

## Liquid phase synthesis of lanthanum chromite in induction furnace with slitted copper crucible

I. Pozniak, A. Pechenkov, S. Suvorov, A. Zuev, B. Nacke, B. Niemann, M. Kudryash

### Abstract

Induction melting in cold crucible (IMCC) of nonmetallic compounds is perspective for production of melted materials and products [1-8]. This technology is widely used for syntheses of high temperature oxidic compounds and remelting high temperature oxides to ingots at the present time. Materials, which were produced by IMCC technology, are stable at high temperature in comparison with fritted one. Small shrink and deformation during roasting, well physical-mechanical and thermomechanical properties characterize the products from melted materials.

Induction melting in cold crucible of high temperature oxidic compounds is possible to view as an alternative to solid-phase synthesis. Investigation of materials by X-ray, petrographic and SEM/EDX shown that content of initial unreacted components is no more than 0,01-0,1 wt % [5, 8]. At that time it is possible additional cleaning of the target material from impurities.

### 1. Objects and investigation methods

Liquid-phase synthesis and melt crystallization tests of lanthanum chromite was realized using lanthanum chromite oxide of «LaO-D» quality, chrome oxide of pure for analysis qualification, from account to receive  $\text{La}_{0,975}\text{Ca}_{0,025}\text{CrO}_3$  solid solution. The tests were realized at research test bench at St.Petersburg state Electrotechnical University (SPbGETU) and at research installation for melting of oxides and glasses at Institute of Electrothermal Processes (ETP), Hannover University. Characteristics of the induction furnaces are given at Tab. 1.

Tab. 1. Characteristics of lanthanum cromite melting

Characteristics	Installation at SPbGETU	Installation at ETP
Type of power supply	Lamp generator	Transistor generator
Frequency, kHz	1760	100
Indictor active power, kW	29	94
Diameter of crucible, mm	70	145
High of crucible, mm	250	300

Microstructure and average content of oxides in the simples at the points 1-6 (Fig. 1.) were investigated at scanning electron microscope TESCAN VEGA II LMU with energy-dispersing analyzer INCA Energy.

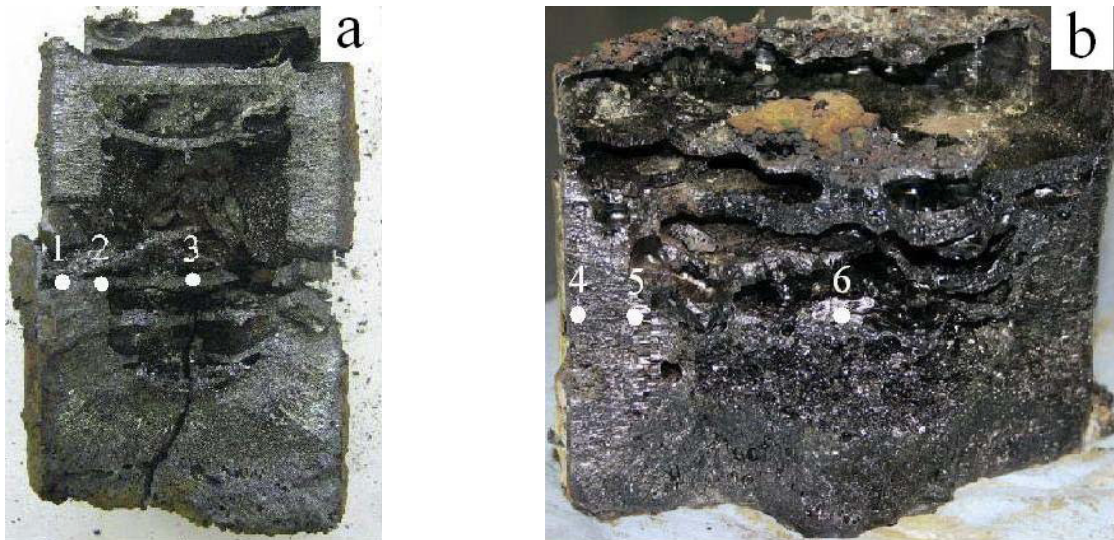


Fig. 1. Structure of the ingots profile and sampling points for investigations (points 1-6).  
 a - ingot with diameter 70 mm                                    b - ingot with diameter 145 mm

Apparent density and open porosity were defined by means of hydrostatic weighing accordingly Russian State Standard 2409-95.

Dynamic modulus of elasticity was defined by measuring instrument of own oscillation frequency «Zvuk-130».

Coefficient of thermal expansion was defined at horizontal dilatometer DIL 402C of «NETZSCH» company accordingly with DIN 51045. Measurements were realized at air atmosphere in temperature range 25-1500°C for heating velocity 5°C/min.

Electrical conductivity was defined on the base of contact two-electrode method [9] using Precision LCR meter QuadTech 7600. To avoid of contact resistivity it was burned-in platinum black to ends of the investigated samples.

## 2. Results of the investigations

### 2.1. Liquid phase synthesis of lanthanum chromite

Chemical interaction velocity of the initial components, which it is equal specific melting rate of the furnace charge, was calculated on the base of received experimental data during liquid phase synthesis of lanthanum chromite composition  $\text{La}_{0,975}\text{Ca}_{0,025}\text{CrO}_3$ :

$$v = \frac{m}{\tau \cdot S},$$

where:  $m$  – material mass, kg;  $\tau$  – melting time, h;  $S$  – cross section area of cold crucible,  $\text{cm}^2$ .

Specific velocity of the melting rate (it is the same as specific synthesis productivity) at air atmosphere at the temperature 2600°C was 0,06-0,09  $\text{kg}/(\text{h} \cdot \text{cm}^2)$ .

Kinetic curves of solid and liquid phase synthesis of 100 g of lanthanum chromite with composition  $\text{La}_{0,975}\text{Ca}_{0,025}\text{CrO}_3$  are shown at Fig. 2. Analyzing of the curves indicates about advantages of liquid phase synthesis as compared to solid phase one. Transformation degree of reaction achieves 98 % for 1 hour at the temperature 1400°C during solid phase synthesis. Specific expenditure of energy is 17,5 kW/h/kg. Liquid phase synthesis of lanthanum chromite allows to receive the same quantity of material for 2-3 minutes at the

temperature 2600°C and specific expenditure of energy will 23-33 kW·h/kg. Content of the target material is no less 99,9 % [5, 8].

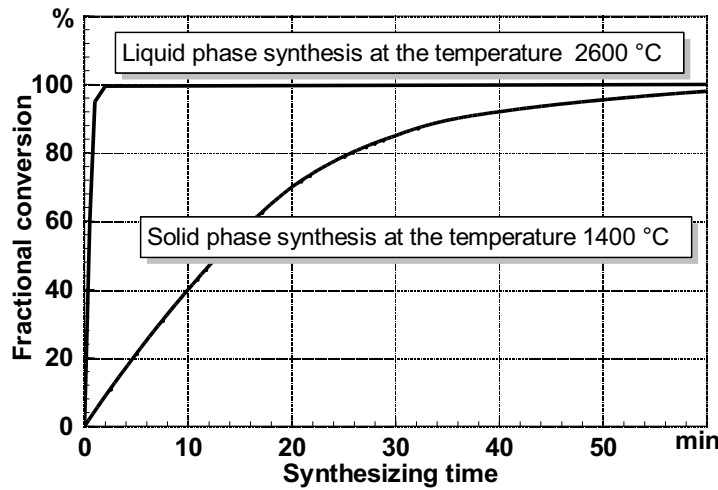


Fig. 2. Kinetic curves of  $\text{La}_{0,975}\text{Ca}_{0,025}\text{CrO}_3$  synthesis at air atmosphere

shown at Tab. 2.

Tab. 2. General experimental and calculated characteristics of lanthanum chromite melting in induction furnace with cold crucible

General geometrical characteristics of the induction system	$T_{melt}$ , °C	$f$ , MHz	$U_{ind}$ , kV	$I_{ind}$ , A	$P_{\Sigma}^t$ , kW	$P_{ind}$ , kW	$\rho_{melt}$ , Ohm·m	$\delta_{sum}$ , %
$H_{melt}=95$ mm $R_{melt}=35$ mm $H_{ind}=93$ mm $R_{ind}=63$ mm	2600	1,82	4,18	235	25,16	1,65	$6,5 \cdot 10^{-5}$	$\pm 17$

where:  $H_{melt}$ ,  $R_{melt}$  – high and radius of the melt pool accordingly;  $H_{ind}$ ,  $R_{ind}$  – high and internal radius of the inductor;  $f$  – power supply frequency;  $U_{ind}$  – inductor voltage;  $I_{ind}$  – inductor current;  $P_{\Sigma}^t$  – total thermal losses in the induction system;  $P_{ind}$  – thermal losses in the inductor;  $\rho_{melt}$  – melt electrical resistivity;  $\delta_{sum}$  – error definition of the melt resistivity.

Value of electrical resistivity, namely express analyzing of the magnitude, can be used in control system of IMCC to keep set value of melt temperature [12, 13].

## 2.2. Microstructure of the ingots and average oxides content

*Ingot with diameter 70 mm.* The ingot has polycrystalline structure with crystalline layers. Thickness of skull layer is about 0,1 mm. Porosity of the ingot is dispersed and concentrated mostly in the central area of the ingot. Overall porosity of the ingot is 26 %. Dissolution of air oxygen in melt results, obviously, formation of shrinkage cavity at central area of the ingot.

Electrical resistivity of the lanthanum chromite melt at air atmosphere was defined by noncontact method which is based on measured thermal, electrical and geometrical characteristics and parameters of induction system and solution of inverse electromagnetic problem [10, 11]. General experimental and calculated characteristics including melt resistivity and its error definition of lanthanum chromite melting in induction furnace with cold crucible at research test bench SPbGETU are

Structure of peripheral area at point 1 is presented non-oriented crystals of angular shape, which was formed at fast cooling of the melt (Fig. 3a.). Width of the peripheral area is not exceed 2 mm and forms about 10 % of the ingot volume.

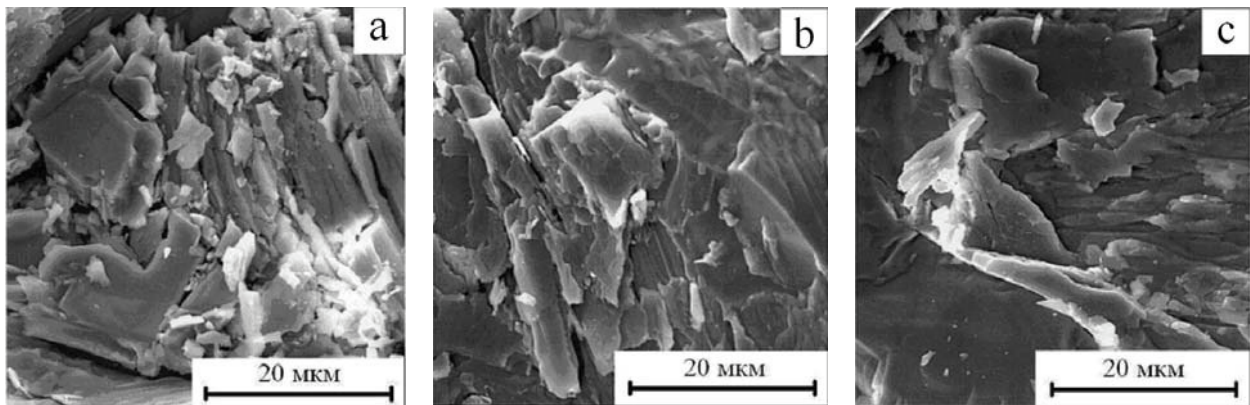


Fig. 3. Fragments of ingot microstructure: a – at the point 1; b – at the point 2; c – at the point 3

Mostly compact area is columnar crystals area and it is placed between peripheral and central areas (Fig. 3b.). This area forms about 60 % of the ingot volume. Porosity in the area is practically absent.

Central area of the ingot has friable structure. Shrinkage cavity and general porosity of the ingot is placed here (Fig. 1a.). This area forms about 30 % of the ingot volume. Structure of crystals is angular and columnar shape (Fig. 3c.).

*Ingot with diameter 145 mm.* The ingot has polycrystalline structure with crystalline layers. Thickness of skull layer is about 0,1 mm. Porosity of the ingot is dispersed and concentrated mostly in the central area of the ingot. Overall porosity of the ingot is 17,6 %.

Structure of peripheral area is presented non-oriented crystals of angular shape, which was formed at fast cooling of the melt (Fig. 4a.). Width of the peripheral area is not exceed 1,5 mm and forms about 6 % of the ingot volume.

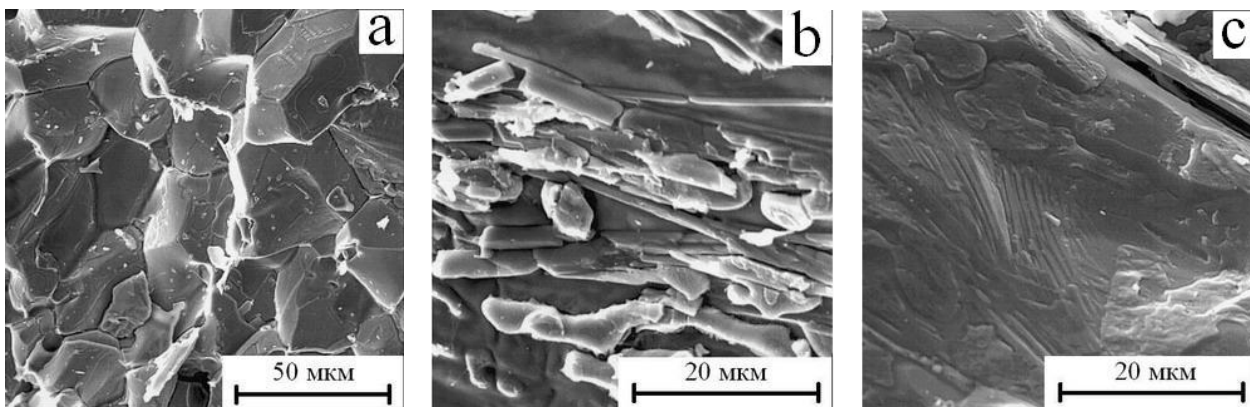


Fig. 4. Fragments of ingot microstructure: a – at the point 4; b – at the point 5; c – at the point 6

Mostly compact area is columnar crystals area and it is placed between peripheral and central areas. This area forms about 70 % of the ingot volume. Porosity in the area is practically absent (Fig. 4b.).

Central area of the ingot has friable structure. Shrinkage cavity and general porosity of the ingot is placed here (Fig. 1b.). This area forms about 24 % of the ingot volume. Structure of crystals is angular and columnar shape (Fig. 4c.).

The results of scanning electron microscopy are shown at Tab. 3.

Tab. 3. Crystals size and average oxides content on the base of data of X-ray analysis

№ sample	Crystals size, mkm	Oxide content, wt. %		
		Cr <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	CaO
1	5-10	31,12	68,18	0,70
2	50-180	31,80	67,56	0,63
3	15-50	32,07	67,06	0,87
4	25-30	31,71	67,60	0,69
5	120-300	31,86	67,48	0,66
6	50-90	32,03	67,28	0,82

During liquid phase synthesis of lanthanum chromite seems cleaning of the material due to volatilization impurities from the melt (Tab. 4.)

Tab. 4. Volume-averaged impurity composition of the lanthanum chromite

Impurity	Max. content at the initial furnace charge, wt. %	Impurity composition at the melted material, wt. %		
		Ingot 70 mm	Ingot 145 mm	Rod samples
Na, K	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	No detected	$1 \cdot 10^{-4}$
Mg	$1 \cdot 10^{-4}$	No detected	No detected	No detected
Ce	$3 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Pr	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	No detected	No detected

### 2.3. Physicotechnical properties

Ingots were crashed to fine particles with size 0,63-0 mm, after that it was grinded in jar mill for 8 hours. Cylindrical simples with diameter 10 mm and height 50 mm were pressed under pressure 160 MPa and burned at 1650°C for 1 hour in argon atmosphere. After that the simples were kept at 1500°C for 5 hours in air atmosphere. Physicotechnical properties of the simples are shown at Tab. 5.

Tab. 5. Physicotechnical properties of the melted lanthanum chromite at room temperature

Attribute Name	Ingot material, diameter 70 mm	Ingot material, diameter 145 mm
Spurious density $\rho_k$ , g/cm <sup>3</sup>	4,98	4,99
Open porosity $\Pi_{otk}$ , %	18,9	18,1
Dynamic modulus of elasticity $E_d$ , 10 <sup>9</sup> Pa	76	74
Coefficient of thermal expansion $\alpha_{25\div 1500}$ , 10 <sup>-6</sup> 1/K	12,0	12,1
Electrical conductivity $\sigma$ , 10 <sup>-3</sup> Sm/m	2,10	1,97

### Conclusions

Presented basic advantages of liquid phase synthesis of lanthanum chromite composition La<sub>0,975</sub>Ca<sub>0,025</sub>CrO<sub>3</sub> in comparison with solid phase synthesis. Induction melting in cold crucible provides high fullness and reaction quickness, homogeneity distribution of components in the melt and therefore receiving monophasic target material. Size of cold crucible and power supply frequency do not influence considerably to physicotechnical properties of the melted lanthanum chromite.



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## Authors

Dr. Pozniak, Igor, Dr. Pechenkov, Andrey Department of Electrotechnology St. Petersburg Electrotechnical University Prof. Popov str., 5 197376, St. Petersburg, Russia E-mail: ivpozniak@mail.eltech.ru, aypechenkov@mail.eltech.ru	Prof. Suvorov, Stanislav, Zuev, Andrey Department of High Temperature Materials St. Petersburg State Technological Institute Moskovsky pr., 26 198013, St. Petersburg, Russia E-mail: av.zuev@mail.ru
Prof. Dr.-Ing. Nacke, Bernard, Kudryash, Maxim, Niemann, Benjamin Institute of Electrotechnology Leibniz University of Hannover Wilhelm-Busch-Str. 4 D-30167 Hannover, Germany E-mail: nacke@ewh.uni-hannover.de	