Research Article

Corundum Molds for Investment Casting from Refractory Alloys and Metals

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Production procedure, physical-chemical, and performance properties of ALUMOX silica-free binder used for the production of high-heat-resistant corundum shell molds by consumable patterns employed in the production of critical molds from superalloyed reactive metals and alloys are described. ALUMOX usage allows obtaining casts from reactive metals and alloys with surface roughness up to $R_z < 10 \mu\text{m}$ (basic casts— $R_z > 60 \mu\text{m}$), which, in its turn, increases fatigue parameters of the material (endurance, durability).

1. Introduction

Contemporary development of aircraft engine building is connected with continuous improvement of performance characteristics of heat-resistant alloys for gas-turbine engine vanes. In such vanes, fabrication directional crystallization technique allowing heat-resistant alloys quality improvement by means of transverse grain boundaries removal is used. However, at directional crystallization and single crystal blade casting exclusive requirements to shell molds are imposed in terms of flame resistance, durability, thermal conductivity, and deformational and thermochemical stability [1].

Conventional corundum shell molds based on ethyl silicate binder and containing silicon dioxide that interacts with heat-resistant alloy components and alkaline admixtures present in corundum as well as partly decomposes at high temperatures under vacuum do not comply with these requirements. Mold binder destruction occurs resulting in its weakening and porosity increase, and molten metal penetrates intergranular space forming a burning-in zone. Attempts to fabricate high-refractory (up to 2000°C) monoxide mold consisting of $\alpha\text{-Al}_2\text{O}_3$ were restrained by the

unavailability of a binder transforming into α -alumina after calcination.

On the basis of chelated alkoxyalumoxane oligomers relatively stable in the air, the researchers of SSC GNIChTEOS developed silica-free binder ALUMOX [2–4] used in the fabrication of high-refractory mold consisting of $\alpha\text{-Al}_2\text{O}_3$ only, for casting heavily alloyed steel, heat-resistant alloys, and refractory metals with directional and single crystal structures [4–8].

2. Experimental

Silica free ALUMOX binder was obtained by a patent [4]. Aluminum content was determined by trilonometry. Thermogravimetric analysis (TGA) was conducted on TGA/SDTA 851 Mettler Toledo.

X-ray phase analysis (XPhA) of organoalkoxyalumoxanes and ceramics on their basis was performed on X-ray diffraction meter DRON-3M ($\text{CuK}\alpha$ -irradiation) with graphite monochromator. The X-ray diffraction meter is combined with personal computer. The experimental data

FIGURE 1: TGA and SDTA curves at ethylacetoacetatealkoxyalumoxanes pyrolysis.

were processed by KO-IMET complex. Qualitative and quantitative X-ray spectroscopic analysis was carried out using XRAYAN software and PDF (POWDER DIFFRACTION FILE) database.

Ceramic suspension was prepared according to the patents [5, 7]. Corundum mold on ALUMOX was produced in air environment with humidity of 60% maximum. Ceramic shells were produced conventionally: consequential model immersion into suspension and its dusting with refractory granular fused α -alumina-based material.

In order to obtain high-grade shell molds, they were dried in two independent stages: the first one—holding every layer in a high-humidity chamber till full solvent removal, the second stage—free water efflorescing from each layer.

Model composition may be removed from shell molds by any available method (hot water, pattern melt, boilerclave, or microwave heating).

Ceramic molds were calcined in a furnace at the temperature of 1250–1350°C within 4–6 hours.

3. Results and Discussions

Researches of GNIChTEOS investigated most promising synthesis area of organoalumoxane oligomers that were sufficiently stable in air environment and that may be used as raw material for the production of silica-free binder of α -alumina composition [2–8].

Chelated alkoxyalumoxane oligomers were synthesized through consistent hydrolysis and alcoholysis of organoaluminum compounds in the presence of stabilizers (chelate compounds). Compounds that are characterized by keto-enol tautomerism were used as stabilizers.

Alkoxyalumoxanes (ethylacetoacetatealkoxyalumoxanes) modified by chelate compounds were synthesized according to the following scheme [2–4]:

where $k = 3 \div 12$; $s + x + 2y + z = 3$; $\text{R} = \text{C}_n\text{H}_{2n+1}$, $\text{C}_n\text{H}_{2n+1}\text{O}$, $(\text{C}_n\text{H}_{2n+1})_2\text{Al}-\text{O}-[(\text{C}_n\text{H}_{2n+1})\text{Al}-\text{O}]_m$, $n = 2 \div 4$, $m = 3 \div 10$, $\text{R}^* = \text{Et}$, $i\text{-Pr}$, $n\text{-Bu}$; $\text{R}^{**} = \text{C}(\text{CH}_3) = \text{CHC}(\text{O})\text{CH}_3$; $\text{C}(\text{CH}_3) = \text{CHC}(\text{O})\text{C}_2\text{H}_5$.

FIGURE 2: (a) RPhA spectrum of ethylacetoacetatealkoxyalumoxanes pyrolysis products at 1000°C. (b) RPhA spectrum of ethylacetoacetatealkoxyalumoxane pyrolysis at 1200–1280°C.

Thermal destruction of the produced ethylacetoacetatealkoxyalumoxanes was studied by thermogravimetric analysis (Figure 1).

X-ray phase analysis showed that the sample pyrolyzed at a temperature below 900°C just like initial ethylacetoacetatealkoxyalumoxane was in amorphous state. Pyrolysis at 1000°C results in two-phase system consisting of low-temperature fine δ - Al_2O_3 and cubic γ - Al_2O_3 phases (Figure 2(a)).

X-ray phase analysis (Figure 2(b)) showed that the sample pyrolyzed at 1200–1280°C was in crystalline state (100% α - Al_2O_3), so pure α -alumina was the end product of ethylacetoacetatealkoxyalumoxanes.

On the basis of the obtained results, major thermal destruction stages may be presented by Scheme 1.

Chelated alkoxyalumoxanes are either brittle solids or highly viscous fluids, and they cannot be used in a pure form for ceramic suspensions preparing, therefore our target was to develop such formulation that would be a fluid capable of forming suspensions with fused corundum powders of good sedimentation stability and well-wetting model compositions.

This problem was successfully solved, and on the ground of chelated alkoxyalumoxane alcoholic solution new silica-free binder [2–4] was developed; the binder when mixed with

SCHEME 1

FIGURE 3: Ceramic samples strength as a function of Al₂O₃ content in ALUMOX.

TABLE 1: Basic characteristics of ALUMOX binder.

Characteristic	
Viscosity of ALUMOX, ν , cSt	2.24–2.30
Mass fraction of Al ₂ O ₃ , wt%,	10.0–12.0
Gel time of ALUMOX, min.	Not less than 30
Relative viscosity of suspension when applied in 1 and 2 layers, sec.	40–42
Relative viscosity of suspension when applied in 3–7 layers, sec	28–30
Bending strength of noncalcined shell molds, MPa	2.2–3.0
Bending strength of calcined shell molds at 1250–1350°C, MPa	14–20

a filler (fused corundum powders) formed ceramic suspension not tending to foaming, having enhanced sedimentation stability and well-wetting model compositions.

The silica-free binder called ALUMOX is chelated alkoxyalumoxanes solution in aliphatic alcohol of 25–35 wt% concentration, its major characteristics are presented in Table 1.

ALUMOX with Al₂O₃ content from 10 to 12 wt% provided ceramic sample production (without sintering activator) in noncalcined condition with maximal strength about 3.0 MPa (Figure 3).

The conducted comprehensive research proved high stability of ALUMOX and ceramic suspensions based on it as well as property retention on long storage. Thus, when stored

FIGURE 4: ALUMOX Shell Mold Mechanical Properties Dependence on Calcination Temperature.

TABLE 2: Technical features of ALUMOX.

Concentration wt %	Shelf life, months	Kinematic viscosity, cSt.	Shell mold stress limit, MPa
Al = 5.85	1–12	2.34	2.2
Al ₂ O ₃ = 11.05	12–24	2.35	2.2
	24–36	2.37	2.18

in a closed container with periodical use of binder portion for various studies, ALUMOX composition and properties did not change within three years (Table 2).

Al₂O₃ content modification in binder composition results in latter viscosity and density change. Binder viscosity value allows judging about the possibility to use it for suspension production. Investigation results showed that ALUMOX viscosity did not differ from that of ethyl silicate binder that provided the possibility to use suspensions with similar filling rate. However, in contrast to the suspension based on ethyl silicate binder whose survivability constituted no more than two weeks, the survivability of ceramic suspension obtained on ALUMOX base in a tight container was retained within a year and a half (Table 3).

The study of ALUMOX shell molds drying kinetics demonstrated a need in two independent drying stages of different durability and different temperature depending on mold moisture content.

We found that the first drying stage must be conducted in high air humidity chamber (95% as a minimum) till full organic ligand removal. Oligomer molecular weight growth, 3D cross-linking and boehmite kind $[Al(O)(OH)]_n$, and structure production took place therewith due to hydrolysis of alkoxy groups at Al.

TABLE 3: ALUMOX-based ceramic suspension bonding properties stability.

Property	The 1st month	The 18th month
Relative viscosity of suspension when applied in 1 and 2 layers, sec.	40	42
Relative viscosity of suspension when applied in 3–7 layers, sec	28	28
Bending strength of noncalcined shell molds, MPa	4.2–4.8	4.4–5.1

TABLE 4: Relationship between ALUMOX-based shell mold mechanical properties and activator amount.

ASD-4 amount, wt. %	5	7	10	12
Liquid : Solid : ASD-4	25 : 70 : 5	25 : 68 : 7	25 : 65 : 10	25 : 63 : 12
Amount of layers	6 layers completely, 7 ones without dusting			
$\sigma_{\text{bend.}}$ of dry sample, MPa	2.2	2.4	2.7	3.0
$\sigma_{\text{bend.}}$ of calcined samples at 1250°C, MPa	7.0	7.4	9.4	14.1
$\sigma_{\text{bend.}}$ of calcined samples at 1350°C, MPa	11.8	15.5	20.5	19.2

The second drying stage—adsorbed moisture removal—must be conducted by means of convection drying till equilibrium moisture content in respect to environment is achieved.

ALUMOX-based shell molds must not be calcined at conventional temperatures of 900–1000°C, as within this temperature range they actually loose strength (Figure 4) since ALUMOX at 900–1000°C according to XPhA data (Figure 2) is two-phase system consisting of δ -Al₂O₃ and γ -Al₂O₃ phases.

In order to improve mechanical properties of corundum shell molds at high-temperature casting conditions, we proposed to introduce sintering activator-aluminum metal powder ASD-4 into the suspension [7, 8]. It was found that the higher is the amount of the introduced activator, the better is shell strength both in cold and calcined states thus allowing selecting optimum calcinations temperature for corundum shell molds (Table 4).

On the basis of ALUMOX binder, silica-free shell molds may be fabricated according to conventional investment casting technique. ALUMOX apparent advantage consists in the fact that it is a finished binder requiring no hydrolysis or any other reprocessing (in contrast to ethyl silicate which employment requires complex hydrolytic operation-hydrolysis in cast shops). Moreover, ALUMOX allows to produce by the conventional technique high-refractory monoxide shell mold consisting of α -Al₂O₃ only, for monocrystal and aligned current structure parts casting.

It should be emphasized that in equiaxial casting processes combined shell molds, where one-two top layers are made of ALUMOX-based suspension, may be used.

Combined molds not only warrant perfect reproduction of model configuration and surface microrelief, but also the most important thing is that they make chemically inert barrier, preventing melt interaction with a shell mold (at 1600–1800°C), it allows obtaining casts from reactive metals and alloys with surface roughness up to $R_z < 10 \mu\text{m}$ (basic castings have $R_z > 60 \mu\text{m}$). This, in its turn, improves fatigue performance of the material (strength, service life).

Thus, new manufacturing process for corundum molds by consumable patterns for refractory and reactive metal and alloys casting has been developed, regularities of α -alumina-based ceramic composite have been investigated.

4. Conclusion

- (1) Production technique of ALUMOX silica-free binder of α -alumina composition based on stabilized alkoxyalumoxanes was developed.
- (2) ALUMOX is a finished binder that can be stored in a sealed container for indefinite period, and there is no need in any additional adaptation under foundry conditions.
- (3) ALUMOX use raises ceramic suspension survivability (suspension shelf life in a sealed container actually is not limited).
- (4) ALUMOX allows obtaining monoxide high-heat-resistant refractory corundum mold with required mechanical characteristics according to conventional process of investment casting.
- (5) ALUMOX use for corundum-based shell molds fabrication eliminates metal penetration in metal-mold interface and provides for up to 95% raw material recycle.

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