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(54) **MATERIAU MOULE A ECOULEMENT LIBRE BASIQUE ET PIECES PROFILEES FABRIQUEES EN CE MATERIAU**

(54) **BASIC FREE-FLOWING CASTING MATERIAL AND PREFORMS PRODUCED THEREFROM**

(57) L'invention concerne un matériau moulé à écoulement libre basique ainsi que des pièces profilées fabriquées en ce matériau. Des matériaux moulés réfractaires, basiques et non basiques, sont connus depuis longtemps. Les matériaux moulés réfractaires traditionnels présentent des propriétés thixotropes et doivent être revêtus en recourant à des techniques de vibration. Les matériaux moulés à écoulement libre n'ont pu être préparés jusqu'à présent qu'à partir de matières premières à base d'alumine. La fabrication d'une suspension basique aqueuse hautement concentrée, constituant le matériau moulé à écoulement libre s'est heurtée jusqu'à présent à l'exigence visant à assurer les propriétés rhéologiques correspondantes et le faible degré d'hydratation des matériaux à base de MgO. L'invention vise, d'une part, à obtenir un matériau moulé du type précité pour le revêtement monolithique ou la réparation d'ensembles soumis à de hautes températures et, d'autre part, à fabriquer des pièces réfractaires. Ce but est atteint suivant une variante à grains fins et une variante à grains fins et grossiers. Pour la variante à grains fins, on utilise un matériau réfractaire à base de MgO favorisant la dilatance, d'une grosseur de grains comprise entre 0,1 et 45 µm, ainsi qu'au moins un dispersant et un agent gélifiant favorisant la dilatance, avec addition d'une quantité prédéterminée d'eau à gâcher. Pour la variante à grains fins et grossiers, également à base de MgO, on utilise complémentairement un matériau réfractaire de grosseur de grain atteignant 15 mm ainsi qu'un liant. Dans les deux variantes, des adjuvants réfractaires et autres adjuvants améliorant la qualité du produit final peuvent en outre être utilisés.

(57) The invention relates to free-flowing casting material and preforms produced therefrom. Refractory non-basic and basic materials have been known per se for a considerable amount of time. Traditional refractory casting materials have thixotropic properties and need to be lined using vibration technology. In the past, free-flowing casting materials were solely based on aluminium oxide starting materials. Attempts to produce an aqueous, highly concentrated, basic suspension which would form the basis of free-flowing casting materials failed to meet the requirements in terms of rheological properties and to achieve the low degree of hydration for MgO based materials. The aim of the invention is to provide the above-mentioned casting material for the monolithic lining or repair of high temperature aggregates in addition to producing refractory preforms. This is achieved by providing a fine grained and fine-course grained alternative. A refractory MgO-based material promoting dilatancy and possessing a grain size of 0.1-45 µm is used along with at least one dispersing agent and cross-linking agent also promoting dilatancy, whereby a given amount of tempering water is added. A refractory material with a grain size of up to 15 mm and a bonding agent are used for the fine-coarse grained alternative which is also MgO based. Refractory and other additives improving the quality of the final products can also be used in both alternatives.

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(54) Bezeichnung: BASISCHE FREIFLIESSENDE GIESSMASSE SOWIE DARAUS HERGESTELLTE FORMTEILE

(57) Abstract

The invention relates to free-flowing casting material and preforms produced therefrom. Refractory non-basic and basic materials have been known per se for a considerable amount of time. Traditional refractory casting materials have thixotropic properties and need to be lined using vibration technology. In the past, free-flowing casting materials were solely based on aluminium oxide starting materials. Attempts to produce an aqueous, highly concentrated, basic suspension which would form the basis of free-flowing casting materials failed to meet the requirements in terms of rheological properties and to achieve the low degree of hydration for MgO based materials. The aim of the invention is to provide the above-mentioned casting material for the monolithic lining or repair of high temperature aggregates in addition to producing refractory preforms. This is achieved by providing a fine grained and fine-course grained alternative. A refractory MgO-based material promoting dilatancy and possessing a grain size of 0.1-45 μm is used along with at least one dispersing agent and cross-linking agent also promoting dilatancy, whereby a given amount of tempering water is added. A refractory material with a grain size of up to 15 mm and a bonding agent are used for the fine-coarse grained alternative which is also MgO based. Refractory and other additives improving the quality of the final products can also be used in both alternatives.

(57) Zusammenfassung

Die Erfindung betrifft eine basische freifliessende Giessmasse sowie daraus hergestellte Formteile. Feuerfeste nichtbasische und basische Giessmassen sind seit langem bekannt. Die traditionellen feuerfesten Giessmassen weisen thixotrope Eigenschaften auf und müssen mittels Vibrationstechnik zugestellt werden. Die freifliessenden Giessmassen konnten bisher nur auf Basis von Tonerderohstoffen entwickelt werden. Die Herstellung einer wässrigen, hochkonzentrierten basischen Suspension als Grundlage der freifliessenden Giessmasse scheiterte bislang an der Voraussetzung, die entsprechende rheologische Eigenschaften und den niedrigen Hydratationsgrad von Materialien auf Basis MgO zu gewährleisten. Ziel der Erfindung ist, die eingangs genannte Giessmasse für die monolithische Zustellung bzw. Reparatur von Hochtemperaturaggregaten sowie zur Herstellung von feuerfesten Formteilen zur Verfügung zu stellen. Gelöst wird die gestellte Aufgabe durch eine feinkörnige und eine fein-grobkörnige Alternative. Für die feinkörnige Alternative wird ein feuerfestes dilatanzförderndes Material auf Basis MgO mit einer Korngrösse zwischen 0,1 und 45 μm sowie mindestens ein dilatanzförderndes Dispergiermittel und Netzmittel mit der Zugabe von vorbestimmten Mengen Anmachwassers eingesetzt. Für die fein-grobkörnige Alternative, ebenfalls auf Basis MgO, gelangt zusätzlich ein feuerfestes Material mit der Körnung bis 15 mm sowie Bindemittel zur Anwendung. In beiden Alternativen können weiters feuerfeste und andere, die Qualität der Endprodukte verbessernde Zusätze Verwendung finden.

Free-flowing basic casting slip and castings produced therefrom

The invention concerns a basic dilatant refractory, free-flowing casting slip and castings produced therefrom, such as bricks, prefabricated elements, low-weight refractory products and/or functional products such as perforated bricks, porous plugs, and casings.

Casting slips are defined as refractory materials introduced or shaped by casting. The appropriate consistency of the slips is achieved by mixing dry components with mixing water or mixing solution.

The casting slip can solidify by hydraulic setting of the calcium aluminate cements without heating, by chemical bonding or micropowder bonding without and with heating, and by sinter processes at operating temperatures. Examples for chemical bonding are a phosphate bonding, water glass bonding, microsilica bonding, or bonding arising when metal powders are used. Micropowder bonding is chiefly a result of the operation of London-van der Waals attraction forces. Refractory casting slips exhibiting more than one bonding type at once are advantageous for numerous applications, as they show the desired strength over a wide temperature range.

Refractory casting slips have been known for a long time. Depending on their chemical composition and on the raw materials used, one distinguishes nonbasic and basic casting slips. Alumina casting slips and zircon-containing casting slips are among the nonbasic ones. Basic raw materials for basic casting slips are magnesia, magnesiochromite, chromium ore, chromium oxide and spinel, for instance $MgCr_2O_4$. Different metal oxides, metal carbides, metal powders or carbon supports are used as refractory additives.

Traditional refractory casting slips lined with the aid of vibration technology are thixotropic. Thixotropy implies a decrease in apparent viscosity with the time of load at constant shear velocity or increase in apparent viscosity (thixotropic rigidification) with decreasing shear velocity. Compaction aids such as pneumatic or electrical vibrators must be used for fluidification and compaction of a thixotropic slip, since this slip is half-dry and stiff after mixing with water. An inhomogeneous distribution of coarse and fine grains, or demixing, is obtained when a thixotropic casting slip is fluidified by an overdose of mixing water, which may be necessary for a lining of narrow cracks and/or complex shapes. An overdose of water will moreover produce a decrease in physical test parameters, such as open porosity and strength. Such monolithic refractory linings have a lower resistance against infiltration and corrosion when used in metallurgical equipment.

Using mechanical compaction aids such as vibrators and/or bottle vibrators has the following disadvantages:

- The compacted casting slip does not always possess optimum homogeneity, that is, shrinkage cavities may be present;
- Problems when lining narrow cracks and complex shapes, since bottle vibrators have a reduced radius of action;
- physical stress for operators.

A thixotropic casting slip on the basis of magnesite preferred for the lining of steel foundry ladles is know from EP 0,248,171 B1. The bonding of this slip consists of boric acid, alkali polyphosphates and calcium hydroxide. Vibrators are used in order to achieve sufficient density during lining.

A hydrous, refractory casting slip on the basis of MgO and having a carbon content between 3 and 10 % by weight, a dispersing agent in an amount between 0.1 and 2.0 % by weight, and a reactive silicic acid in an amount between 1 and 10 % by weight is described in DE 195,18,468 A1. According to this document (see column 2, lines 4 to 7) the silicic acid is decisive for preventing a hydration of the sintered magnesia. This slip, too, which is used for a monolithic lining of metallurgical melting vessels, and preferably of the slag region of foundry ladles, is compacted by vibration technology.

The use of an oxide-type micropowder dispersed in a nonaqueous dispersion medium is known from EP 0,573,029 B1. This fine-grained suspension on the basis of MgO,

Al_2O_3, Cr_2O_3 and/or TiO_2 can be used to produce refractory ceramic materials and castings of high density and strength. The risk of hydration of MgO is reduced since nonaqueous solvents are used to prepare the suspension. Tests have shown that the castings can be made by dry pressing from a slip containaing 85 % by weight of coarse-grained matrix material in the grain fraction between 1.0 μm and 3 mm as well as 15 % by weight of a finely divided, previously dispersed MgO micropowder. The raw density and strength of the green compact and of fired castings is distinctly higher than that known in the art. The use of nonaqueous MgO suspensions for the preparation of casting slips is little appropriate on account of the environmental impacts and of safety risks during the drying and heating of lined equipment.

The use of basic aqueous suspensions having a high concentration of MgO micropowder could be advantageous for the production of castings, for instance by dry pressing or ramming, if it was possible the prepare such suspensions. However, it would be necessary not to have an excessive degree of hydration of the MgO-based materials in the suspension.

A process for the preparation of magnesia of low hydration is further known from the document EP 0,448,156 A1. However, it is not possible to produce a casting slip with free-flowing properties by this process, even when hydration is low and a large amount of mixing water is used. In this context the reader is referred to the reference examples cited at the end of the description.

Free-flowing alumina casting slips are a relatively new development. In contrast to the thixotropic casting slips, mechanical compaction aids are not needed in order to achieve an appropriate consistency and physical test parameters comparable with those of the thixotropic slips. Free flow is promoted by dilatant properties of the slip. Dilatancy is defined as a decrease in viscosity occurring with decreasing shear velocity, here in the sense of so-called rheological dilatancy.

A nonbasic refractory, hydraulically bonded casting slip is described in EP 0,525,394 B1. This casting slip on the basis of alumina raw materials is composed as follows, and exhibits free flow when 3.5 to 7.0 parts by weight of mixing water are added for each 100 parts by weight of solids:

- 65 to 87 % by weight of a refractory matrix material on the basis of Al_2O_3, ZrO_2 and/or Cr_2O_3 with a grain size between 0.1 and 10 mm;
- 7.0 to 22.0 % by weight of a reactive refractory component on the basis of Al_2O_3, ZrO_2 and/or Cr_2O_3 with a grain size between 0.1 and 10 μm:
- 0.5 to 10.0 % by weight of a hydraulic binder with an Al_2O_3 content above 68 % by weight;
- 0.2 to 6.5 % by weight of one or several stabilizing additives and/or additives promoting the water retention of the casting slip.

Decisive for the desired flow properties of the free-flowing alumina casting slip are the adjustment of the grain size ranges in the refractory matrix material and the reactive refractory component as well as the adjustment of the mixing water with the additives named.

The fluidity of a free-flowing casting slip is rated according to the flow value. The flow value Fo is determined immediately after mixing with the mixing water with a vibration-free consistency test, and using the formula:

$$Fo = [(dm,mm - 100mm)/100mm] \times 100, \%$$

where dm is the mean diameter of the sample after a certain time of flow, and 100 mm is the lower diameter of the truncated cone.

The consistency test of the free-flowing casting slips is performed at present, most often using a truncated cone of ø100 x ø70 x 50 mm and a flow time of 60 sec in accordance with ASTM C-860. The casting slip is considered free-flowing when the flow value Fo is at least 80 % when determined with the vibration-free consistency test using above truncated cone. A European standard for the consistency testing procedure and evaluation of the flow value for free-flowing casting slips is still in preparation. It has been proposed that the truncated cone should measure ø100 x ø70 x

80 mm and the flow time should be 120 sec. One must expect that the flow value will be correspondingly larger when using this truncated cone.

A high market acceptability and good practical results are recorded at present with free-flowing, hydraulically bonded casting slips on the basis of alumina raw materials in several industries. They have found applications, both in all those cases where thixotropic nonbasic casting slips had already been used in the past, and in the new applications involving high-temperature equipment which are difficult to open up.

From a knowledge of rheological properties of the Al_2O_3 suspensions and from experience with free-flowing alumina casting slips, so far it had not been possible to provide free-flowing basic casting slips. Experts evidently have believed up to now that the properties of materials on the basis of magnesia and the rheological requirements constitute essential obstacles for the development of a free-flowing basic casting slip. This refers to a relatively high demand of mixing water and the hydrating tendency of magnesia-based raw materials. Free flow of a basic casting slip requires above all an optimum dispersion and distinct dilatancy of the highly concentrated aqueous MgO suspension. The flow behavior of a refractory casting slip mainly depends on the rheological properties of the suspension developing from the fine-grained components of the slip.

The present invention has the aim of providing a dilatant refractory basic, free-flowing casting slip on the basis of magnesia and/or chromium ore. Both an exclusively fine-grained and a mixed fine and coarse-grained alternative are to be provided.

The present aim of providing a fine-grained alternative is met by the elements of claim 1. The casting slip prepared according to the compulsory elements of claim 1 can be used to seal very narrow cracks, for instance <10 mm, or as a highly concentrated aqueous suspension, to produce compact bricks, for instance dry-pressed or rammed. It has further been found to be advantageous when, still according to the elements of claim 1, binders, refractory or other additives are used as an option.

Dilatant properties can only be attained with an excellent dispersion, i.e., comminution of large, hard particle agglomerates in the suspension. This finding is used when an aqueous, highly concentrated suspension prepared according to the elements of claim 1 is used to produce bricks. A very good dispersion of the suspension is needed in this case in order to attain a dense, homogeneous matrix of the bricks.

The aim of providing a mixed fine and coarse-grained alternative is met while using the elements of claim 2. Here again the elements mentioned in connection with claim 1 are needed in order to attain free flow of the basic casting slip according to the invention, but now the use of binders is compulsory. The introduction or shaping of the casting slip can in this alternative occur by pouring or pumping. This alternative is applicable primarily for a monolithic lining or repair of high-temperature equipment and/or the production of prefabricated elements, functional products or low-weight refractory products.

The basic casting slip according to the elements of claims 1 and 2 has the effect of flowing freely and homogeneously after addition of the mixing water and mixing, but without the vibratory compaction needed for the thixotropic casting slips, i.e., without the input of external energy. The fluidity is rated in terms of the consistency test following ASTM C-860 described earlier, where the flow value should be at least 80 %.

It is a condition for practical applications of a free-flowing basic casting slip that the hydration of the MgO-based materials used to prepare the slip is markedly retarded. This is achieved with the dispersion agents and binders used, the latter being utilized optionally, i.e., when needed in the case of claim 1, and definitely in the case of claim 2. The degree of hydration of the caustic-calcined MgO after contact with the dispersing solution used here was five times smaller than after contact with water. The test was performed over a period of 30 min at 25 °C followed by rapid drying at 160 °C. The degree of hydration was determined gravimetrically, a degree of hydration of 100 % corresponding to complete transformation of the MgO to $Mg(OH)_2$. The dried or fired test bodies produced from the free-flowing basic casting slip revealed no hydration damage. The use of MgO powders pretreated e.g. with carboxylic acids is a further possibility for reducing the hydration of the free-flowing, basic casting slips.

The document EP 0,525,394 B1 discloses a free-flowing nonbasic casting slip, while with the process described in the document EP 0,448,156 A1 a casting slip having free-flowing properties cannot be achieved, hence even a pooling of these two documents will not suggest the solution offered in claims 1 and 2.

The advantages of the free-flowing basic casting slip according to the invention over the free-flowing alumina casting slip can become apparent in numerous applications, such as a better corrosion and erosion resistance toward aggressive slags, molten metals, and furnace atmospheres and/or a favorable price/performance ratio.

The ranges of application of the fine-grained and the mixed fine and coarse-grained casting slip will be clarified later by the elements cited in the dependent claims and underpinned by the examples.

The following elements are decisive for the distinct dilatant properties - as shown by the shape of the flow curves in Fig. 1 - and for free flow of the basic casting slip according to the invention:

- adjusted grain composition,
- the chemical and physical properties of the grain fraction <45 µm,
- the type and amount of dispersing agent. According to a preferred embodiment the mixing solution is added in amounts accurate to 0.2 percent by weight.

Further advantageous embodiments of the invention become apparent from the dependent claims 3 to 10.

Claim 3 expresses that fact that the dispersing agents and binders used will substantially retard the MgO hydration of the casting slip according to the invention.

The refractory MgO-based materials used in the grain fraction <45 μm according to the elements of claim 1 are preferably the synthetic magnesia types such as caustic-calcined magnesia, sintered magnesia and fused magnesia. The MgO powders obtained by spray-calcining are also designated as caustic-calcined magnesia. Such dilatancy-promoting refractory materials can be used advantageously, both according to claim 1 and according to the elements of claim 2. The refractory material, again on MgO basis, in the grain size fraction up to 15 mm consists of sintered magnesia, fused magnesia, magnesiochromite co-clinker, and/or magnesiochromite fused grains, according to further elements of claim 4.

It is one of the advantages of the free-flowing casting slip according to the invention that it can be provided with one or several types of binders. According to the elements of claim 5, both different chemical, hydraulic but also temporary binders can be used, and in its hardened state the casting slip has physical test parameters comparable to those of a basic thixotropic casting slip.

The refractory additives according to claim 6 have a grain fraction between 0.1 μm and 3 mm and can influence both the properties and the applications of the casting slip, depending on the type of additive. The refractory additives can substantially raise the thermomechanical resistance, the infiltration resistance and/or the thermal endurance of the casting slip.

Investigations of surface-chemical and rheological properties of aqueous MgO suspensions <45 μm have substantially contributed to finding a solution to the aims set for the invention. A knowledge of the dispersion mechanism is advantageous when selecting refractory additives and, if necessary, the type and amount of binder. An interaction of these components with the fine-grained fraction of the refractory material on the basis of MgO and/or chromium ore can suppress or reinforce dilatant properties and free flow. In the group of phosphates known as chemical binders, for instance, only few are suitable to prepare free-flowing basic casting slip if - as indicated in a modification of the elements of claim 7 - a particular type of polyelectrolyte is used as the dispersing agent.

A positive effect on dispersing action and dilatant properties of a free-flowing basic casting slip has been attained according to the elements of claim 8 of the invention by using particular amines. This effect can be attributed to the adsorption of amines and change in zeta potential of the MgO particles in suspension.

The additives employed according to the elements of claim 9 have diverse effects. Thus, organic fibers can prevent cracks due to drying during heating. Steel fibers can improve the thermal endurance of a free-flowing basic casting slip. A lower degree of infiltration of molten metal and slag by capillary action can be attained when for instance adding, according to the invention, spherical materials having diameters of 5 to 80 μm which will evaporate or burn away.

According to the elements of claim 10, the free-flowing basic casting slip according to the invention can be employed on account of its properties in all those applications where up to now the thixotropic basic casting slips are used, i.e., for the refractory monolithic lining or repair of high-temperature equipment, as well as for vibration-free production of refractory castings such as prefabricated elements, functional products, low-weight refractory products, and above that for the production of dry-pressed or rammed, compact bricks. High-temperature equipment which according to experience is lined with refractory basic products includes, according to the elements of claim 10, ladles, reactors, vessels for treatments, vessels for transport, storage tanks, tundishes, furnaces, converters, regenerators, and runners in the steel, metal, cement, lime and gypsum, chemical and other industries.

In the following the invention will be explained in the instance of embodiments. Examples 1 to 3 refer to the free-flowing casting slips of different compositions according to the elements of claim 2 of the invention, examples 4 and 5 refer to the dilatant casting slips according to the elements of claim 1.

Example 1

A free-flowing dilatant casting slip according to the invention on the basis of magnesia with phosphate/microsilica bonding has the following composition:

Sintered magnesia 98.5 % MgO	0.045 to 5 mm	66.0 % by weight
Fused magnesia 98.3 % MgO	<0.045 mm	15.0 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	15.0 % by weight
Phosphate binder		1.0 % by weight
Binder on microsilica basis		2.0 % by weight
Silicon powder		1.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		0.7 % by weight
Water		7.8 % by weight
Mixing solution, relative to solids fraction of dry mass		8.5 % by weight

Example 2

A free-flowing dilatant casting slip according to the invention on the basis of magnesia hydraulically bonded has the following composition:

Sintered magnesia 98.5 % MgO	0.045 to 5 mm	65.0 % by weight
Fused magnesia 98.3 % MgO	<0.045 mm	15.0 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	12.0 % by weight
Calcined alumina	0.2 to 6.0 μm	3.0 % by weight
Alumina cement > 69 wt.% Al_2O_3		5.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		0.4 % by weight
Amine		0.2 % by weight
Water		6.9 % by weight
Mixing solution, relative to solids fraction of dry mass		7.5 % by weight

Example 3

A free-flowing dilatant casting slip according to the invention on the basis of magnesia and chromium ore with phosphate/microsilica bonding has the following composition:

Sintered magnesia 98.5 % MgO	0.045 to 5 mm	31.0 % by weight
Chromium ore Transvaal	0 to 1.5 mm	35.0 % by weight
Fused magnesia 98.3 % MgO	<0.045 mm	15.0 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	15.0 % by weight
Phosphate binder		2.0 % by weight
Binder on microsilica basis		2.0 % by weight
Dry mass		100.0 % by weight
Sodium salt of polybasic carboxylic acids		0.4 % by weight
Amine		0.3 % by weight
Water		7.8 % by weight
Mixing solution, relative to solids fraction of dry mass		8.5 % by weight

Example 4

A fine-grained dilatant casting slip according to the invention on the basis of magnesia with microsilica bonding has the following composition:

Fused magnesia 98.3 % MgO	<0.045 mm	49.8 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	47.0 % by weight
Natural organic polymer		0.2 % by weight
Binder on microsilica basis		3.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		1.8 % by weight
Amine		0.3 % by weight
Water		23.4 % by weight
Mixing solution, relative to solids fraction of dry mass		25.5 % by weight

The dry components of the slip in examples 1 to 4 were mixed in a forced-action mixer for 6 to 15 minutes, first dry and then with the amount of mixing solution indicated. The fluidity after mixing and the physical test parameters of casting slip hardened and dried at 160 °C, calcined at 900 °C, and calcined at 1500 °C can be seen from Table 1.

Table 1

Table 1

The flow value Fo and the physical test parameters of the free-flowing basic casting slip of examples 1 to 4 (RD: raw density; OP: open porosity; CCS: cold crushing strength)

	Example 1	Example 2	Example 3	Example 4
Mixing water, wt.%	7.8	6.9	7.8	23.4
Fo, %	**105**	**90**	**120**	**130**
After drying at 160 °C:				
RD, g/cm^3	2.71	2.78	2.84	2.17
OP, vol.%	17.7	16.8	14.0	28.3
CCS, N/mm^2	34	39	44	32
After calcining at 900 °C:				
RD, g/cm^3	2.68	2.75	2.78	2.06
OP, vol.%	22.1	19.5	23.1	36.8
CCS, N/mm^2	17	23	12	8
After calcining at 1500 °C:				
RD, g/cm^3	2.82	2.92	2.94	2.23
OP, vol.%	18.7	14.3	20.6	27.4
CCS, N/mm^2	45	41	27	28

The physical test parameters of the free-flowing dilatant basic casting slip of examples 1 to 3 listed in Table 1 show that the level of the values for thixotropic, MgO-based casting slips with comparable bonding was attained. A higher strength of the casting slip according to the invention can be attained when using larger amounts of binders. However, in some cases this may affect the chemical resistance and refractoriness under load.

For the basic aqueous dilatant casting slip in example 4, a basic thixotropic casting slip with comparably fine grain composition is not available as a reference from prior art.

The degree of hydration of the casting slip of example 4 was determined in a hydration test of 24 h at 60 °C and a relative humidity of 100 %, and found to be 21 %.

Example 5 and the reference examples to examples 4 and 5 were introduced in order to describe even better the hydration resistance of the MgO materials and the fluidity of the casting slips produced or not produced according to the elements of this invention.

Reference example to example 4

A fine-grained casting slip on magnesia basis with microsilica bonding:

Fused magnesia 98.3 % MgO	<0.045 mm	49.8 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	47.0 % by weight
Sodium hexametaphosphate		0.2 % by weight
Binder on microsilica basis		3.0 % by weight
Dry mass		100.0 % by weight
Boron oxide		0.9 % by weight
Water		34.1 % by weight
Mixing solution (saturated boric acid solution), relative to solids fraction of dry mass		35.0 % by weight

Flow value Fo = 0, casting slip not free-flowing

Degree of hydration 0.1 %, test at 60 °C, 24 h, relative humidity 100 %

Despite a very low degree of hydration this casting slip lacks free-flowing properties.

A casting slip according to the invention or a highly concentrated MgO suspension can be formulated in such a way that MgO hydration is particularly effectively retarded by the action of dispersing and binding agents used according to claim 1 or claim 2. This was shown in the instance of example 5, where a caustic-calcined magnesia that was very fine-grained and hence prone to undergo hydration was employed.

Example 5

A dilatant, fine-grained casting slip on magnesia basis according to the invention:

Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	94.0 % by weight
Hydraulic binder		6.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		2.0 % by weight
Dispersing agent		1.0 % by weight
Water		35.0 % by weight
Mixing solution, relative to solids fraction of dry mass		38.0 % by weight

Flow value Fo = 120 %

Degree of hydration 5 %, Test at 60 °C, 24 h, relative humidity 100 %.

Reference example to example 5

A fine-grained casting slip on magnesia basis:

Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	94.0 % by weight
Hydraulic binder		6.0 % by weight
Dry mass		100.0 % by weight
Sodium hexametaphosphate		0.2 % by weight
Boron oxide		1.3 % by weight
Water		50.0 % by weight
Mixing solution (saturated boric acid solution with sodium hexameta-phosphate), relative to solids fraction of dry mass		51.5 % by weight

Flow value Fo = 0, slip not free-flowing

Degree of hydration 31 %, test at 60 °C, 24 h, relative humidity 100 %

It can be seen from reference examples 4 and 5 that MgO hydration is reduced when employing known prior-art hydration retardants for MgO, viz., a saturated boric acid solution, as well as sodium hexametaphosphate as a dispersing agent, but free flow of the basic casting slip cannot be achieved despite a very large amount of mixing water. In the above reference examples, MgO materials promoting dilatancy and hence free flow were used but a dispersing agent according to the invention was not used.

From the reference example 5 it can be seen that a very fine-grained caustic-calcined magnesia could not be protected from hydration as efficiently as in example 5 with saturated boric acid solution. Moreover, it is known that boric acid, already from a concentration of 0.05 %, when used as hydration retardant for magnesia has a negative effect on refractoriness.

For comparison: the degree of hydration of a very fine-grained caustic-calcined magnesia was 85 % in water without dispersing and binding agents, when determined at 60 °C, 24 h, relative humidity 100 %.

Figure 1 shows the flow curves (arrows indicate the curves for increasing and decreasing shear velocity) of dilatant aqueous suspensions on the basis of MgO <45 μm prepared with two different MgO concentrations (75 % and 78 %). The composition of the mixing solution corresponds to that of Example 4. The flow curves were determined with the cone-plate system.

Claims

1. Refractory free-flowing basic casting slip or highly concentrated aqueous suspension on the basis of MgO and/or chromium ore, characterized by the following composition:

   a) 76.0 to 100 wt.%, preferably 80.0 to 98.5 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size between 0.1 and 45.0 μm, preferably with a grain size below 25.0 μm,
   b) 0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, with the addition of 20 to 30, preferably 21 to 26 parts by weight of mixing water, referred to the solids fraction of the slip,
   c) if necessary 0.1 to 15.0 wt.%, preferably 0.5 to 12.0 wt.% of one or several binding agents,
   d) if necessary up to 6.5 wt.% of one or several refractory additives on the basis of Al_2O_3, Cr_2O_3, ZrO_2, TiO_2, SiC, metal powder, carbon support, with a grain size below 3 mm,
   e) if necessary 0.05 to 2.5 wt.% of one or several additives for preventing cracks arising during drying when heating or for raising the thermal endurance and for preventing the infiltration of molten metal and/or slag,

   further characterized in that after adding the mixing water and mixing it has a flow value of at least 80 %.

2. Refractory free-flowing basic casting slip on the basis of MgO and/or chromium ore, characterized by the following composition:

   a) 35.0 to 85.0 wt.%, preferably 55.0 to 75.0 wt.% of a refractory material on the basis of MgO and/or chromium ore with a grain size between 0.045 and 15.0 mm,

b) 15.0 to 50.0 wt.%, preferably 25.0 to 42.0 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size between 0.1 and 45.0 μm, preferably with a grain size below 25.0 μm,

c) 0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, with the addition of 5 to 10 parts by weight of mixing water referred to the solids fraction of the slip,

d) 0.1 to 15.0 wt.%, preferably 1.0 to 10.0 wt.% of one or several binding agents,

e) if necessary up to 6.5 wt.% of one or several refractory additives on the basis of Al_2O_3, Cr_2O_3, ZrO_2, TiO_2, SiC, metal powder, carbon support, with a grain size below 3 mm,

f) if necessary 0.05 to 2.5 wt.% of one or several additives for preventing cracks arising during drying when heating or for raising the thermal endurance and for preventing the infiltration of molten metal and/or slag,

further characterized in that after adding the mixing water and mixing it has a flow value of at least 80 %.

3. Casting slip or highly concentrated aqueous suspension according to claim 1 or 2, characterized in that the dispersing and binding agents employed have distinct MgO hydration retarding properties.

4. Casting slip according to claim 1 or 2, characterized in that the refractory dilatancy-promoting material on the basis of MgO consists of sintered magnesia, fused magnesia and/or caustic-calcined magnesia, and the refractory material, again on the basis of MgO, consists of sintered magnesia, fused magnesia, magnesiochromite coclinker and/or magnesiochromite fused grain.

5. Casting slip according to claim 1 or 2, characterized in that one or several binding agents are selected from the group of phosphates, sulfates, microsilica, water glasses, alumina cements, clays, boron compounds and/or temporary binding agents.

6. Casting slip according to claim 1 or 2, characterized in that the refractory additive consists of calcined alumina, fused corundum, MA spinel, chrome oxide green, baddeleyite, titanium oxide, silicon carbide, magnesium powder, silicon powder, aluminum powder, iron powder, ferrochrome powder, soot and/or graphite, the refractory additives having a grain size between 0.1 μm and 3 mm.

7. Casting slip according to claim 1 or 2, characterized in that the dispersing and wetting agent is a polyfunctional polyelectrolyte or a salt of polybasic carboxylic acids.

8. Casting slip according to claim 1 or 2, characterized in that the dispersing agent is an amine which contains one or several nitrogen substituents: $-C_2H_4OR$, -H, $-CH_3$, $-C_2H_5$, $-C(CH_3)_2CH_2OH$ where R = H or R = C_2H_4.

9. Casting slip according to claim 1 or 2, characterized in that the additive consists of organic fibers and/or steel fibers and/or spherical, evaporating or combusting materials, the latter having a diameter of 5 to 80 μm.

10. Casting slip according to one of the claims 1 to 8, characterized by its use both for the refractory monolithic lining or repair of high-temperature equipment and for the production of refractory castings such as prefabricated elements, functional products, low-weight refractory products and/or dry-pressed or rammed, compact bricks, the high-temperature equipment contemplated being a ladle, a reactor, a furnace, a vessel for treatment, transport or storage, a tundish, a converter, a regenerator and a runner in the steel, metal, cement, lime, gypsum, chemical industry and other industries.

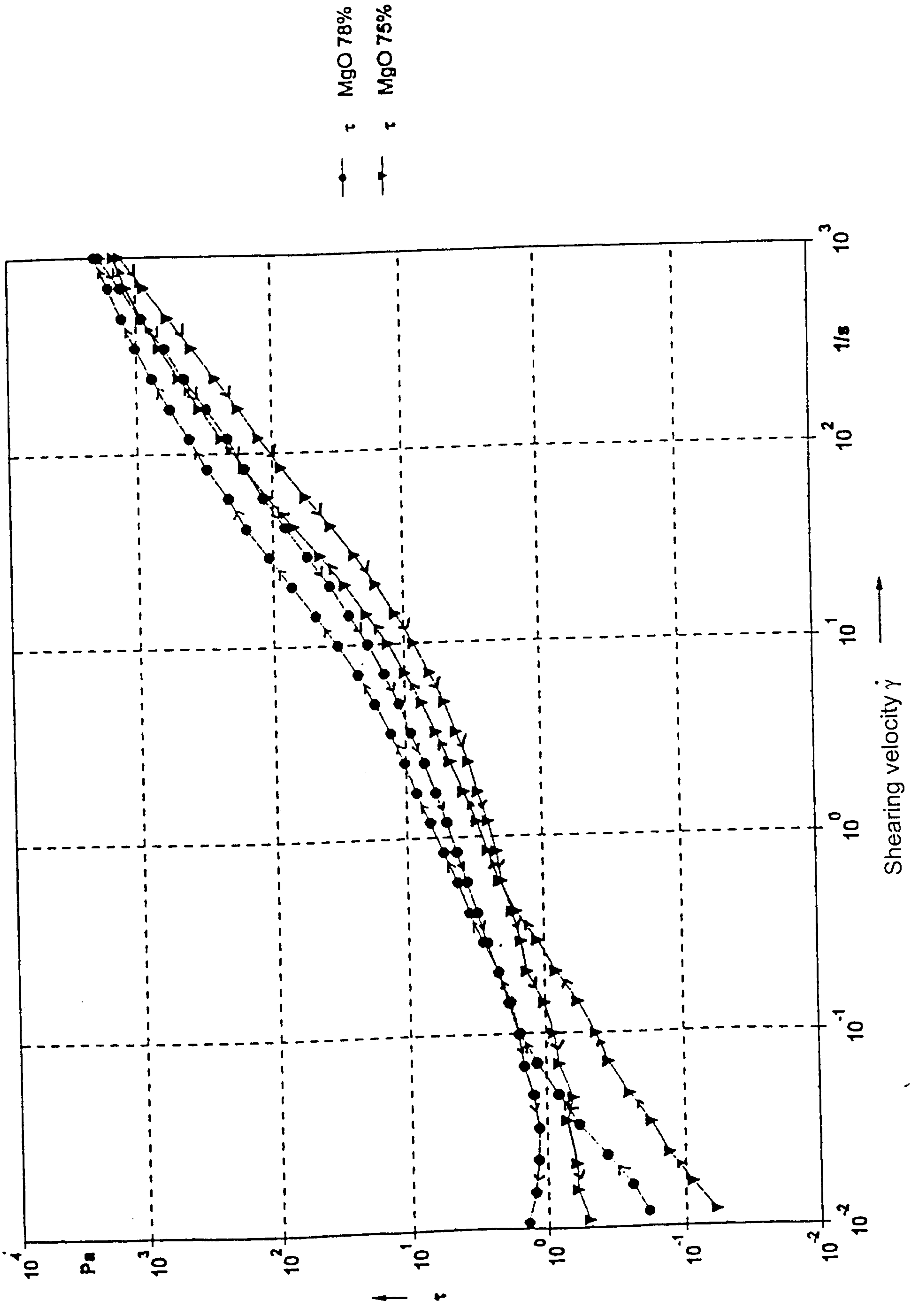
τ MgO 78%
τ MgO 75%
τ
Pa
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
Shearing velocity $\dot{\gamma}$
1/s
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

Fig. 1