is increased, the high-temperature creep time and heat resistance increase, while the yield point and tensile strength decrease. Castings with a fine-grained structure show higher tensile strength and yield point [18]. The relationship presented in Fig. 3 is based on data from the literature – the author has not conducted research in this direction.

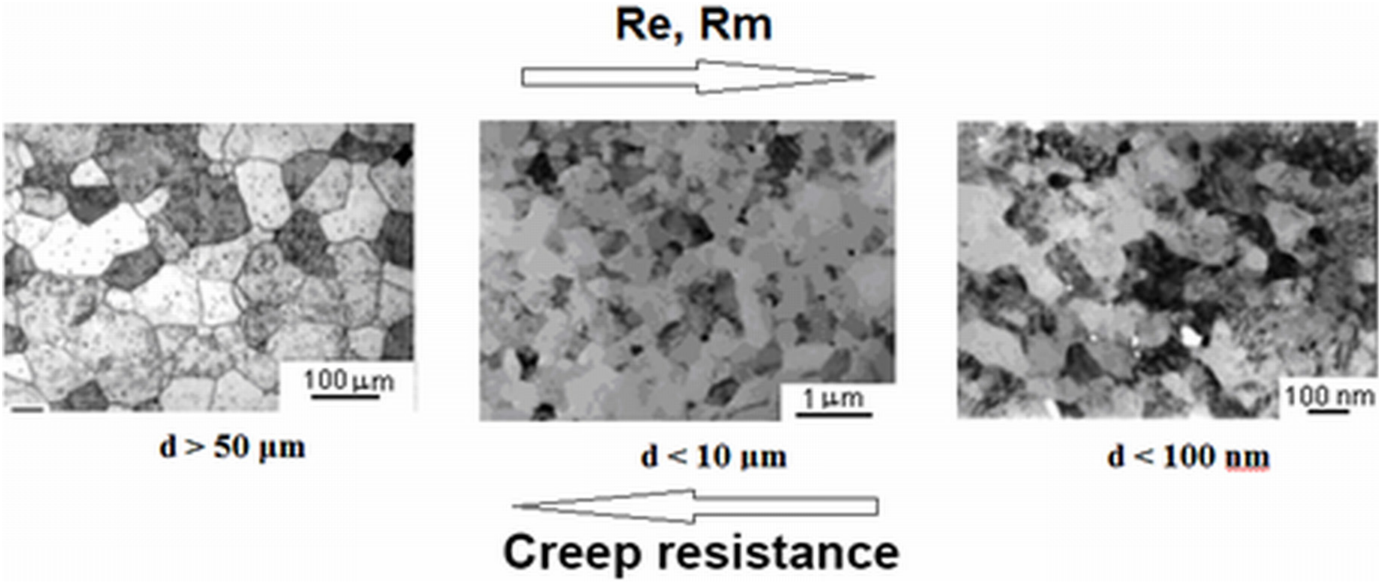

Fig. 3. The influence of grain size on the properties of nickel superalloys castings

The fragmentation of the structure can be achieved by the use of modifiers introduced into the surface layer of the mould. Experiments with cobalt aluminate $CoAl_2O_4$ as a component of the mould coating have shown that it is likely that atomic cobalt, released from aluminate (as a result of reduction by some alloy components), may act as a nucleus [19,20]. Hafnium, niobium, aluminium, titanium and chromium have the strongest reduction effects [21]. Under certain temperature conditions (supercooling and cooling intensity), the formed Co particles are stable and can combine into groups (clusters) of over critical size. The lower the casting temperature and the thinner the walls of the casting, the more clusters are formed – the final macrostructure of the casting is therefore more fine-grained.

Thermodynamic calculations

There are valuable components in the form of metal and non-metal oxides in copper slag and steel dust. The use of these materials in the process of surface modification of nickel alloy castings will require the separation of pure elements from their oxides. One such proven reducer for most oxides is coal, preferably in the form of ground coke breeze [22]. Carbon reducing abilities were confirmed by appropriate calculations of the free enthalpy of the chemical reaction. It was assumed that these elements, similarly to atomic cobalt (as described earlier), would be able to act as seeds of near-surface crystallization.

These processes will be favored by high temperature, in the first stage when pre-heating of the moulds at a temperature of about 950°C and in the second stage during casting in the temperature range of 1350 to 1500°C.

Thermodynamic calculations were performed in the HSC Chemistry computer program by Outotec (formerly Outokumpu Technology) version 4.1 [23,24]. The Reactions Equations module was used for the calculations, which enables the determination of the thermodynamic potentials of chemical reactions in any selected temperature ranges.

The calculations were performed for the chemical reactions presented in Table 2.

TABLE 2

Reactions of oxides with carbon

Symbol	Reaction equations
1-A	$Cu_2O + C = 2Cu + CO(g)$
1-B	$MnO + C = Mn + CO(g)$
1-C	$TiO + C = Ti + CO(g)$
1-D	$FeO + C = Fe + CO(g)$
1-E	$Fe_2O_3 + 3C = 2Fe + 3CO(g)$
1-F	$MgO + C = Mg + CO(g)$
1-G	$Na_2O + C = 2Na + CO(g)$
1-H	$K_2O + C = 2K + CO(g)$
1-I	$Cr_2O_3 + 3C = 2Cr + 3CO(g)$
1-J	$ZnO + C = Zn + CO(g)$

Free enthalpy calculations were carried out in the temperature range of 1000 to 1500°C (step 50°C). For the sake of comparison, the mean change in free energy ΔG was calculated in the range from 1350°C to 1500°C related to one mole of the tested reagent. In casting conditions of nickel superalloys, this is the temperature range on the mould – liquid alloy interface. These are the conditions at the mould-metal interface at the time of casting the alloy. The results of these calculations are shown in Fig. 4.

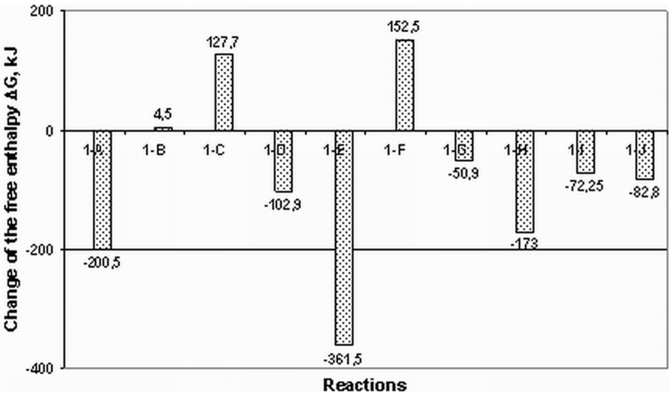

Fig. 4. Average change of the free enthalpy ΔG as a function of temperature for the considered reactions of oxides with carbon

The occurrence of the reaction is possible only with a negative value of the free energy, while the negative value is higher, the more intense the reaction is. Thus, in the studied temperature range, the reactions of carbon with oxides of MgO, TiO and MnO are impossible. The highest negative value of the free enthalpy shows the reactions of carbon with oxides Fe_2O_3, Cu_2O, FeO, K_2O, ZnO, Cr_2O_3 and CaO.

Thus, at a temperature above 1350°C (conditions in the case of casting nickel and cobalt alloys), on the border of the mould surface – liquid alloy, presence of metallic Cr, Fe, Cu and Zn atoms is possible.

The method and direction of modifying the impact of the above-mentioned components on the fragmentation of the macrostructure of nickel alloy castings is related to the physical properties of potential modifiers and main alloy components, i.e. Ni (IN-713C). and Co (MAR-247). An important parameter is the melting point and the type and parameters of the crystallographic lattice at a temperature close to the temperature prevailing at the "mould-alloy" interface at the time of casting, ie above 1350°C. A summary of these parameters is presented in Table 3.

Table 3 shows that a potential modifier for nickel alloys may be chromium, which at a temperature above 1350°C (average solidification point of the IN-713C alloy), has an A3 crystal lattice identical to Ni (hexagonal compact) and with similar parameters [28].

The activation energy of the nucleation process ΔG decreases when there is a similarity of the crystal lattice and the interatomic distances of chromium and nickel.

The chromium particles can therefore take part in the nucleation process, thus causing grain refinement on the surface

TABLE 3

Melting point and crystal lattice type

Element	Ni	Co	Fe	Cr	Cu
T_{mel}, °C	1453	1495	1535	1857	1083
T < 400°C	A1 a = 0,3523 nm	A3, Co_α a = 0,2580 nm, c = 0,4069 nm	A2 a = 0,286 nm (<768°C)	A2, Cr_α	A1 a = 0,362 nm
T > 1350°C	A3 a = 0,2622 nm	A1 , Co_β (>400°C) a = 0,3545 nm	A1 a = 0,365 nm (910-1390°C)	A3, Cr_β (>1350°C)	A1 a = 0,374 nm (>950°C)

of the castings. In the case of copper, its modifying effect on the form-liquid alloy interface may consist in causing a local temperature decrease as a result of immediate melting, after reducing the slag coating from the mixture. The effect of lowering the temperature is the occurrence of supercooling which promotes the nucleation process.

The experiments

For the preparation of modifying coatings, zirconium flour, cobalt aluminate, a mixture of copper slag and steel slag with a grain size of less than 0.071 mm and colloidal silica were used, which allowed to obtain a thick suspension that could be applied to the surface of the mould. Three experiments were performed:

- 1st mould – without modifying coating,
- 2nd mould – a coating of zirconium flour and 5% cobalt aluminate $CoAl_2O_4$ (existing technology),
- 3rd mould – a coating of zirconium silicate (40%) and a slag mixture (ratio 1: 1) (60%) and 5% ground coke breeze.

The ceramic mould, made by the lost wax method, is shown in Fig. 5.

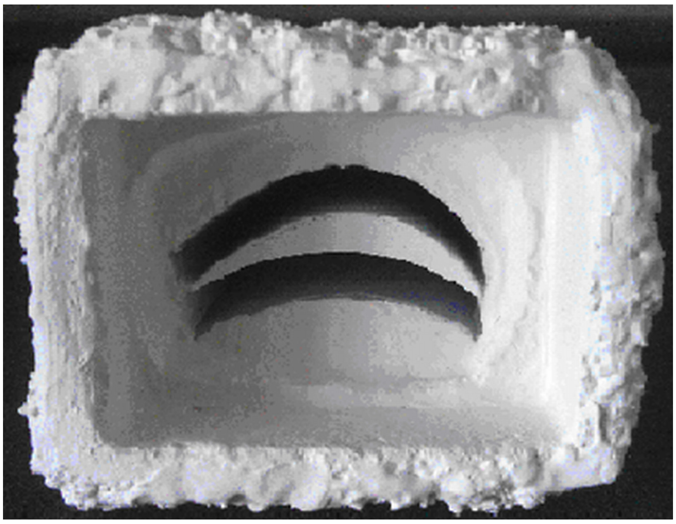

Fig. 5. The cavity of the ceramic mould

The IN-713C nickel alloy was melted in the Balzers VSG-02 induction furnace. About 1.2 kg of the alloy was placed in the Al_2O_3 crucible. Melting was performed under a vacuum of about 10^{-3}. Before being put into the induction furnace chamber, the mould was heated in a chamber furnace for 1 hour at a temperature of about 850°C. An example casting (height 100 mm, wall thickness: top – 6 mm, bottom – 0.5 mm, weight about 1 kg) is shown in Fig. 6.

Fig. 6. Cast from experiment no. 2

Microstructure examination

The surfaces of the castings and samples were etched in Marble's reagent. Images of the surface macrostructure of the castings (mould-metal boundary) at the height in relation to the position in the mould are shown in Fig. 7. A strong influence of the solidification intensity on the grain size can be observed. As the wall thickness of the casting decreases (the intensity of solidification increases), the grain size decreases.

Observations of the microstructure were carried out on samples from the side of the modified surface, taken in the middle of the casting height. The samples were digested in Marble's reagent. The obtained images were processed in the Met-Ilo

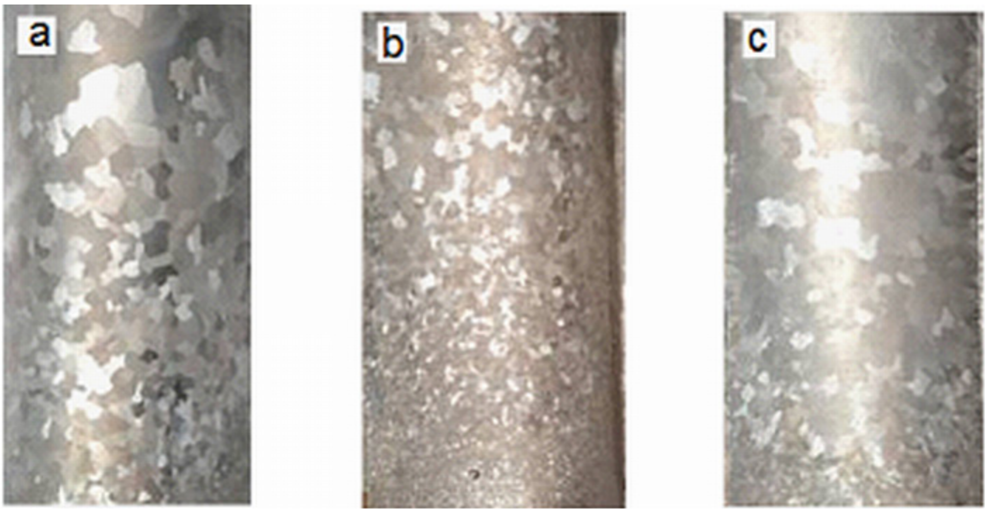

Fig. 7. Change of the surface structure at the height of the castings: unmodified (a)

program and appropriate calculations were made [25]. The following macrostructure parameters were assessed:

- number of grains per unit area L_g [per 1 mm^2],
- average grain area A_g [mm^2].

The results of the macrostructure examinations are presented in Fig. 8, while the results of the calculations of the stereological parameters are presented in Figs. 9-10.

The strongest surface modification effect was found for the casting made in a mould with a coating containing cobalt aluminate. The obtained effect confirms the results obtained so far for the technology used currently [26-29].

Encouraging results were obtained for the casting made in a mould with a coating containing a mixture of copper slag and steel dust. The average grain size of about 4.78 mm^2 indicates

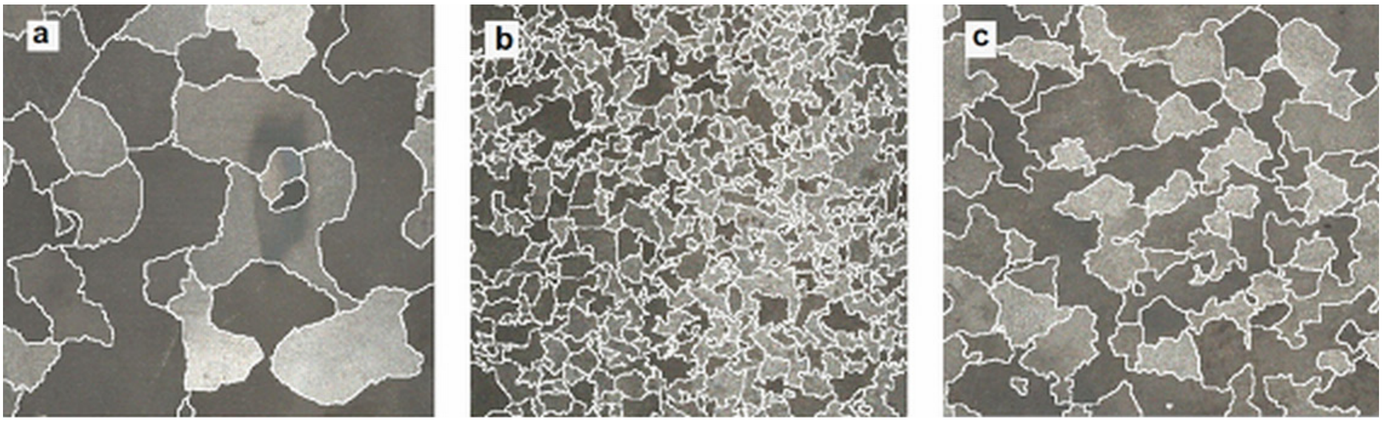

Fig. 8. Microstructure of castings: unmodified (a), current technology (b), slag mixture in the modifying coating (c)

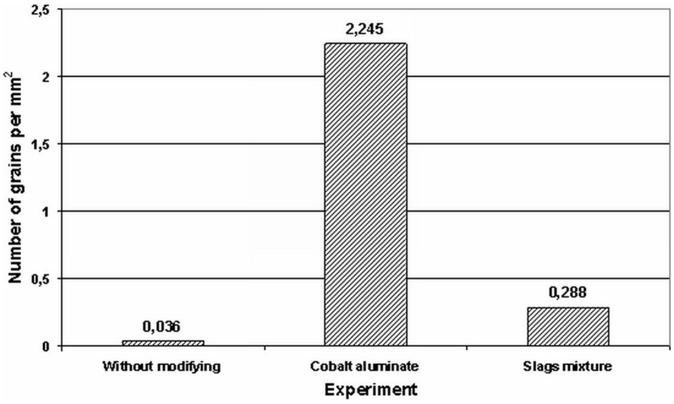

Fig. 9. Influence of technological conditions of casting on the number of grains per mm^2 of the casting surface

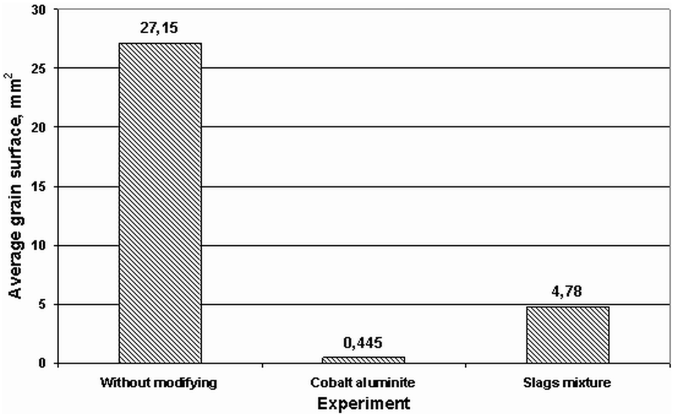

Fig. 10. Influence of technological conditions of casting on the average grain surface

a small but visible grain refinement effect compared to the unmodified casting. Compared to the traditional method, however, this effect is much weaker.

Hypothetical model of the influence of slags on the modification effect

Based on the obtained results and the existing views on the surface modification mechanism of nickel alloy castings [21,28], a hypothetical model of the modifying effect of a mixture of copper and steel slag on the refinement of the IN-713C nickel alloy was developed. The model is shown in Fig. 11.

The observed weak modifying effect may be the result of the formation of crystallization nuclei formed of metallic elements, reduced from slags by the addition of carbon. This is the same mechanism as for cobalt particles in conventional modification [19-21,27].

The lower the casting temperature and the greater the cooling intensity, the more small clusters are formed, and the final macrostructure of the casting is finer [28].

In the case of copper, its modifying effect on the mould-liquid alloy interface may be caused by a temperature reduction (supercooling) as a result of melting, immediately after the separation (reduction) of modifying slags from the coating. Registering such a small undercooling, however, is not easy, in the conditions of pouring in the vacuum chamber of the furnace and requires the installation of a complex system of thermocouples, on the mould-metal interface. Much easier to register the ATD thermal analysis method is supercooling of eutectic solidification, which occurs during sodium modification of a hypoeutectic silumin [13,14].

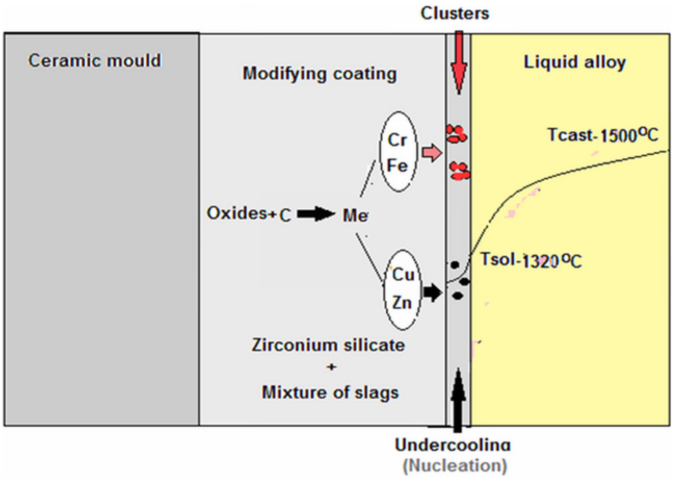

Fig. 11. Hypothetical model of the modifying effect of a coating containing zirconium silicate, a mixture of slags and coke breeze

4. Summary

Metallurgical slag, treated as a waste and a by-product, can be used successfully in many industries, including in the refining and modification of casting alloys. It has been shown that a properly prepared copper slag, introduced in a small amount into the liquid hypoeutectic aluminium alloy, shows noticeable modifying properties.

In the case of the IN-713C nickel alloy, the presence of the slag mixture in the modifying coating modifies the grain refinement. This effect is however less than that of cobalt aluminate. But in some cases a significant grain size reduction is not required. The high casting temperature requires at least 50% zirconium silicate and colloidal silica to be present in the coating as a binder and consistency agent.

Although the obtained results are not fully satisfactory, in the author's opinion, they constitute an incentive to conduct further research on the use of a wider range of slags, e.g. nickel slag for surface modification of nickel alloys and electrowinning sludge and dust for the modification and refining of aluminium alloys, containing compounds phosphorus, sodium and potassium.

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