4. K. Ye, Kapustin and D. Z. Savostin. Looking after hearths and repairing open-hearth furnaces. Kemirovskiy Book Publishing House.

5. A. K. Sokolov and others. Laying and welding on open hearths. Metallurgizdat, 1957.

6. G. Ye. Germaidze and V. G. Pushkov. Metallurg, 1950, No. 3.

7. Ye. F. Kosolapov and I. P. Bas'yas. Proc. East. Inst. Refract., 1960, issue 2.

8. I. P. Bas'yas and A. M. Lepesa. Ibid. 1959, issue 1.

9. I. P. Bas'yas. Ogneupory, No. 10, 1960.

10. I. P. Bas'yas and others. Plant Laboratory, 1959, No. 9.

RESEARCH WORK

TECHNOLOGICAL FEATURES OF CASTING ZIRCONIA PARTS

G. P. KALLIGA, V. A. KOLBASOVA AND D. N. POLUBOYARINOV
(Mendeleyev Chemical Technology Institute)

The technique of casting zirconia parts from aqueous suspensions of stabilized zirconium dioxide is of definite practical value, despite its complexity and laboriousness.

The parts are cast from slurries with a relatively low moisture content and the green ware is fairly dense and strong, which keeps the shrinkage down during firing and reduces the possibility of flaws occurring during this technological process [1-3].

The method makes it possible to use parts made from "damp" mixtures which had been spoiled by firing. The method is also useful for the manufacture of zirconia parts with improved thermal stability by synthesizing them from cubic ZrO_2 with the addition of monoclinic ZrO_2 [4-6].

As a result of a number of investigations [1-3, 7-9], a technological procedure has been worked out for water casting parts from stabilized ZrO_2, and the possibility has been shown in principle of casting parts both in acid and alkaline mediums.

The following methods have been put forward for finely pulverizing the material: a) rubber lined mills with zirconia balls producing "alkaline" slips; b) steel mills with subsequent treatment of the material with hydrochloric acid to remove the iron, producing "acid" slips.

The technological advisability of these methods of preparing the material, however, the acid treatment and casting of the parts in different media have not been described adequately in technical literature.

This article is devoted to the study of these processes.

For the investigation we used zirconium dioxide stabilized with 6% CaO. The industrial zirconium dioxide contained 97.55% ZrO_2 and 1.15% TiO_2. The initial materials were industrial ZrO_2 and $CaCO_3$ (type 'ch') and were pulverized in ball mills by the wet method. The zirconium dioxide spent 40 hours in the metal mill, after which it was washed with HCl and decanted with water unitl the pH value was 3; the $CaCO_3$ was ground in a rubber-lined corundum-ball mill for 15 hours. The amount of corundum impurity was not more than 0.2% of the CaCO weight.

The materials were mixed by the slip method and then dehydrated; the mixutre was dried, pulverized and pressed at 500 kg/cm^2 into cylindrical compacts 50 mm in diameter and length. The compacts were fired at 1750° for 2 hours. the fired compacts were then ground in jaw and roller crushers, the powder was passed through a 0.5 mm screen, and then underwent magnetic separation. Microscopic and x-ray analyses showed virtually complete stabilization of the zirconium dioxide in the fired products.

The slip for casting the parts was made with powder by two methods:

a) by the wet method of grinding for 80 hours in a rubber-lined mill with zirconia cylinders or in certain cases with corundum balls. The weight ratio of the balls, material and water was 2.5 : 1 : 1. The zirconia were made as rolled stabilized ZrO_2 cylinders 15-20 mm in diameter and height; the bulk density of the cylinders was 5.1-5.3 g/cm^3 and their porosity 1-2%.

The grinding impurity resulting from abrasion of the zirconia cylinders amounted to 40% of the weight of the zirconium dioxide charged. A grinding time of 80 hours was selected on the basis of [1] which states that 52 hours grinding produces adequate dispersion of the material.

b) by the wet method of grinding in a steel mill for 45, 60, 80, 100 and 120 hours with similar load ratios and subsequent treatment with hyrdochloric acid and decantation with water to a pH value of 1.5-1.7 (bulk); the effect of the difference in the pulverization time was studied since there is no relevant data on steel-mill grinding.

Thus, for our work we used two types of initial slip: alkaline slip with a pH value of 10.5 and acidic slip with a pH value of 1.5-1.7.

Study of the castability of alkaline slip. Sedimentation analysis of diluted slip suspensions shows that in the alkaline medium the ZrO_2 particles are present in a more aggregated state than in an acid medium at a pH value of 2.0-2.5 (Fig. 1).

The number of ZrO_2 particles less than 5 microns, even in the acid medium, did not exceed 36%, whereas the

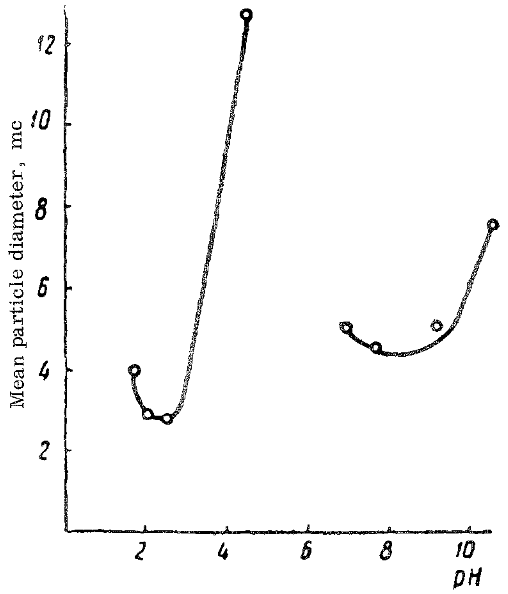

Fig. 1. Variation in dispersion of ZrO_2 particles as function of pH value of medium

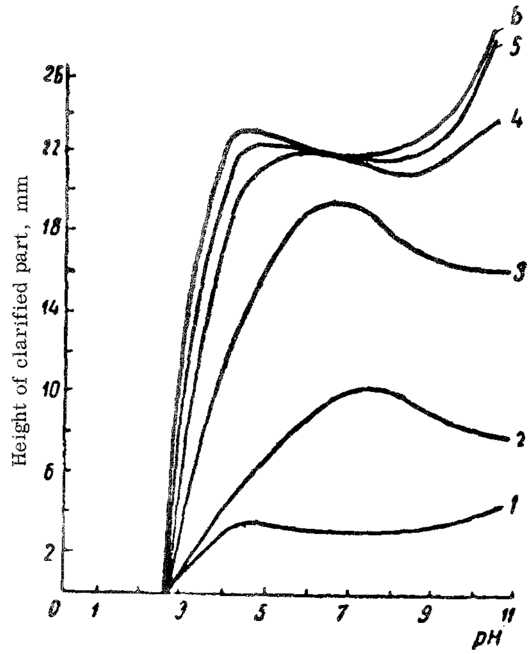

Fig. 2. Variation in height of clarified part of slip at different pH values. Duration of experiment:

1) 10 minutes; 2) half an hour; 3) one hour; 4) two hours; 5) 3 hours; 6) 4 hours

microscope revealed 65–70% of these particles. This indicates the aggregation instability of the suspension, which was further shown by stratification of the slip and low castability. Thus, the stratification, particularly in an alkaline medium, shows up clearly in the curves obtained (Fig. 2) for the dependence of the height of the clear part of the slip on the pH value of the medium when it has been left to stand for different periods of time.

The greatest degree of clarity was observed between pH values of 10 and 5 with a subsequent reduction to pH = 2.5. At pH values of 2.5 and 2, the slip did not become completely clear.

The casting properties of the slip were checked at the initial pH value 10.5, with slight acidification to pH = 2.5, and with the addition of 0.8% sulfite-cellulose base to the initial alkaline slip (in terms of dry weight) in order to stabilize the suspension.

For purposes of comparison we also cast experimental speciments (crucibles 40 mm high) from the initial acidic slip with pH = 1.7.

The results of experimental castings with pre-vacuumed slip are shown in Table 1. The poorest casting properties (high filling rate of body, large amount of spoilage, low density of the green ware) are shown by the initial alkaline slip. The addition of sulfite-cellulose base and acidulation to a pH value of 2.5 does not improve the strength of the green ware, although it improves the casting properties. At the same time washing the slip with hydrochloric acid does not only improve its casting properties, but increases the density from 2.5 to 2.8 g/cm^3.

The poorer casting properties of the initial slip are evidently due to the presence of calcium compounds (on account of the CaO which has not entered the solid solutions), which are frequently leached out by long wet grinding of stabilized ZrO_2, shown by the high pH value of the initial slip (10.5).

The coagulating action of the calcium is not offset by more acidulation of the slip, although the particles do become slightly dispersed. The material has to be washed with hydrochloric acid during which the calcium compounds are completely removed, an acidic medium is created and zirconium oxichlorides are formed, which all together sharply increase the stability of the slip and improve its casting properties.

The positive effect of the oxichlorides and acidic medium is observed, for example, when casting parts from "crude" mixtures, using non-stabilized ZrO_2 washed with hydrochloric acid and supplemented with calcium zirconate as the stabilizer for the zirconium dioxide [2].

The beneficial effect of the zirconium oxichlorides on the stability of the suspension and the d-aggregation of the particles is well illustrated by curves for the precipitation of fine-ground non-stabilized ZrO plotted on the basis of the accumulation of sediment in the plan of a tortion balance (Fig. 3). Here the addition of zirconium oxichlorides, even to a saturated solution of $ca(OH)_2$ results in peptization of the particles in the same way as when the material is washed with hydrochloric acid.

Casting properties of acid slip made by grinding in a steel mill and subsequently washing with hydrochloric acid. Study of the effect of the grinding time on the properties of the slip, green ware and fired product has established the fact that as the grinding time is lengthened, the fineness of the pulverized material increases unevenly. After 60 hours the effectiveness of lengthening the grinding time is sharply reduced (Fig. 4). When the grinding lasts 45 hours, the material is still more coarsely dispersed and high-grade parts cannot easily be cast from this slip (Table 2). After 60 hours of grinding, it is possible to cast parts from the slip, but the green ware shows a low bulk density of 2.54 g/cm^3.

TABLE 1

VARIATION IN CASTING PROPERTIES OF SLIP, CHARACTERISTICS OF GREEN AND FIRED MATERIAL

Initial slip	Slip			Green material			Quality of casting	Specimens fired at 1700°			
	pH	Moisture content, %	Thickness of gathered body in 15 secs., mm	Bulk density, %	Porosity, %	Bending strength*, kg/cm^2		Bulk density, %	Moisture absorption, %	Apparent porosity, %	Shrinkage, %
Alkaline	10,5	45	10	2,49	52,4	6,1	Extremely unstable casting; large number of crystals were cracked	5,18	0,2	1,0	21,9
Alkaline with addition of 0.8% sulfite-cellulose base	9,5	45	4,2	2,49	52,4	10,7	Specimens cast well; no cracks or flaws	5,27	0,2	1,0	22,5
Alkaline, acidulated with hydrochloric acid	2,5	45	3,7	2,56	—	6,4	Unstable casting; some cracking	5,17	0,2	1,0	21,0
Treated with hydrochloric acid and then decanted with water to pH = 1.7	1,7	45	1,2	2,80	48,4	7,5	Very good specimens cast	5,24	0,2	1,0	19,0

*Determined on bars 65 × 15 × 8 mm in size.

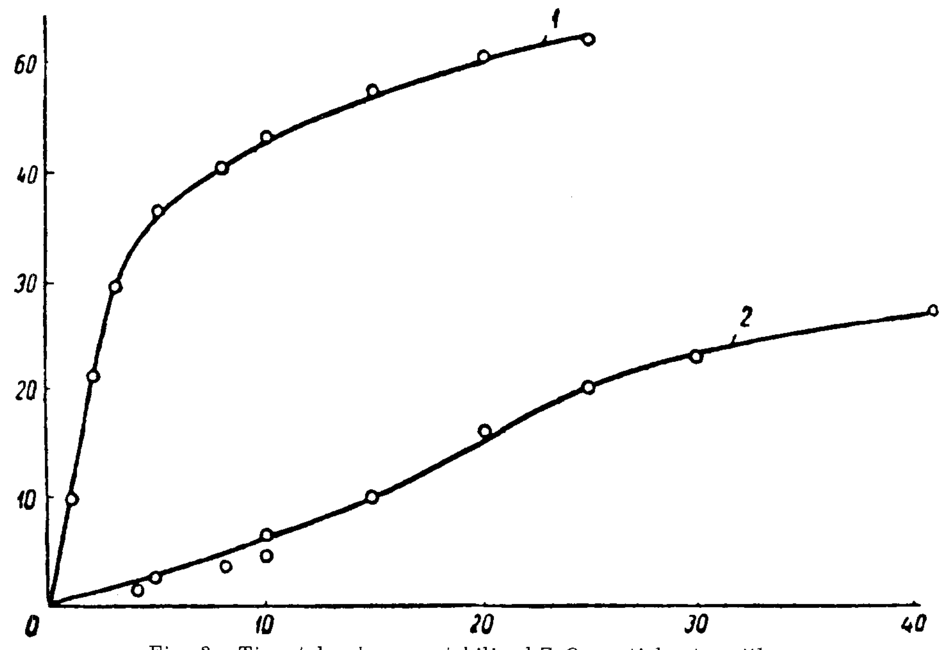

Fig. 3. Time taken by non-stabilized ZrO_2 particles to settle:

1-in medium of saturated $Ca(OH)_2$ solution; 2-in medium of saturated $Ca(OH)_2$ solution and in presence of zirconium oxichlorides.

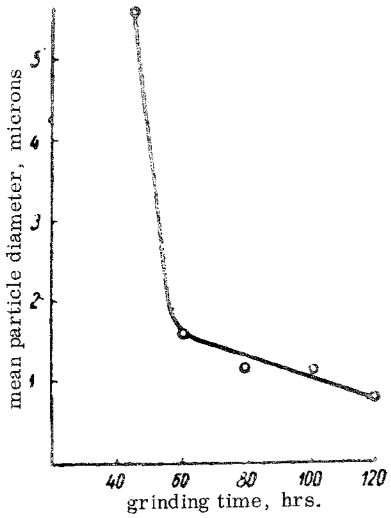

Fig. 4. Variation in mean diameter of ZrO_2 particles as function of pulverization time

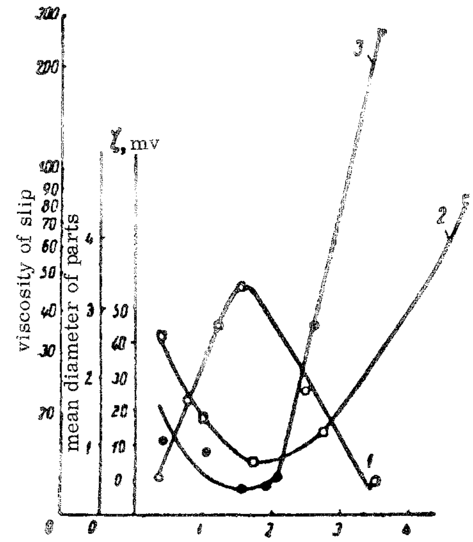

Fig. 5. Effect of hydrogen iron concentration on: 1-variation in ζ potential; 2- degree of dispersion of particles; 3-viscosity of slip

Slip obtained after grinding for 80-120 hours shows good casting properties, ensures a high and even degree of density in the green material, and specimens fired at 1700° are close in density (5.43-5.50 g/cm³). Densities of this kind in the green and fired material were not obtained when zirconia parts were cast from "crude" mixtures.

Thus, in our experiments an 80-hour grinding period provided sufficient for high-grade casting and for producing green and fired material with a degree of density. All further experiments were conducted with slip obtained after this amount of grinding.

TABLE 2

EFFECT OF GRINDING TIME ON CASTING PROPERTIES OF SLIP, CHARACTERISTICS OF GREEN WARE AND FIRED MATERIAL

Grinding time, hours	Slip*			Quality of casting	Green material			Material fired at 1700°			
	Moisture content %	Viscosity, centipoise	Thickness of collected body in 60 sec, mm		Bulk density, g/cm³	Moisture absorption, % (from kerosene absorption	Porosity, %	Bulk density, g/cm³	Moisture absorption, %	Apparent porosity, %	Theoretical linear shrinkage, %
45	45	—	—	All crucibles cast were cracked	—	—	—	—	—	—	—
60	45	6	10	Specimens cast well; no flaws	2,54	—	—	5,3	—	—	—
80 a	45	5	0,7	" "	2,79	17,3	48,3	5,40	0,1	0,5	19,6
80 b					2,81	17,0	48,0	5,43	0,1	0,5	19,7
100 a	45	5	0,6	" "	2,78	17,4	48,4	5.50	0	0	20,4
100 b					2,81	17,0	48,0	5,45	0,1	0,5	19,8
120 a	45	4	0,6	" "	2,79	17,3	48,3	5,50	0	0	20,2
120 b					2,77	17,4	48,5	5,48	0	0	20,3

* pH value of slip = 1.2-1.9
a specimens made by casting
b specimens made by modling dried slip

TABLE 3

Quality of Casting and Properties of Green and Fired Material at Various Moisture Contents of Original Slip.

Slip*		Quality of casting	Green material		Material fired at 1700°			
Moisture content, %	Viscosity, centipoise		Bulk density, g/cm³	Porosity, %	Bulk density, g/cm³	Water absorption, %	Apparent porosity, %	Theoretical linear shrinkage, %
20	75	Slip is less mobile	2.81	48.1	5.45	0.3	1.6	19.8
25	33	Slip is more mobile	2,82	47,8	5.44	0.3	1,6	19,6
30	17	Product casts well	2.80	48.4	5,45	0,3	1,6	19.8
45	13	Product casts well	2,79	48,3	5,50	0	0	20,2

*pH value of slip = 1.5.

TABLE 4

Duration of Standing Time and its Effect on the Slip Properties and Density of the Castings.

Bulk number	Duration of standing time, days	Slip			Green material		Quality of casting
		Moisture content, %	pH	Viscosity, centipoise	Thickness of gathered body in 60 secs., mm	Bulk density, g/cm³	
1	0	28,2	0,5	36	2,5	2.74	Casting difficult to remove from mold; after 4 days of standing the quality of the casting improves.
	1			—	—	2.79	
	4			—	—	2,89	
	6			—	—	2,93	
	55			—	—	2,98	
2	0	28,2	1,1	30	2,0	2,85	Product casts well. Castings have no deffects.
	2			26	1,6	—	
	4			24	1.5	3.00	
	9			22	1,1	3,01	
	55			21	1,0	3,02	
3	0	28,0	1,9	22	1,1	2,95	Product cast well. Castings have no defects.
	1			—	—	3.10	
	2			—	—	3,16	
	7			—	—	3,16	
	55			—	—	3,16	
4	0	28,5	2,5	40	2,7	2.86	Part of the products cracked. Products difficult to remove from mold. After 55 days of standing the quality of the casting improves.
	1			—	—	2,86	
	4			—	—	2,86	
	55			—	—	2,86	
5	0	42*	4,2	—	6,2	2,72	Products crack on casting.
	2			—	—	2,72	

*At a moisture content of 28% the slip was too thick for casting.

Experiments on the aggregation of particles in diluted suspensions made with the 80-hour slip, washed to a pH value of 4.8, with variation of the acidity of the medium, showed that the greatest peptization is achieved between pH values of 1.5 and 2.5 (Fig. 5).

When the pH value of the slip is 1.5, the working moisture content can be selected (Table 3). Parts without cracks or any other flaws were cast with slip of all the conventional percentages of moisutre (20, 25, 30 and 45%). In all cases the density of the green ware was 2.8 g/cm^3 and that of the fired material 5.45 g/cm^3.

When slip with a moisture content of 20% was cast, however, the operation proved rather difficult on account of increased viscosity and a relatively high gathering rate of the body. When the moisture content was 25%, there was far less difficulty, and at 30% there was none at all.

The viscosity of the slip and the zeta-potential as a function of the pH value of the medium (see Fig. 5) were determined concurrently with the research described. The optimum point on the curves lies at close pH values ranging from 1.2 to 2.0. The slight shift in the optimum values is apparently due to the experimental conditions (at different concentrations, experiments at different times, and so on).

During the investigation we observed a change in the casting properties of the slip with time. Similar changes due to ionic exchange, dispersion of the particles and other factors have been observed during the casting of parts from clay slip [10] with the addition of fluidizing additives.

On account of this some of the slip was washed until the pH value was 0.5, 1.1, 1.9, 2.5 and 4.2; after this treatment and after being allowed to stand from 1 to 55 days, experimental castings were made with subsequent determination of the bulk density of the green material and other characteristics (Table 4).

When the slip with initial pH values of 0.5-1.9 was allowed to stand, its properties changed and showed a reduction in the gathering rate of the body, a slight reduction in viscosity and an increase in the bulk density. Over the pH range 1.1-1.9, when the green ware has stood for 2 to 4 days, the increase in bulk density is 0.15-0.2 g/cm^3.

A further period of standing has virtually no effect on the density. The increase in the density of the green material should increase its strength and reduce shrinkage during firing. For example, if the bulk density is 3.1 g/cm^3 for the green ware and 5.5 g/cm^3 for fired parts, the theoretical linear shrinkage is 17% as opposed to 20 when the bulk density of the green ware is 2.8 g/cm^3.

CONCLUSIONS

Alkaline slips made of zirconium dioxide stabilized with calcium oxide, which have been obtained by grinding the materials in a rubber-lined zirconium-ball mill, exhibit poor casting properties and a tendency to stratification. The green ware obtained shows a low bulk density of the order of 2.5 g/cm^3. The inadvisability of preparing material for casting in this way is further confirmed by the need to restore a large number of the grinding balls which quickly wear out during operation. In order to obtain a uniform degree of fineness of the material, the grinding time for zirconium balls, as opposed to the process in metal mills, should be increased.

A sharp improvement in the casting properties of slip, an increase in the porosity of the green ware and a reduction in shrinkage during firing can be obtained by casting acidic slips treated with hydrochloric acid. This determines the technological advisability of washing the stabilized ZrO_2 with acid after grinding, and the possibility, therefore, of grinding for a shorter period in steel metal-ball mills.

The most favorable conditions for casting slip made of stabilized ZrO_2 treated with hydrochloric acid are a moisture content of about 30% and a pH value of 1.5-2. Here the density of the casting is 2.8 g/cm^3 and the density of the fired part 5.45 g/cm^3.

The casting properties of slip are improved and the density of the green ware is raised by 0.2 g/cm^3 if the materials are left to stand for 2 to 4 days after treatment.

REFERENCES

1. A. A. Grebenyuk and Z. I. Zhuravleva. Ogneupory, 1959, No. 7.
2. G. P. Kalliga and others. Ogneupory, 1960, No. 7.
3. S. G. Tresvyatskiy and A. M. Cherepanov. Super-duty materials and parts made of oxides. Metallurgizdat, 1957.
4. C. E. Curtis. Journ. Am. Cer. Soc., 1947, 30, No. 6.
5. G. K. Basalova and others. Coll. Scientific Papers, UNIIO, 1960, issue 3.
6. L. A. Kachalova and A. I. Avgustinik. J. Phys. Chem., 1959, 32.
7. St. Pierre. Trans. Brit. Cer. Soc., 1952, 51, 260.
8. M. A. Schwartz, G. D. White and C. E. Curtis. Atomic Energy Comp. Inform. Service Oak Ridge, 1953, 1354, 28.
9. B. C. Weber, P. E. Rempes and M. A. Schwarz. Journ. Am. Cer. Soc. 1958, 37, No. 7.
10. Ye. I. Zavarzina. Papers of NIIstroykeramika, issue 15, Gosstroyizdat, 1960.
11. G. V. Kukolev and other. DAN Uk. SSR, "Chemical Technology", series, 1961, No. 2.