THE SYNTHESIS OF NANO-SIZED POWDERS IN THE ZrO$_2$-HfO$_2$-Y$_2$O$_3$ SYSTEM

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Abstract. The powders with a crystallite size of 3-5 nm have been prepared by the reverse coprecipitation. The effect of coprecipitation temperature on the size of crystallites and agglomerates has been studied. The cubic phase alone has been found to exist at temperatures above 550 °C in the compositions under investigation.

1. INTRODUCTION

Fluorite related solid solutions of a cubic structure based on Y$_2$O$_3$-stabilized ZrO$_2$ are widely used as solid electrolytes in high-temperature oxygen sensors for the analysis of gaseous media [1,2]. The application of such a type of sensors for the gas/liquid monitoring in glass and blast furnaces is humpered by a number of physico-chemical processes. First, Zr$_4$Y$_3$O$_{12}$ rhombohedral phase can be formed [3,4], this process leads to the sharp change in the elementary cell volume and, consequently, to the destruction of a solid electrolyte material. Next, the yttria-zirconia-compositions are not stable enough in the oxide melts [5,6]. A transitional layer is formed at the boundary between the solid electrolyte and the melt, this layer contains the products of the ceramic destruction. As a result, a significant error may be introduced into the measurements because of the indefinite contribution of the junction potential in the e.m.f. (electric moving force) of a galvanic cell. The above factors confine the use of yttria-zirconia compositions as electrode materials in the sensors for controlling oxygen in oxide melts and high-temperature gaseous media. In contrast to Y-Zr-compositions, the isomorphic solid solutions based on hafnium dioxide have a number of advantages as an electrode material, since they

do not form Hf$_4$Y$_3$O$_{12}$ [8] and possess sufficiently high chemical stability [9]. At the same time, its oxygen conductivity is similar to their of solid solutions based on ZrO$_2$. However, a high cost of hafnium compounds hinders the wide use of them. This hindrance can be overcomed by using the compositional materials including HfO$_2$ as a component.

The aim of the present work was to produce nano-dispersed precursor powders in the ZrO$_2$-HfO$_2$-Y$_2$O$_3$ system and to study their basic physico-chemical properties, i.e. to evaluate the dispersity and agglomerate size and to determine the temperature of amorphous-crystalline transition.

2. THEORY

Having analyzed the phase diagram of the ZrO$_2$-HfO$_2$-Y$_2$O$_3$ system [8,10], one can conclude that the partial substitution of ZrO$_2$ by HfO$_2$ up to 15 mol. % (at 8 mol. % Y$_2$O$_3$) retains the fluorite structure of the solid solution. Also it can be suggested that the obtained isomorphic solid solution will exhibit the properties peculiar to the HfO$_2$-Y$_2$O$_3$ system. The compositions chosen for the present investigation are listed in Table 1.

As it has been already mentioned, the electrode material must have a sufficient chemical stability to oxide melts to achieve high metrological character-

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Table 1. The compositions under investigation.

Com- position	HfO$_2$, mol.%	ZrO$_2$, mol.%	Y$_2$O$_3$, mol.%
N1	5	87	8
N2	7	85	8
N3	10	82	8

Fig. 1. Dependencies of pH on the volume of 1 M NH$_4$OH: 1 – Zr(OH)$_4$, 2 – Hf(OH)$_4$, 3 – Y(OH)$_3$.

istics of an oxygen sensor. A comparison between two sintered ceramic samples of the same composition shows that the sample, which has more fine-grained structure with the average crystallite size less than 100 nm and a density close to the theoretical one, exhibits the higher chemical stability. Thus, to produce the high-density electrode material, the precursor powders should be nano-dispersed, with a crystallite and agglomerate sizes less than 10-20 nm and 5 mm, respectively [11].

We should emphasize that the structure and properties of intermediate compounds determine the agglomeration level of oxide precursor powders and their agglomerate properties. The method of amorphous hydroxide coprecipitation from salt solutions is known to be optimal for preparing of precursor powders in the system under study because this technique provides a high-homogeneity distribution of reagents and a low level of powder agglomeration. Nano-dispersity of the powders obtained by the coprecipitation method is due to the fact that a sufficient number of nuclei-crystallization centres is formed during the solution mixing [12]. The products of coprecipitation are amorphous gels containing nano-sized particles of Zr(OH)$_4$, Hf(OH)$_4$, and Y(OH)$_3$. During further thermal decomposition, they form nano-sized crystallites of the ZrO$_2$-HfO$_2$-Y$_2$O$_3$ system. As shown in [12], the structure and the size of particle agglomerates in the crystalline oxide system will be identical to the structure and the size of particle agglomerates in coprecipitation products, i.e. amorphous hydroxides. Therefore, it is very important to gain a low level of particle agglomeration at the coprecipitation stage. Note that sizes, density, and strength of agglomerates can be varied by changing the conditions of hydroxide synthesis. The following conditions must be kept to prepare low-agglomerated high-dispersed precipitates:

1) the precipitation from diluted salt solutions should be done using a diluted precipitant solution;
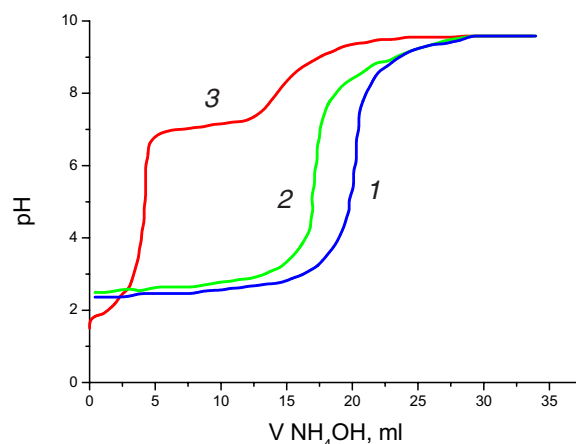
2) the rate of precipitation must be as low as possible;

3) solutions should be vigorously stirred at mixing;

4) reactions must be conducted at room or reduced temperature since the dispersity increases with the decrease in coprecipitation temperature, while the size and the strength of agglomerates decrease [11];

5) to eliminate the agglomerate growth during the aging process, the duration of the precipitate residence in a mother solution should be minimal after the end of the reaction.

3. EXPERIMENTAL

The starting aqueous solutions were prepared from the following salts: HfOCl$_2$·6H$_2$O (p.p.a.), ZrO(NO$_3$)$_2$ ·2H$_2$O (p.p.a.), Y(NO$_3$)$_3$·6H$_2$O (c.p.g.). The precipitation was conducted from the decimolar diluted salt solution. 1M ammonia solution was used as a precipitant.

The starting decimolar salt solutions were titrated by a 1M ammonia solution to determine the pH values required for the precipitation of the amorphous zirconium, hafnium, and yttrium hydroxides. The obtained dependencies of pH on the volume of NH$_4$OH are shown in Fig.1. As can be seen from the figure, the pH values for precipitation of Zr(OH)$_4$ and Hf(OH)$_4$ are close and equal to 2,3 and 2,5 respectively; and the precipitation pH value is about 7 for Y(OH)$_3$. Taking into account these results, the method of reverse precipitation was used to obtain high-homogeneity powders. The salt solution was added drop by drop at a rate of 10 ml/min to the
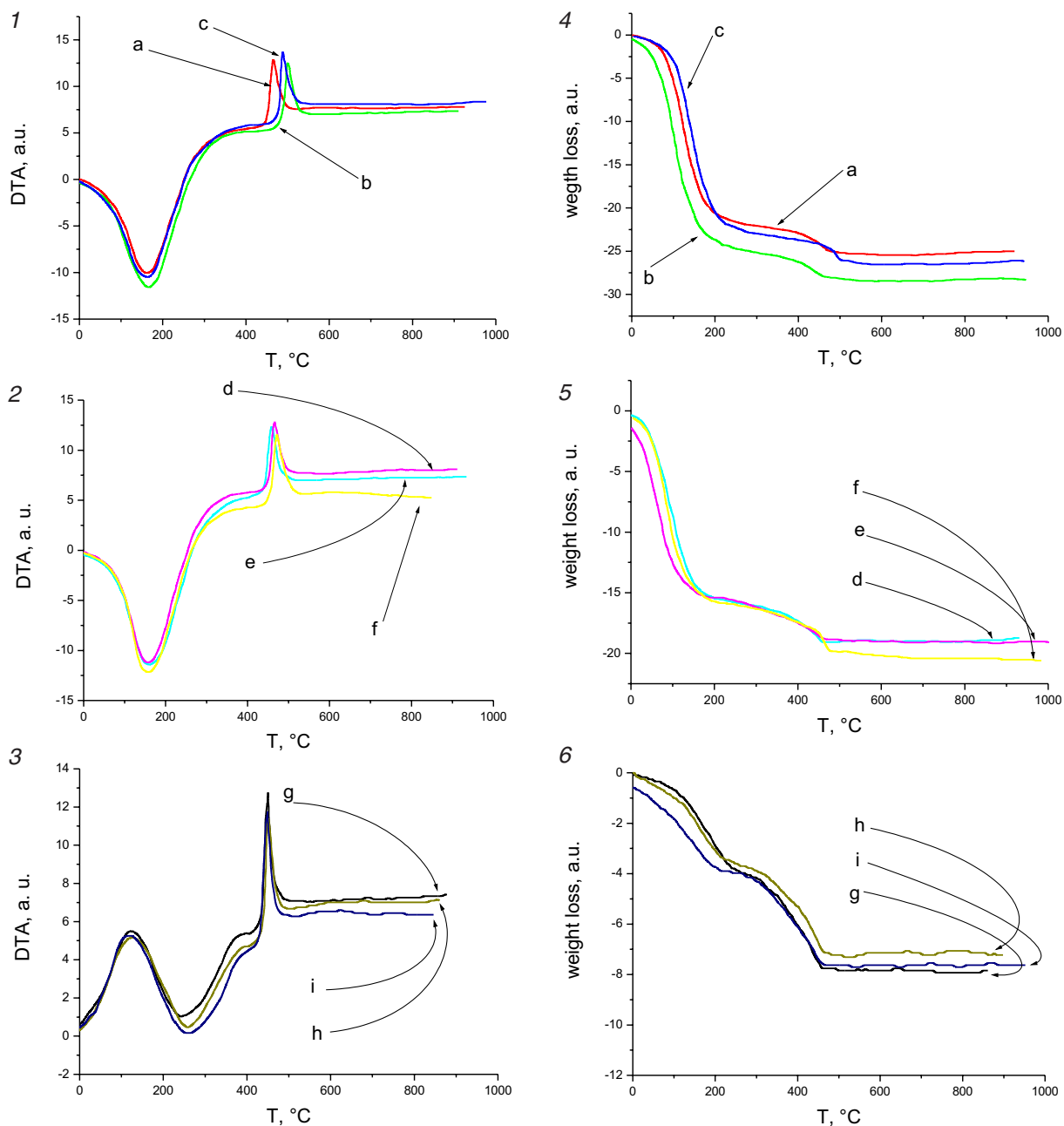
Fig. 2. DTA (1-3) and TG (4-6) curves of the amorphous hydroxide samples: a, d, g – composition N1; a, b, c – precipitation temperature 20 °C; b, e, h – composition N2; d, e, f – precipitation temperature 0 °C; c, f, i – composition N3; g, h, i – precipitation temperature –5 °C.

precipitant solution at vigorous stirring with a paddle glass mixer. The constant pH value of 9.5, which corresponds to the basicity of 1M ammonia solution, was maintained during this process. The precipitate was separated from the solution and washed right after the end of the reaction.

The precipitation was carried out at three temperatures: 20, 0, and –5 °C. The resultant amorphous hydroxide precipitates were calcined at 300
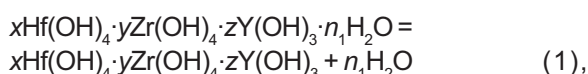
°C for 1 hour. Subsequently they were annealed at 550 °C for 30 min and at 1000 °C for 10 min. As-treated powders were investigated by thermal analysis (MOM-3 Derivatograph) and X-ray diffraction (D-500/HS Diffractometer, Siemens). The agglomerate size was determined using the laser sedimentograph "HORIBA LA-920". The crystallite size was calculated from the XRD data by the "WinFit" program using the Fourier transform method.

Table 2. The temperatures of the effects on heating of synthesized powders according to DTA.

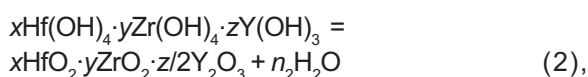| Sample effect	T,^{0}C								
	a	b	c	d	e	f	g	h	i
exo	–	–	–	–	–	–	120	120	120
endo	165	165	165	160	160	160	205	210	220
exo	480	480	500	460	465	480	460	460	460

4. RESULTS AND DISCUSSION

DTA curves of amorphous hydroxide samples are presented in Fig.2. As is seen, the a-f samples have similar DTA curves exhibiting a deep endothermal peak at 160-165 °C (see Table 2). This effect is due to a loss of structural water from amorphous hydroxide crystallohydrates. As this takes place, a considerable weight loss is observed in TG-curves (Fig.2). The dehydration effects in DTA curves of the j-i samples are shifted to the temperature range of 205-220 °C. In case of these samples, the exotherms at 120 °C are also noted which are not accompanied by a weight loss. These effects are likely to result from the formation of amorphous hydroxide crystallohydrates with a low content of water. They are formed from hydrated adducts of variable compositions obtained by precipitation at –5 °C. Such an explanation of the observed exotherms was subsequently confirmed by calculations. The decomposition reaction of the amorphous hydroxide crystallohydrates can be written as follows:

$$x\text{Hf(OH)}_4 \cdot y\text{Zr(OH)}_4 \cdot z\text{Y(OH)}_3 \cdot n_1\text{H}_2\text{O} =$$
$$x\text{Hf(OH)}_4 \cdot y\text{Zr(OH)}_4 \cdot z\text{Y(OH)}_3 + n_1\text{H}_2\text{O} \qquad (1),$$

where x, y, z – stoichiometric coefficients corresponding to the mole fractions of the compositions of amorphous hydroxide crystallohydrates (see Tab.1), n_1 – a number of moles of the structural water lost at dehydration.

DTA curves of all the samples demonstrate exothermal effects (Tab.2) in the temperature range from 460 to 500 °C attributed to a crystallization process revealed by X-ray diffraction (Fig.3). A weight loss observed in this temperature range allows us to conclude that the crystallization process is accompanied by the amorphous hydroxide decomposition, which can be assumed as follows:

$$x\text{Hf(OH)}_4 \cdot y\text{Zr(OH)}_4 \cdot z\text{Y(OH)}_3 =$$
$$x\text{HfO}_2 \cdot y\text{ZrO}_2 \cdot z/2\text{Y}_2\text{O}_3 + n_2\text{H}_2\text{O} \qquad (2),$$

where n_2 – a number of moles of water lost at hydroxide decomposition.
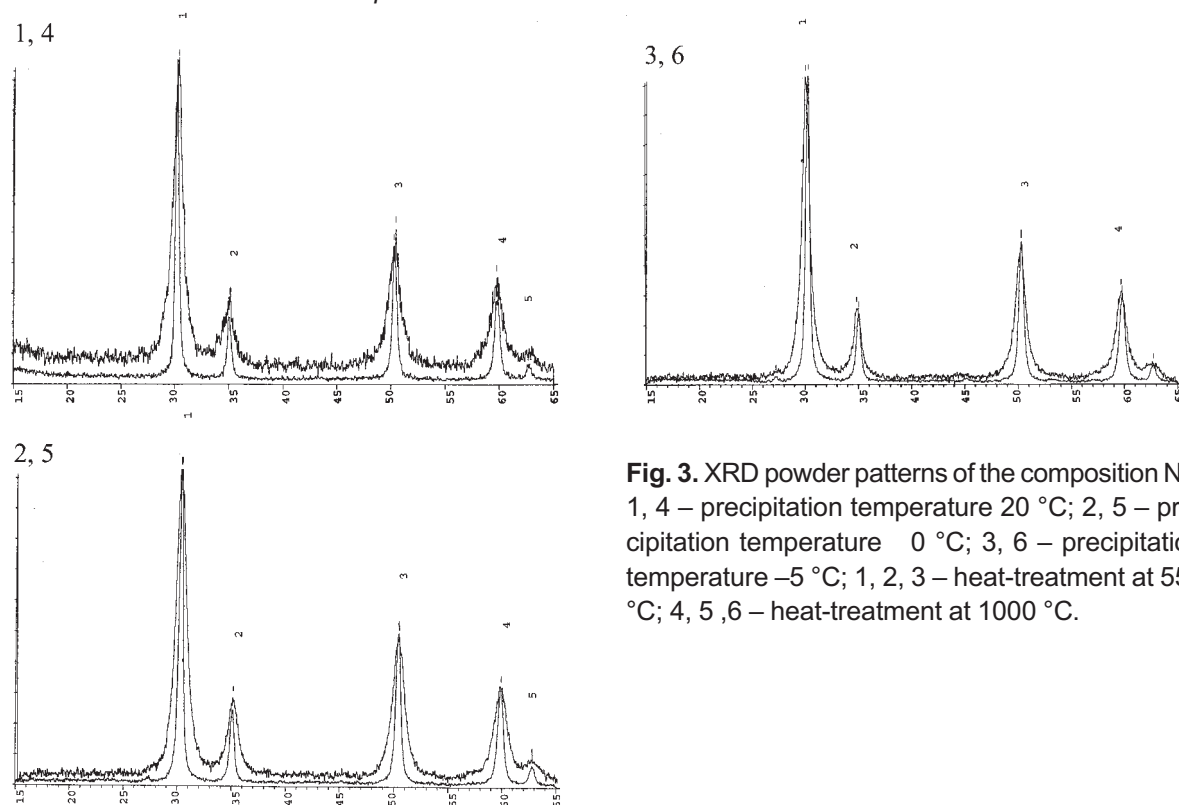
Using DTA and TG data, the values of variables n_1 and n_2 were estimated for the studied samples (see Tab.3). One can see from the table that the content of water in amorphous hydroxide crystallohydrates diminishes with the decrease in precipitation temperature. The average values of n_1 are 5,0; 2,4 and 0,57 and of n_2 are 0,48; 0,21 and 0,19 at the precipitation temperatures of 20, 0, and –5 °C, respectively. The calculated water losses at stoichiometric hydroxide decomposition are equal to 0,230; 0,227 and 0,223 moles of H_2O per 1 mole of the composition N1, N2, and N3 respectively. The analysis of the data obtained gives us the opportunity to suggest that the crystallohydrates are not completely decomposed in case of samples a, b, c. Low-water compounds are formed here and these compounds are similar to the crystallohydrates which are produced from the j, h, and i samples precipitated at –5 °C. The exotherm effect observed in the DTA curve at 120 °C , Fig. 2, supports this assumption. The stoicheiometric value of a weight loss is achieved for the hydroxide decomposition in case of the samples d, e, and f precipitated at 0 °C, while for the j, h, and i samples, precipitated at –5 °C, the weight loss values are observed to be less than those predicted by theory. These data may indicate that the hydroxides of non- stoicheiometric composition are formed at dehydration.

XRD analysis of the ZrO_2-HfO_2-Y_2O_3 powders revealed that the diffraction peaks of the fluorite related cubic structure are only observed for all compositions studied. Fig.3 demonstrates XRD patterns of the powders of composition N3 (see Tab.1) obtained at 20, 0, and –5 °C. XRD patterns identical with those shown in Fig.3 were detected for the powders of compositions N1 and N2 synthesized under the same conditions. The only difference in the XRD patterns of the samples heat-treated at 550 and 1000 °C was in the half-width of the diffraction peak; in turn, this value is proportional to the average crystallite size (see Tab.4). As seen from the table, the crystallites of all the powders under study

Table 3. Weight losses of powder samples calculated from TG data.

Sample	Composition number	Precipitation temperature, ^0C	*Losses on dehydration n_1, mol. H_2O	*Losses on hydroxides decomposition n_2, mol. H_2O	Total losses, mol. H_2O
a	1	20	4.3	0.56	4.86
b	2	20	6.2	0.32	6.52
c	3	20	4.6	0.57	5.17
d	1	0	2.4	0.21	2.61
e	2	0	2.3	0.23	5.17
f	3	0	2.5	0.14	2.64
g	1	-5	0.67	0.20	0.87
h	2	-5	0.50	0.19	0.69
i	3	-5	0.53	0.18	0.71

* *Calculated to 1 mole of composition*

1, 4

3, 6

2, 5

Fig. 3. XRD powder patterns of the composition N3: 1, 4 – precipitation temperature 20 °C; 2, 5 – precipitation temperature 0 °C; 3, 6 – precipitation temperature –5 °C; 1, 2, 3 – heat-treatment at 550 °C; 4, 5 ,6 – heat-treatment at 1000 °C.

are nano-sized. The average sizes are 3-5 nm and 20-28 nm for crystallites of powders heat-treated at 550 and 1000 °C, respectively [13, 14]. The data obtained reveal that an average size of crystallites does not depend on the temperature of precipitation. This phenomenon is probably connected with the fact that a number of crystallization centres appearing on precipitating is not temperature dependent over the temperature range of the present investigation.

Of considerable interest was also to study the processes of nano-particle agglomeration. Fig.4 presents the distribution of agglomerate sizes in the powders of the compositions N3 obtained at different temperatures. As one can be seen from the figure, agglomerate sizes are reduced with decreasing temperature of precipitation. An average size of agglomerates amounted to 14,41; 5,91, and 5,01 mm at the precipitation temperature of 20, 0, and –5 °C respectively.

Table 4. The average sizes of crystallites calculated from XRD data.

Sample	N of composition according to Tab. 1	Precipitation temperature, ^{0}C	The averege size of crystallites, nm	
			550 ^{0}C	1000 ^{0}C
a	1	20	4.5	22.8
b	2	20	4.4	23.8
c	3	20	3.7	27.6
d	1	0	3.9	22.8
e	2	0	3.5	23.6
f	3	0	5.0	23.3
g	1	-5	4.4	28.3
h	2	-5	3.1	19.6
i	3	-5	2.7	26.5

CONCLUSION

The powders of the ZrO_2 -HfO_2 -Y_2O_3 system have been prepared by the reverse coprecipitation. The crystallite size of the powders heat-treated at 550 °C is less than 3-5 nm. It has been shown that the reduction of the precipitation temperature does not influence on an average size of crystallites. The fluorite related cubic phase alone has been found to exist at temperatures above 550 °C in all the compositions studied. It has been revealed that the content of structural water in amorphous hydroxide crystallohydrates decrease with the decrease in the precipitation temperature. The powders produced at reduced temperatures are less agglomerated as compared to those obtained at room temperature. The agglomerate size in the powders synthesized at 0 and -5 °C is 5-6 mm. Thus, the produced precursor powders are the perspective reagents for the synthesis of the novel compact materials with a density close to the theoretical one and with a crystallite size less than 100 nm.

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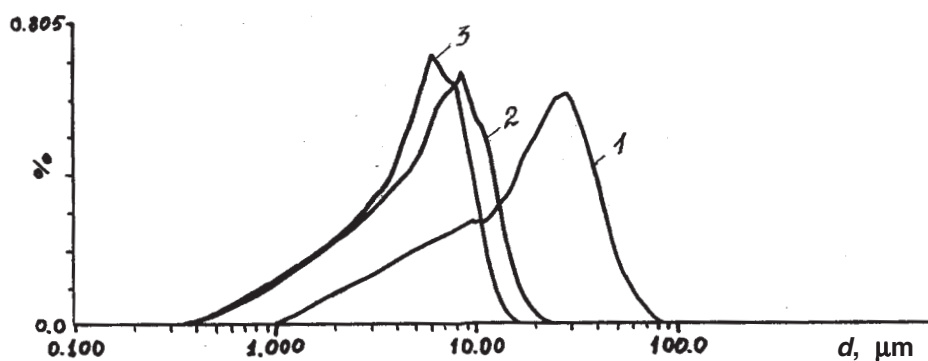[9] V.B. Glushkova, M.V. Kravchinskaya, A.K. Kuznetsov and P.A. Tikhonov, *Hafnium dioxide*

Fig. 4. The distribution of the agglomerates size in the powder of the composition N3 heat-treated at 550 °C; precipitation temperature is 20 °C (1), 0 °C (2) and –5 °C (3).

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