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X-RAY PHASE ANALYSIS (XPA) OF A COLD-HARDENING MIXTURE (CHM) AND THE EFFECT OF THE MIXTURE PROPERTIES ON THE CASTING

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The objectives of this type of research are as follows: identifying the phase composition of the samples under study; assessing the effect of the composition on the mechanical properties of the samples. Prior to the study by the XPA, the authors obtained 9 samples of different compositions to select the optimal composition of cold-hardening mixture (CHM). The method of X-ray phase analysis was selected for the phase composition of the CHM samples. After examining the samples using XPA analysis, molds were made from CHM (resin+clay) according to the composition of sample No. 3. To evaluate the quality of the castings, there was measured roughness.

Key words: steel, casting, CHM, XPA, properties.

INTRODUCTION

One of the promising developments in the area of making molds for producing thin-walled castings is the use of cold-hardening mixtures (CHM). The scale of CHM use is constantly growing. The method of obtaining castings with the help of CHM was introduced into production in the 80 s of the last century but due to a high cost of materials and their harm to human health and the environment, they have not been used in the production of the RK.

At the same time, neighboring countries, such as Russia and Ukraine, widely use this process to obtain castings of various sizes, including those with walls thinner than 5–10 mm [1].

CHM is also a mixture based on sand but compared to sand-clay mixtures (SCM) it has a number of advantages: increased accuracy of the geometry and dimensions of castings made in them, decreased surface roughness. It does not require heat drying, transport operations are reduced, labor productivity increases, etc. [2].

The relevance of this work is studying the use of a complex composition of the binder in cold-melting molds in order to obtain thin-walled castings with high dimensional accuracy and reduced cost due to the partial use of a cheap binder: clay. Three components are used in this technology: sand (a filler), clay (a binder), epoxy resin with a hardener (a binder). Since epoxy resin does not have hardening qualities, it is used in combination with a hardener to obtain CHM.

The objectives of this type of research are as follows:

- identifying the phase composition of the samples under study;
- assessing the effect of the composition on the mechanical properties of the samples.

To study the phase compositions formed in the complex binder, the method of X-ray phase analysis (XPA) was selected. This method is known to use X-ray diffraction on the crystal lattice of the powder. In this study the powder is a ready-made cured sample of CHM in crushed form. Grinding was carried out on an Emax nanomill (Retsch, Germany) at 1 000 rpm within 5 minutes.

RESEARCH METHODS

Prior to the study by the XPA, the authors obtained 9 samples of different compositions to select the optimal

Table 1 **CHM composition with different binders**

Composition No.	Filler (quartz sand, sand fraction)	Binder (clay)	Epoxy resin EP-SM-PRO+ hardener 921OP (2/1)	Composition average hardness / unit
1	25 g (125 mm)	5 %	2 %	the sample did not harden
2		10 %	2 %	82
3		15 %	2 %	81
4	25 g (250 mm)	5 %	2 %	the sample did not harden
5		10 %	2 %	54
6		15 %	2 %	59
7	25 g (250 mm)	5 %	LG 2 %	77
8	25 g (250 mm)	10 %	LG 2 %	68
9	25 g (250 mm)	-	LG 2%	76

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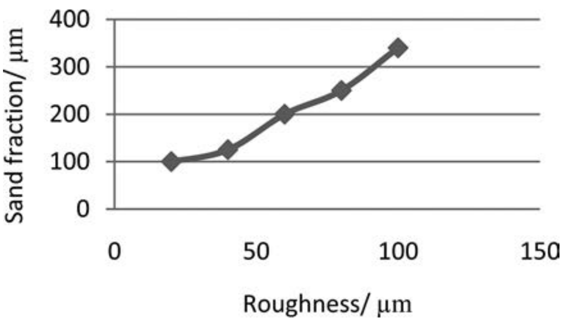
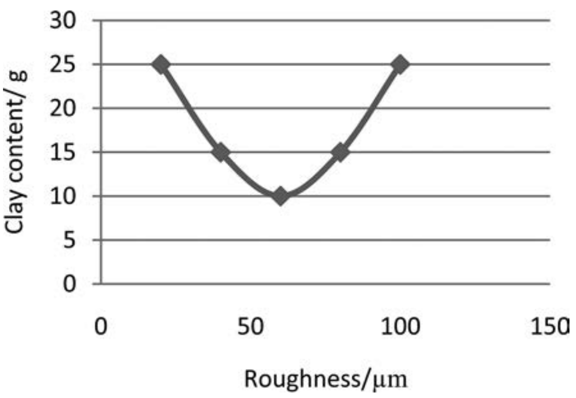
composition of CHM [3]. For comparison, samples were obtained from sand-clay mixtures (SCM) and liquid-glass mixtures (LGM). To select the optimal composition of CHM, samples were made with different ratios of the binding elements of the mold, such as clay, epoxy resin, liquid glass (Table 1). Several clay deposits were considered for the experiments: the Darat, the Fedorovskoye, the Beloe Glinische, the Karasor MPP. Sand and kaolin clay from the Karasor deposit were selected for the further work. The clay of this deposit complies with the SS 3 226 of classification of kaolin clays for manufacturing cold-hardening mixtures. The clay of the Karasor Mining and Processing Plant is finely dispersed, the particle size is 20 microns.

When pouring and solidifying the alloy, the mold must have high qualities such as strength, gas permeability, fluidity [4]. Fluidity of the mold is to a certain extent affected by the absence of blockages and flaking of the mixture that are in turn determined by the mold hardness. This Table considers several samples with different constituents. It is seen that hardness in many samples is very low, and according to the standard hardness should exceed 80 units [5]. Hardness was determined with a hardness tester for green molds, rods, model 04421 No. 295, Usman. The surface quality of the mold also affects low surface roughness [6]. The surface roughness of the mold is shown in Figure 1.

Therefore, the following composition was selected for the further work: quartz sand 80 %, sand fraction 125 mm, kaolinite clay 15 %, epoxy resin with hardener 5 % (sample No. 3).



a)



b)

Figure 1 The CHM surface roughness:
a) relative to the sand fraction;
b) relative to the clay content

The sample was dried at the room temperature within 24 hours. In this mode, the granular base of the mixture receives the most durable and uniform connection through a binder. This in turn provides a smooth surface of the mold. The mold with low roughness contributes to increased fluidity of the alloy poured into it, since the liquid metal flow under the condition that it is uniformly poured into the gating bowl, does not have turbulences and has the character of laminar motion. Since there are considered thin-walled castings, such a property as fluidity plays an important role in this type of casting.

Grinding was carried out within 5 minutes at the speed of 1 000 rpm.

RESULTS

The method of X-ray phase analysis was selected for the phase composition of the CHM samples. The XPA method was implemented on an Empyrean diffractometer (PANalytical, Holland). The method used makes it possible to identify the qualitative and quantitative composition of the samples. The diffractometer uses the tomographic scanning method, which allows examining the samples in any plane and displays the internal structure in the three-dimensional range. The measurements were carried out at the room temperature with stepwise scanning.

Then, when processing the results using the HighScore Plus program in sample No. 3 (quartz sand 80 %, sand fraction 125 mm, kaolinite clay 15 %, epoxy resin with a hardener 5 %), 400 phases were identified (Figure 2).

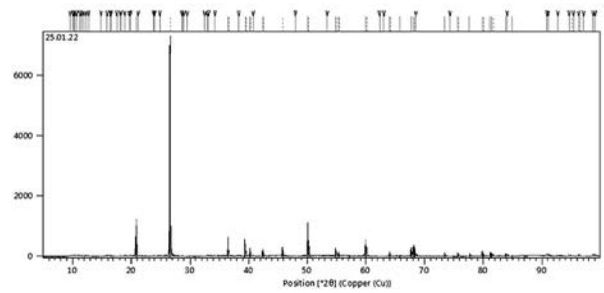


Figure 2 X-ray spectrum in the powdered form of the CHM sample (phase peaks are shown, sample No. 3). Peaks of quartz sand

As the analysis of the diffraction pattern of monocompositions and complex mineral compositions shows, the most common constituents of sand are silica (SiO_2), usually in the form of quartz, which, due to its chemical inertness and significant hardness, is resistant to weathering. The composition of sand is very diverse depending on local rock sources and conditions. As a result of XPA analysis, it shows 85 % with the chemical formula SiO_2, which corresponds to the standard designation of quartz sand (Table 2).

The next component in the mixture is epoxy resin with a hardener. In the test sample, there is 5 % of this

Table 2 **Quartz low phase**

№	Compound Name	Chemical formula	Score	Scale
1	Quartz Low	O_2Si	85	0.955

Table 3 **XPA results in the HighScore Plus program (sample No. 1)**

№	Compound Name	Chemical formula	Score	Scale
1	Aluminium Phosphide	$Al_1 O_4 P_1$	16	0,05316
2	Aluminium Gallium	$A_{l0,75} Ga_{0,25} O_4 P_1$	16	0,027
3	Berlinite	$A_{l1} O_4 P_1$	16	0,034
4	Scandium Nickel	$C_2 Ni_{0,83} Sc_1$	14	0,008
5	Aluminium Gallium	$A_{l0,58} Ga_{0,42} O_4 P_1$	13	0,027
6	Berlinite	$A_{l1} O_4 P_1$	12	0,036
7	Sodium Dioxoco	$Co_1 Na_{0,75} O_2$	5	0,016
8	Holmium Manganese	$Ga_1 Ho_1 Mn_1$	2	0,323
9	Terbium Gallium	$Ga_{1,17} Si_{0,83} Tb_1$	2	0,026
10	Manganese Germfn	$Ge_1 Mn_1$ 10.250	2	10,250
11	Erbium Tris	$H_3 Er_1 O_{12} S_3$	1	0,018
12	Ytterbium Silver	$Ag_{0,28} Si_{1,72} Yb_1$	1	0,025
13	Jeremejevite	$H_3 A_{l6} B_5 O_{18}$	1	0,015
14	Hydrodresserite	$C_2 H_{10} A_{l2} Ba_1 O_{13}$	1	0,023
15	Jeremejevite	$H_3 Al_6 B_5 O_{18}$	1	0,015

type of binder (Table 3). The molding mixture that uses epoxy resin, has high dielectric properties after curing, chemical resistance and mechanical strength. It is also supported in the program by many different elements. The main ones are positions 56, 57, 61 (C12H32Li-2O2Pt1, C2Y13Cu2N1J11S2, C8H32Co1N2J32) and so on (Table 4). These elements correspond to the constituents of epoxy resin according to the standard.

The authors also studied another sample. As part of the next sample (sample No. 2), kaolnite clay from the Kazakhstan deposit was added. The identified positions of the phases are shown in Table 4.

The clay from the Karasor deposit is koalinite clay. Since clay is a binder, it must be evenly distributed throughout the mixture. The composition of the clay in the mixture is 5 %.

Table 4 **XPA results in the HighScore Plus program (sample No. 2)**

№	Compound Name	Chemical formula	Score	Scale
56	Dilithium Tetram	$C_{12} H_{32} Li_2 O_2 Pt_1$	1	0,898
57	Tetrakis(dimethyl oxide)	$C_2 H_{13} Cu_2 N_1 O_{11} S_2$	1	0,217
58	Cordierite	$Al_4 Mg_2 O_{18,45}$	1	0,391
59	Dilithium Tungsten	$Li_2 O_4 W_1$	1	0,084
60	Dioxonium hexacyanidoferrate	$H_{14} Br_{14} O_6 W_6$	1	0,041
61	Bis-tetramethyl hydroxypiperidinyl	$C_8 H_{32} Co_1 N_2 O_{32}$	1	0,545

In positions 2 and 6, new phases of aluminum gallium (Al 0,75Ga0,25O4P1) were formed. In the composition of the phase gallium does not occur in nature in its pure form. These elements were formed when clay and epoxy resin came into contact. This compound belongs to the group of organic aluminum compounds; its amount is 0,027 % of the total composition. When the required concentration of reacting substances is reached on the surface of gallium, the phenomenon of surface tension appears, from which, due to the constant changing of the amount of substances obtained, a drop of liquid metal acquires the ability to «pulsate». These expansions and contractions are reminiscent of the work of the heart, from which this experience received the name «Gallium Heart».

XPA analyzes were obtained by examining two samples within 1 hour.

The new phases found as a result of XPA of sample No. 2, in accordance with the literature data and laboratory experiments [2], had a positive assessment of strength. As a result of providing high strength and low friability of the mixture, low surface roughness of the mold is achieved, which in turn has a positive effect on fluidity, as noted above.

After examining the samples using XPA analysis, molds were made from CHM (resin+clay) according to the composition of sample No. 3. For comparison, a mold was prepared using PCM and CHM with only resin. St30 steel was selected for pouring.

After preparing the mixture, its technological and physical and mechanical properties were determined: compressive strength (wet mixture), tensile strength (dry mixture), gas permeability and humidity. To determine the work for the knockout, a special technological test was developed. The molds were used to produce castings with the wall thickness of 5, 10, 15, 20 mm. Tables 5 and 6 show the results of the experiments.

Table 5 **Specific work for the knockout**

Casting wall thickness/ mm	Specific work spent for the knockout/ J/g	
	Basic mixture (CHM with only resin)	Mixture under study (CHM resin+clay)
5	0,54	0,19
10	0,51	0,14
15	0,50	0,11
20	0,49	0,09

Table 6 **Technological properties of the mixtures under study**

Mixture properties	Basic mixture (CHM with only resin)	Mixture under study (CHM resin+clay)
Compression strength (green)/ MPa 10^{-1}	0,18	0,26
Fracture strength (dry)/ MPa	2,9	3,4
Gas permeability/ un.	140	250
Humidity/ %	5	5

As a result of the studies, the fundamental expediency of using complex additives that improve the properties of CHM has been established. The combination of clay and epoxy resin in the CHM significantly improves its strength and smooth surface.

CONCLUSIONS

After carrying out research work, the following conclusions can be drawn on the use of a complex binder in CHM molds:

- High dimensional accuracy of the casting is ensured due to uniform increased strength and low shattering of the CHM mold.
- The need for machining castings is reduced, as the molds provide high dimensional and geometric accuracy.
- Energy consumption for cleaning and final processing of castings is also reduced, since the mold provides low roughness of the castings and the absence of burn marks on its surface.

According to the results of XPA analysis, different phases were identified. There were discovered new phases 56, 57, 61 (C12H32Li2O2Pt1, C2Y13Cu2N-1J11S2, C8H32Co1N2J32) that appeared due to the combined composition of the binders, which ultimately had a positive effect on the quality of the mold.

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Note: Responsible for the English language is Natalya Drak, Karaganda, Kazakhstan.