Studying of High-alumina and Al_2O_3–MgO Crucibles Interaction with Heat-proof Alloys Based on Nickel and Cobalt

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The research of high-alumina and Al_2O_3–MgO (alumina-spinel, alumina-magnesia and magnesia-spinel) crucibles interaction with heat-proof alloys based on nickel and cobalt was carried out. It is determined that resistance to impregnation of the tested samples is practically the same for nickel and cobalt alloys, and increases in the line high-alumina < alumina-magnesia < alumina-spinel < magnesia-spinel content. Petrographic research had shown that in the alumina-magnesia, alumina-spinel and magnesia-spinel samples the alloy penetration into the refractory practically is not observed (imperceptible through the binder and into the low depth). Refractory interaction with alloy, mainly takes place in the contact of refractory and alloy. Cobalt and nickel oxides penetrate into refractories, forming solid solutions with crucible materials. Thin slag crust is principally consisting of nickel ($NiAl_2O_4$) or cobalt ($CoAl_2O_4$) spinel. Taking into consideration the research results of the crucible stability to the two type alloys on nickel and cobalt base and properties of crucibles (adsorption ability and thermal shock resistance), the alumina-spinel and alumina-magnesia crucibles were produced and tested successfully at Ukraine enterprises.

1 Introduction

One of key units among electric heating equipment used in metallurgy and mechanical engineering for melting of heat-proof alloys are induction crucible furnaces. Their application allows melting of alloys of complex compositions, realizing deep metal degassing, floatation and removal of nonmetallic inclusions, carrying out scavenging of volatile components, obtaining homogeneous structure of ingots and automatizing melting processes. One of the ways to improve the alloys induction melting effectiveness are fired crucibles of different composition application (Fig. 1). In service the melting crucible is exposed to thermal loadings, as a result of high temperature differences on height and thickness of crucible walls [1]. Intensive circulation of molten metal promotes not only good additives recovery, acceleration of chemical reactions and receipt of homogeneous metal according to chemical composition, but also scavenging of refractory grains [2]. In the case of neutral gaseous atmosphere application, the interaction of molten metal with the refractories runs slowly and in the case of prolonged curing of metal erosion occurs in the crucible. However, while operation in vacuum environment (10^{-3}–10^{-5} Pa) and high rates of temperature rise (90–110 K/min), high erosion influence resistance of crucible material remains actual. Just as, in melting process from metallic melt, oxide elements of the alloy – oxide scab escape and concentrate on its surface which get into the foundry during metal tapping are one of the reasons of low-quality production receipt. Choice of the crucible material have to be done depending on the melting alloy composition, temperature and melting period, necessary to adsorb oxide scabs of the alloy (requirements for metal ingots). In Ukraine for induction melting of heat-proof alloys high-alumina, alumina-spinel, alumina-magnesia and magnesia-spinel crucibles are widely used, which are produced in *Ukrainian Research Institute of Refractories* named after *A.S. Berezhnoy* [4–6].

Earlier the institute has published the research results of the high-alumina, alumina-spinel, alumina-magnesia and magnesia-spinel crucibles interaction with heat-proof alloys on ferroniobium base [7]. In the present work it has been studied the interaction of the crucibles with the same composition with alloys on nickel and cobalt basis, with an objective to determine the optimal composition of the crucible for melting of these alloys in production of one of the engine-building company that has provided the alloys. Melting of these alloys, that characterized by significant scabs formation, is carried

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out at temperature ~1680 °C in vacuum (from 10^{-3} to $5 \cdot 10^{-5}$ Pa) for 1,5 h (including loading and melting of the charge 70–80 kg of metal) at stopping operation.

2 Experimental

For the research, the following raw materials were used – fused white alumina, fused mullite and fused alumina-rich alumina-magnesia spinel (further spinel) from own production, fused magnesia produced by *Magnezit Group*/RU, alumina produced by *PJSC-Zaporojsky aluminum integrated plant*/UA. Chemical composition of these raw materials is given in the Tab. 1. For the investigation of the high-alumina (HA), alumina-spinel (AS), alumina-magnesia (AM) and magnesia-spinel (MS) crucibles with alloys, laboratory samples (cubes with edge size 50 mm) of the same composition were produced by vibrocasting method at the following vibration parameters: frequency 50 Hz, vibration amplitude 0,5 mm. The shaped samples were dried at temperatures of 80–90 °C during 12 h and fired at a temperature of 1580 °C with 10 h soaking time. The samples properties determination was carried out in accordance with the standards of the Ukraine. Cold crushing strength of the fired samples was determined in accordance with GOST 4071.1-94, open porosity and apparent density with GOST 2409-95, thermal shock resistance with GOST 7852-94 (950 °C – water) and GOST 7875.1-94 (1300 °C – water).

Metal resistance was determined by the crucible method on samples with a cylindrical hole with diameter 25 mm and height 25 mm, filled with metal. For the research the following alloys were taken: alloy on the nickel base (nickel ~43 %, chrome ~20 %, cobalt ~22 %, aluminum ~9 %, other ~6 %), alloy on the cobalt base (cobalt ~63 %, chrome ~27 %, aluminum ~9 %, other ~ 1%). As alloys on nickel and cobalt induction melting goes at temperature ~1680 °C, the research of the samples interaction with the alloys was carried at the temperature 1750 °C with soaking time during 8 h. After a metal resistance test the samples were cut along the centre pin. On these samples the area of the refractory impregnation by alloy was determined.

Petrographic structure research under microscope in the reflected light on polished sections and in transmitted light in immersion liquids was carried out.

The main properties of fired samples before metal resistance tests are given in the Tab. 2.

3 Results and discussion

The impregnation area of the HA, AS, AM and MS samples by alloys on the nickel and cobalt base is given on the Fig. 2.

The analysis of graphical data, given on the Fig. 2, certifies that the resistance to impregnation of the tested samples is practically the same for nickel and cobalt alloys, and increases in the line HA < AM < AS < MS.

Petrographic structure research of the HA, AS, AM and MS samples after metal resistance tests showed, that in the result of alloys (on nickel and cobalt base) influence phase-structure changes took place, introduced by a zone formation. Under influence of all above given factors less changeable zone, working zone and slag crust were formed. Phase composition of the samples after metal resistance test depending on the alloy type is given in the Tab. 3 and 4.

Characteristics analysis in the Tabs. 3–4, indicates that difference in the samples phase compositions after impregnation by alloys (on nickel and cobalt base) consists of a formation with refractory components solid solutions correspondingly with nickel or cobalt oxide. Thereby the petrographic research of the samples interaction with alloy on nickel base are given more detailed in this paper as interaction with alloy on cobalt base goes in the same way.

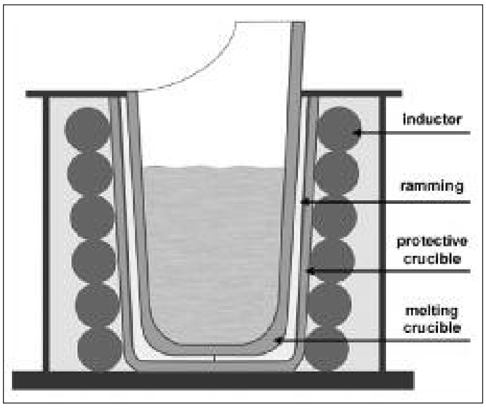

Fig. 1 Scheme of crucibles installation in an induction furnace

3.1 HA sample petrographic research

The structure and phase composition of the less changeable zone of HA sample is similar to the structure before tests (represented by grains of corundum, mullite and fine binder)

Tab. 1 Raw materials chemical composition

Material	Content of Oxides [%]						
	SiO_2	Al_2O_2	Fe_2O_3	CaO	MgO	Na_2O	L.O.I.
Fused alumina	0,05	99,38	0,05	0,02	0,03	0,32	0,15
Fused mullite	26,07	73,30	0,18	0,10	0,08	0,23	0,04
Fused spinel	0,17	84,78	0,13	0,18	14,60	–	0,14
Fused magnesia	0,97	0,41	0,57	1,31	96,50	–	0,24
Alumina	0,04	99,47	0,05	0,02	0,02	0,29	0,11

Tab. 2 Main properties of HA, AS, AM and MS samples

Properties		Sample Name			
		HA	AS	AM	MS
Content of oxides [%]	SiO_2	6,65	–	–	0,71
	Al_2O_3	93,00	93,00	92,80	22,67
	MgO	–	5,80	5,70	75,82
	Fe_2O_3	0,10	0,23	0,26	0,80
Open porosity [%]		12,3	16,8	22,8	17,3
Cold crushing strength [N/mm²]		133	185	50	36
Thermal shock resistance [thermal cycles]					
950 °C – water		>20	>20	>20	>20
1300 °C – water		>20	4–8	3–6	~2

Tab. 3 Phase composition of the samples after determination of metal resistance to alloy on nickel base

Sample	Zone	Depth of Zone [mm]	Content of Phase [vol.-%]					
			Corundum	Mullite	Spinel	Periclase	Glass Phase	Ni and Ni Oxide
HA	less changeable	base	65–70	25–30	–	–	2–4	–
	working	2–7	65–70*	5–15*	10–15**	–	6–8	2–5
	slag crust	0,1–0,4	traces	–	85–95**	–	3–5	5–7
AS	less changeable	base	75–77	–	23–25	–	<1–2	–
	working	0,5–2,5	60–65*	–	30–35*	–	<1–2	1–2
	slag crust	0,1–0,4	traces	–	93–95**	–	<1	3–5
AM	less changeable	base	65–70	–	25–30	traces	<1–2	–
	working	0,5–2,9	60–65*	–	30–35*	traces	<1–2	1–2
	slag crust	0,1–0,5	traces	–	93–95**	–	<1	3-5
MS	less changeable	base	–	–	25–30	70–75	<1	–
	working	0,5–2,0	–	–	34–37*	60–65*	<1–2	1–3
	slag crust	0,05–0,1	–	–	85–90**	3–5*	<1–2	5–10

*contain Ni oxide in solid solution; **spinel $NiAl_2O_4$ (or close in its composition)

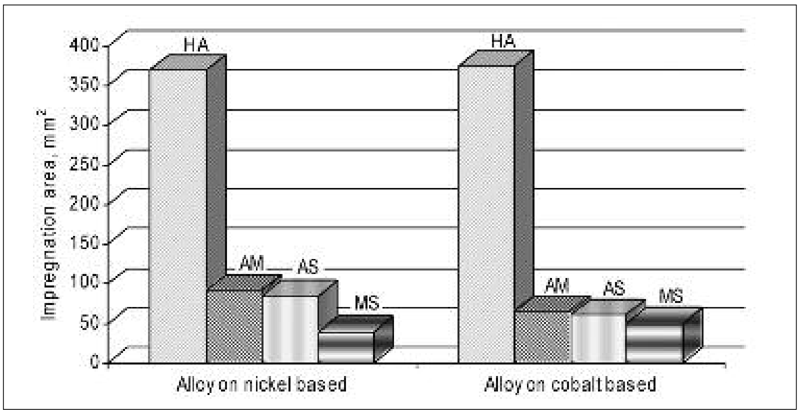

Fig. 2 Impregnation area of the HA, AS, AM and MS samples by alloy on the nickel and cobalt base

and differs by the presence some mullite grains, dissociated into the needle-shaped corundum and glass phase along the edge.

Working zone depth basically is 2,0–7,0 mm. In the working zone (Fig. 3) the most part of the mullite (small grains completely) along the edges and cracks dissociated into the needle-shaped corundum and glass phase, partially forming spinel $NiAl_2O_4$, possibly contains in the solid solution chrome and cobalt oxides, with optical refraction indexes N ~1,875. Mullite grains have an increased optical refraction index, which means nickel oxide content in the solid solution. Corundum grains also

Tab. 4 Phase composition of the samples after determination of metal resistance to alloy on cobalt base

Sample	Zone	Depth of Zone [mm]	Content of Phase [vol.-%]					
			Corundum	Mullite	Spinel	Periclase	Glass Phase	Co and Co Oxide
HA	less changeable	base	65–70	25–30	–	–	2–4	–
	working	3–7	65–70*	5–10*	10–15**	–	8–10	3–6
	slag crust	0,2–0,4	traces	–	94–95**	–	3–5	4–7
AS	less changeable	base	75–77	–	23–25	–	<1–2	–
	working	0,5–2,4	60–65*	–	30–35*	–	<1–2	1–2
	slag crust	0,05–0,2	traces	–	94–96**	–	<1	1–3
AM	less changeable	base	65–70	–	25–30	traces	<1–2	–
	working	0,5–2,7	60–65*	–	30–35*	traces	<1–2	1–2
	slag crust	0,05–0,2	traces	–	95–97**	–	<1	1–3
MS	less changeable	base	–	–	25–30	70–75	<1	–
	working	0,5–2,0	–	–	35–40*	60–65*	<1–2	1–2
	slag crust	0,05–0,1	–	–	85–90**	5–10*	<1–2	5–7

*contain Ni oxide in solid solution; **spinel $NiAl_2O_4$ (or close in its composition) have an increased optical refraction indexes (N up to 1,780), which means nickel oxide content in the solid solution ((Al, Ni)$_2$O$_3$). In the binder, besides corundum, there is also spinel (grains with size 4–40 µm) close in its composition to NiAl$_2$O$_4$, possibly contains in the solid solution chrome and cobalt oxides, and glass phase films. Comparatively to the less changeable zone more big size cracks can be observed.

The slag crust consists of spinel close to composition NiAl$_2$O$_4$ (possibly contains in the solid solution chrome and cobalt oxides) with N ~1,875 (grains with size from 4–40 µm to 12–60 µm, max. 80 µm), nickel and its oxides.

3.2 AM samples petrographic research

The structure and phase composition of the less changeable zone of the AM sample is similar to the structure before tests (represented by grains of corundum and fine binder consisting of corundum and alumina-rich alumina-magnesia spinel of different composition) and differs with increased content (~5 %) of new-forming fine-crystalline spinel. A higher amount of this spinel, from the one side, spends to increasing refractory resistance to impregnation by oxidized alloy elements and from another – to increasing the ability to adsorb oxide scabs of the alloy. On the contact filler-binder and in the fine binder cracks with a width 20–100 µm occur. There are small pores (4–40 µm) sometimes connected between each other, in the binder.

The depth of the working zone is 0,5–2,9 mm. In the working zone (Fig. 4) the corundum quantity decreases, corundum grains have an increased optical refraction indexes (N up to 1,780). Spinel grains also have an increased optical refraction indexes (N from 1,780 up to 1,870), which means nickel oxide content in the solid solution ((Mg, Ni)Al$_2$O$_4$, possibly contains in the solid solution chrome and cobalt oxides). In a small amount there is nickel and its oxides. Many pores can be observed.

The slag crust consists of spinel close to the composition NiAl$_2$O$_4$ (possibly contains in the solid solution chrome and cobalt oxides) with N ~1,870 (grains with size from 4–40 µm to 12–60 µm, max 80 µm), and also in a small quantity nickel and its oxides.

3.3 AS sample petrographic research

The structure and phase composition of the less changeable zone of AS sample is similar to the structure before tests (represented by grains of corundum, spinel and fine binder, also glass phase film can be observed) and differs by increased content of 2–3 % of fine-crystalline corundum, as a result of a solid solution dissolving. On the contact filler-binder grains and in the binder there are cracks with width up to 100 µm.

The depth of the working zone is 0,5–2,5 mm. In the working zone (Fig. 5) the corundum quantity decreases, corundum grains have an increased optical refraction indexes – N up to 1,780. Spinel grains also have an increased optical refraction indexes (N from 1,780 up to 1,870). In small quantity there is nickel and its oxides. Many pores can be observed. The slag crust consists of spinel close to composition NiAl$_2$O$_4$ (possibly contains in the solid solution chrome and cobalt oxides) with N ~1,870 (grains with size from 4–40 µm), and also in a small quantity nickel and its oxides.

3.4 MS sample petrographic research

The structure and phase composition of the less changeable zone of the MS sample is similar to the structure before tests (represented by grains of periclase with N ~1,737, spinel and fine binder, also glass phase film can be observed).

The working zone (Fig. 6) depth is mainly 0,5–2,0 mm. At the contact with metal and its oxides, some periclase grains have an increased optical refraction index (N ~1,780), which means nickel oxide content in the solid solution ((Mg,Ni)O). On the edge part of working zone, periclase sectors fractionized into smaller pieces along cleavage cracks. Spinel grains have an increased op-tical refraction index (N from ≤1,754 up to 1,870). In a small amount there is nickel and its oxides. Many pores can be observed.

Slag crust consists of spinel close to composition NiAl$_2$O$_4$ with N ~1,870 (with size 8–30 µm, max 80 µm), and also in a small quantity nickel and its oxides. In some areas working zone and slag crust separates by interrupting cracks from metal and its oxides, in some areas forms solid union with alloy oxide on the nickel base. Many pores can be observed.

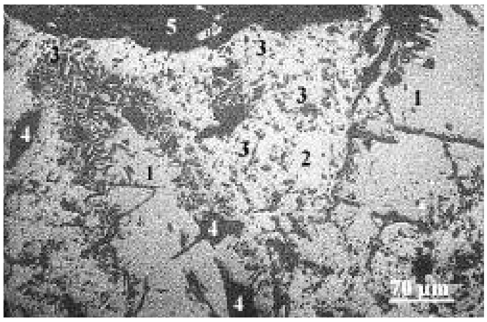

Fig. 3 Working zone and slag crust of the HA sample microstructure: 1 = mullite grains; 2 = corundum grains with nickel oxide in the solid solution; 3 = spinel grains close to composition NiAl$_2$O$_4$ (possibly contains chrome and cobalt oxides); 4 = pores; 5 = slag crust

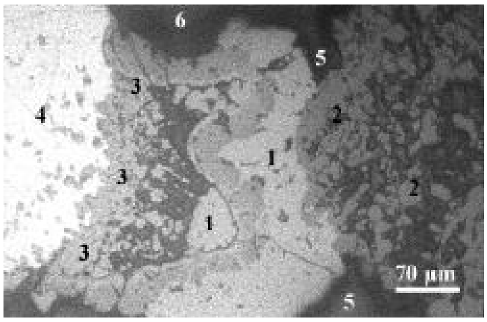

Fig. 4 Working zone and slag crust of the AM sample microstructure: 1 = corundum grains with nickel oxide in the solid solution; 2 = spinel grains with nickel oxide (possibly chrome and cobalt oxides) in the solid solutions; 3 = spinel grains close to composition NiAl$_2$O$_4$ (possibly contains chrome and cobalt oxides); 4 = nickel and its oxides; 5 = pores; 6 = slag crust

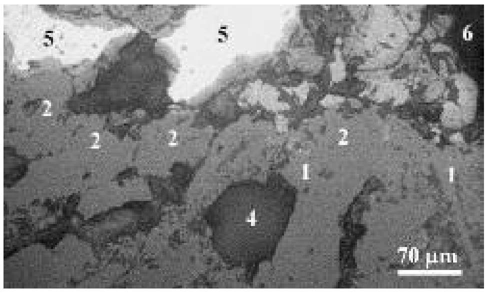

Fig. 5 Working zone and slag crust of the AS sample microstructure: 1 = corundum grains with nickel oxide in the solid solution; 2 = spinel grains with nickel oxide (possibly contains chrome and cobalt oxides) in the solid solutions; 3 = spinel grains close in its composition to NiAl$_2$O$_4$, (possibly contains chrome and cobalt oxides); 4 = pore; 5 = nickel and its oxides; 6 = slag crust

In summary the petrographic research had shown that in the samples, after nickel and cobalt alloy interaction, zone formation can be observed: less changeable zone, working zone and slag crust. In the less changeable zone the processes connected with the tem-

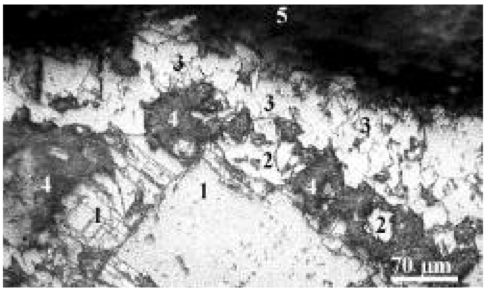

Fig. 6 Working zone and slag crust of the MS sample microstructure: 1 = periclase grains with nickel oxide in solid solution; 2 = spinel grains with nickel oxide (possibly contains chrome and cobalt oxides) in solid solutions; 3 = spinel grains close in composition to $NiAl_2O_4$ (possibly contains contains chrome and cobalt oxides); 4 = pores; 5 = slag crust

Fig. 7 Refractory crucibles for heat-proof alloys induction melting

Tab. 5 Main properties of AS and AM crucibles

Properties	Crucible Composition	
	AS	AM
Content of oxide [%]: Al_2O_3	93,2	92,8
Content of oxide [%]: MgO	5,8	5,7
Open porosity [%]	18,5–18,9	22,7–23,0
Cold crushing strength [N/mm²]	204–263	48–52

perature changes take place, what stipulates their additional sintering. In the HA sample slight alloy penetration occurs through the pores and cracks and at interaction with refractory components with formation of solid solution and fusible glass phase. Mullite partially dissociated into the corundum and glass phase, what happens with porosity increasing. Along the corundum grains perimeter, nickel or cobalt spinel forms. In the AM, AS and MS samples the alloy penetration into the refractory practically is not observed (imperceptible through the binder and into the low depth). Refractory interaction with alloy, mainly, takes place on the contact refractory and alloy. At this interaction nickel and cobalt oxides penetrates into the refractories with a corundum, spinel and periclase content solid solution formation. Along the edge of the sample working zone thin slag crust can be observed, basically consisting of nickel and cobalt spinel. The slag crust in some areas separates by crack from nickel and its oxides or cobalt and its oxides, in some areas forms a solid union with them.

With the result of the carried out research it was stated that the most stable refractories to the nickel and cobalt alloys (what become evident in the less depth of working zone and less interaction intensity with refractory components) are MS, AS and AM refractories. The area of the alloys penetration to HA refractory is the highest, so HA crucibles are not recommended for melting of these alloys on nickel and cobalt base. The minimum interaction observed on MS refractory, but because of lower adsorption ability (oxide scabs in ingots is production reject) and lower thermal shock resistance (stopping operation), compared with AM and AS, the MS crucibles is also not recommended for melting of the above alloys. Optimal is the use of AS and AM crucibles.

AS and AM crucibles were produced (Tab. 5) and tested at vacuum induction melting of heat-proof alloys based on nickel and cobalt at one engine-building production, which provided the alloys. Their application showed the average durability of 15 and 20 melts, correspondingly, that completely meets the requirements of engineering process of melting. According to the results of carried out research and crucibles tests, optimal crucibles composition (AM) for melting the alloys on the nickel and cobalt base was determined.

Developed and manufactured in Ukrainian Research Institute of Refractories named after A.S. Berezhnoy, crucibles (Fig. 7) are successfully used on engine-building and other enterprises of Ukraine for heat-proof alloys induction melting based on nickel and cobalt.

4 Conclusions

The interaction researches of high-alumina (HA), alumina-spinel (AS), alumina-magnesia (AM) and magnesia-spinel (MS) crucibles with alloys on nickel and cobalt base were carried out. It was determined that refractories interaction with these alloys decreases in the line HA > AM > AS > MS.

Petrographic research had shown that refractory and alloy interaction basically takes place on the contact refractory and alloy. At this interaction cobalt and nickel oxides penetrates into the refractories, forming solid solutions with crucible materials. Along the working zone a thin slag crust can be observed, principally consisting from nickel ($NiAl_2O_4$) or cobalt ($CoAl_2O_4$) spinel. Taking into consideration the crucible properties and research results of the crucible stability to the alloys on nickel and cobalt base, the AS and AM crucibles were produced and tested successfully at an engine-building enterprise of Ukraine.

Developed and produced by the Ukrainian Research Institute of Refractories named after A.S. Berezhnoy the crucibles of different composition are successfully used in engine-building and some other Ukraine enterprises at induction melting of heat-proof alloys.

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