

Hermes Schleifmittel GmbH & Co,
Hamburg

RTMP copy

p15564/93

D/fi (#121)

5

Ceramic corundum abrasive

The invention relates to an abrasive of ceramic corundum, to a process for the preparation thereof and to tools manufactured therefrom.

10 Besides fused corundum, use is increasingly made of ceramic corundum which, because of its polycrystalline structure, shows advantageous wear behaviour and which in the machining of special materials, for example of high-alloy stainless steels, makes possible a significant increase in tool life. A widespread process for preparing
15 such ceramic corundum abrasives is the sol-gel process in which a sol containing a water-containing alumina, usually aluminium oxide hydrate, is converted into a gel by addition of acid. After drying, this is calcined, crushed and subsequently sintered. Particularly over the
20 course of the past ten years, many attempts have been made to improve the quality of an abrasive obtained in such a way by particular process steps (EP-B 263 810) or by additions of material. The latter can, in accordance with their action in the sintering process, be classified
25 on the one hand as nucleus formers (M. Kumagai and G.L. Messing: Controlled Transformation ... J. Am. Ceram. Soc. 68 (9), 500-505 (1987)) or on the other hand as modifying components. The latter influence the sintering process and the structure and the properties of the end
30 product in different ways. Modifying components used are, for example, magnesium, hafnium, cobalt, nickel, zinc (EP-B 0 024 099), yttrium (EP-B 228 856), iron oxide (EP-B 200 487), rare earths (EP-B 293 164), lithium (EP-A-441 640). Although some of these additives do cause
35 a significant improvement in the abrasive properties, the values are found to have a wide scatter which has the effect of reducing quality.



The invention starts out from the recognition that besides the physical material properties such as hardness, toughness, resistance to microcrack extension or micro-wear conventionally specified for corundum abrasives, significant importance for the achievement of an increased tool life has to additionally be attached to a high constancy of these values within a particle size fraction.

It is an object of the invention to prepare a corundum abrasive which, besides the usual quality features (in particular a high hardness) has only small quality variations within a batch of grain. It has surprisingly been found that this is achieved by the addition of tin.

Accordingly, an abrasive of the invention comprising mainly ceramic corundum is characterized by it having a tin content. This content should, calculated as tin oxide, lie above 0.01% by weight of the sintered end product. Furthermore, it preferably lies above 0.1% by weight. A content of 5% by weight, preferably 1% by weight, should not be exceeded.

Hardness and a fine grain can, as is known, be improved by the addition of magnesium. It has further proven to be very advantageous if the abrasive also contains lithium, whereby hardness and product uniformity are further improved. Finally, further modifying components such as cobalt, yttrium, hafnium, iron and/or rare earths can be used.

Optical examination of a fractured surface or etched polished surface of the product produced as in the examples given below reveals a structure which is easily distinguishable from conventional products. Between conspicuously larger particles, some of which show a terrace structure typical of alpha-aluminium oxide (Petzold/Ulbricht: Alumina and alumina materials, p. 83, Figure 7.14), there is an accumulation of smaller



particles. The average size ratio. The average size ratio is at least 3 : 1, but is generally greater than 5 : 1. Adjacent larger particles are largely, in most cases almost completely, separated from one another by a layer of the smaller particles. The layers of smaller particles form an essentially continuous matrix in which the larger particles are embedded. Accumulations of smaller particles which are present in the triangular interstices between the larger particles are at least connected to one another through branches over a wide area. The different appearance of the particles corresponds to a different composition. The larger particles contain a higher proportion of alpha-aluminium oxide than the smaller ones, or consist almost exclusively of alpha-aluminium oxide. The tin is preferentially or predominantly contained in the smaller particles. This also applies to any further modifying components, in particular magnesium, yttrium, lithium, cobalt, iron, titanium, rare earths. In this context particles mean those shaped units which in the etched polished section are distinguished from one another by distinct boundaries. In the literature they are also designated as crystallites.

The abrasive of the invention has, besides high hardness, unusually high resistance to, in particular, high thermal and mechanical loads so that, for example in the use of abrasive belts strewn with the abrasive of the invention, a significant increase in the tool life is achieved besides significantly increased abraded masses per time interval.

The abrasive of the invention can be used on substrates, as a component of bonded grinding tools or as loose abrasive, for example in abrasive blasting or lapping. In all application areas, any qualitative and quantitative combination with other abrasives can be used. Of particular advantage is mixing with abrasive grain of higher or particularly high hardness such as, for example,



silicon carbide, cubic boron nitrite [sic] or else diamond. In addition, the abrasive of the invention can also function as a matrix into which one or more qualitatively different abrasives are incorporated. The latter is achieved by mixing the other abrasive into an intermediate, preferably the sol or gel, in the preparation of the abrasive of the invention.

In the preparation process, it is ensured that the material containing the tin is intimately mixed with and finely distributed in the other starting materials. If the preparation starts from pulverulent starting materials which are pressed with one another and then sintered, the material containing the tin is preferably likewise added in powder form. It can also be in liquid form and mixed into or sprayed onto the material to be sintered. Particularly intimate mixing is obtained when using the sol-gel process if the material containing the tin is added to the starting materials prior to formation of the gel so that it is already contained in the dispersion (sol) which leads to the gel. It [lacuna] be present in solid, very finely divided milled form or in solution. It has been established that then even the dried gel has a significantly changed nature able to resist higher mechanical loads compared with the tin-free procedure. This not only infers a considerable modifying action, but also improves the crushing of the dried gel in respect of the yield and the shape of the crushed grains.

A particularly advantageous compound has proven to be tin oxide which is added in the form of pulverulent SnO_2 to the starting materials or to the intermediates. However, it is also possible to use other tin-containing materials such as non-oxidic tin compounds, for example tin salts.

The sol advantageously contains very finely divided, optionally milled, gamma-aluminium oxide.



A particularly advantageous result is achieved by further addition of lithium which is preferably mixed into any intermediate stage as lithium salt dissolved in water. It is particularly advantageous for a lithium compound, preferably a lithium salt, to already be present in the sol in dissolved form. Furthermore, it is advantageous if any further modifying components, in particular those mentioned above, are already contained in the sol in finely divided solid or dissolved form. They can also be introduced into another intermediate. Advantageous amounts (as oxide) are:

	magnesium	0.1 - 1%
	yttrium	0.1 - 1%
	lithium	0.1 - 5%, preferably 1.5 - 3%
15	cobalt	0.1 - 0.4%
	rare earths	0.1 - 2%

Apart from that, the process steps of the sol-gel process do not require any more detailed explanation because they can be taken from the generally available prior art, in particular from the abovementioned patent literature.

The starting material used is advantageously an aluminium hydroxide, preferably an aluminium oxide hydroxide of the boehmite type. For example, Disperal aluminas from Condea-Chemie, Brunsbüttel, have proven useful. After addition of demineralized water and nitric acid there is obtained a suspension which can be centrifuged to remove coarse constituents. It is advantageous, but not strictly necessary, to add a nucleus former or gamma-aluminium oxide. The latter can first be present in an aqueous, nitric acid suspension which is likewise centrifuged. Mixing definite amounts of these suspensions and any further modifying components, preferably in aqueous solutions or suspensions, gives a suspension which is converted into a gel by means of nitric acid and/or salts thereof present in aqueous solution. This gel is dried and calcined. The dried or calcined intermediate is crushed and optionally classified. The calcined



intermediate [lacuna] sintered. Finally the abrasive thereby obtained is sieved and mixed to make batches of grain of uniform grain size.

5 It has been found that the use of lithium, optionally together with the components indicated further above, but without tin, also leads to very good results. This applies in particular to a lithium addition of the order (as oxide in the sintered product) of 2% by weight. Although the addition of lithium is known per se
10 (EP 0 441 640), the amounts are only up to 1.5% by weight of the oxide in the sintered product. Moreover, there is supposed to be a decline in the abrasive qualities. According to the invention, however, the opposite has been established. A product which is advantageous accord-
15 ing to the invention therefore has, independently of the addition of tin, a lithium content (as oxide) of more than 1.5% by weight in the sintered product. However, the combined use of lithium and tin is particularly advantageous.

20 Example 1

2000 kg of demineralized water (50°C), 28 l of HNO_3 solution (53% strength) and 1000 kg of Disperal are mixed to form a suspension from which the precursor 1 is obtained after centrifugation. The solids content is
25 about 30% by weight.

1000 kg of demineralized water (50°C), 27 kg of gamma- Al_2O_3 ("Puralox 400" from Condea, Brunsbüttel) and 5 l of HNO_3 solution (53% strength) form the precursor 2 after centrifugation (solids content 2.5% by weight).

30 1000 kg of the precursor 1, 500 kg of the precursor 2, 1 kg of tin oxide (as aqueous suspension), 3.3 kg of magnesium nitrate hexahydrate (in aqueous solution), 0.2 kg of cobalt nitrate hexahydrate (in aqueous solution) and 1 kg of yttrium oxide are mixed. This gives the
35 precursor 3.



Precursor 4 contains 70 kg of demineralized water and 20 kg of aluminium nitrate nonahydrate.

Mixing 1505.5 kg of the precursor 3 with 115.4 kg of the precursor 4 leads to the formation of a gel which is
5 dried at 130°C for 20 minutes.

After calcining (850°C, 15 minutes), crushing and sintering in a rotary tube furnace (1450°C, 12 minutes) the abrasive grain is sieved and classified. The abrasive grain obtained in this way has a tin content (as tin
10 oxide) of 0.36% by weight. It had an average hardness of 19.1 GPa.

Example 2

The procedure of Example 1 is repeated using 5.6 kg of tin oxide in the precursor 3. The grain prepared had an
15 average hardness of 18.1 GPa. The density was higher than in Example 1.

Example 3

The procedure of Example 1 is repeated, additionally using 25.4 kg of lithium nitrate. The grain obtained had
20 a lithium content (as lithium oxide) of 2%. It had an average Knoop hardness of 22.22 GPa.

Examples 4 to 10

Method and material composition as in Example 3, but the proportion of lithium nitrate is varied in such a way
25 that the lithium oxide content in the end product is

	0.1% by weight	(Example 4)
	0.2% by weight	(Example 5)
	0.3% by weight	(Example 6)
	0.4% by weight	(Example 7)
30	0.5% by weight	(Example 8)
	1.0% by weight	(Example 9)
	3.0% by weight	(Example 10).



The measurement of the hardness (Knoop method) was carried out using a testing apparatus manufactured by Shimadzu, model HMV-2000.

	average Knoop hardness
5	[GPa]
	Example 4 18.9
	Example 5 20.3
	Example 6 20.5
	Example 7 20.5
10	Example 8 20.6
	Example 9 20.7
	Example 10 19.7

Example 11

The procedure of Example 3 was used to produce the abrasive of the invention on an industrial scale, two samples of the abrasive grain being taken from the ongoing production at times 60 minutes apart.

10 abrasive grains of each sample were subjected to hardness measurement with the following results (Knoop GPa).

	<u>Sample 1:</u>
	22.22
	21.21
	20.57
25	21.88
	21.88
	20.72
	21.88
	21.04
30	21.88
	22.22
	$m_A = 21.55$





- 9 -

Sample 2:

	22.22
	23.70
	20.88
5	22.58
	22.22
	21.54
	20.41
	20.72
10	21.04
	21.04
	$m_A = 21.64$

Example 12

To assess the performance of the abrasive of the invention vulcanized fibre grinding wheels were made using the abrasive grain of grain size P 36 prepared in accordance with Examples 1 and 3.

As comparative sample, use was made of vulcanized fibre grinding wheels made in the same way and containing fused corundum (Comparative sample A).

The diameter of the wheels was uniformly 180 mm (cross recess design, rotation rate 6000 min^{-1}). The workpiece ground was a steel pipe ST 37, diameter 195 mm, which had a rotation of 16.3 min^{-1} counter to the grinding wheel.

The numerical values in each case give the abraded mass in [g] achieved in a time interval of 60 s.

Abraded mass in [g]				
Abrasive used	0s-60s	60s-120s	120s-180s	180s-240s
Abrasive grain corresponding to Example 3	65	47	39	35
Abrasive grain corresponding to Example 1	52	35	27	23
Comparative sample A	32	17	12	9

Example 13

For a further comparative test, abrasive belts of dimensions 50 mm x 2000 mm were made using fused corundum (Comparative sample B), abrasive corresponding to Example 1 and abrasive corresponding to Example 3.

The workpiece ground was a steel pipe ST 35-8/I having a diameter of 219.1 mm and a wall thickness of 6.3 mm, which rotated at a speed of 33.4 min⁻¹. The linear speed of the abrasive belt was 38 m/s.

10 The numerical values refer to the total abraded mass in [kg] achieved up to the respective point in time.

	Abrasive used	5	10	15	20	25	30	35	40	45
		min	min	min	min	min	min	min	min	min
15	Comparative sample B	0.91	1.46	1.93	2.35	2.75	2.98	3.16	3.29	3.44
	Example 1:	0.95	1.67	2.29	2.85	3.28	3.73	4.12	4.45	4.71
	Example 3:	1.29	2.27	3.18	4.01	4.80	5.57	6.26	6.87	7.42

Example 14:

20 As in Example 3 without tin. A grain having a hardness of 19.1 GPa results.





Claims

1. Abrasive, which consists essentially of ceramic corundum, characterized by a tin content.
2. Abrasive according to Claim 1, characterized in that
5 the tin content, calculated as tin oxide, lies above 0.01% by weight.
3. Abrasive according to Claim 1 or 2, characterized in that the tin content, calculated as tin oxide, does not lie above 5% by weight.
- 10 4. Abrasive according to one of Claims 1 to 3, characterized in that it contains magnesium.
5. Abrasive according to one of Claims 1 to 4, characterized in that it contains lithium.
- 15 6. Abrasive according to one of Claims 1 to 5, characterized in that it contains cobalt, yttrium, hafnium, iron and/or rare earths.
- 20 7. Abrasive according to one of Claims 1 to 6, characterized in that in the polished section or impression it comprises two particle fractions of significantly different size and having an average dimensional ratio of at least 3 : 1.
- 25 8. Abrasive according to one of Claims 1 to 7, characterized in that the tin and optionally the lithium is present in the smaller particles in a greater proportion than in the larger ones.
9. Abrasive according to Claim 7, characterized in that at least the smaller particles have a submicron average size.
10. Grinding tool characterized in that a substantial





proportion of the abrasive thereof is that according to one of Claims 1 to 9.

- 5 11. Grinding tool according to Claim 10, characterized in that the abrasive thereof comprises at least 5% by weight of that according to one of Claims 1 to 9.
12. Grinding tool according to Claim 10 or 11, characterized in that it additionally contains one or more abrasives of higher hardness such as diamond, cubic boron nitride [sic] and/or silicon carbide [sic].
- 10 13. Process for preparing a ceramic corundum abrasive according to one of Claims 1 to 9, characterized in that it is produced by the sol-gel process.
- 15 14. Process according to Claim 13, characterized in that a material containing the tin is present in the sol in finely divided, solid and/or dissolved form.
15. Process according to Claim 14, characterized in that the sol contains gamma-aluminium oxide.
- 20 16. Process according to Claim 14 or 15, characterized in that a material containing the lithium is present in the sol in finely divided, solid and/or dissolved form.
- 25 17. Process according to one of Claims 14 to 16, characterized in that magnesium is present in the sol in finely divided, solid and/or dissolved form.
18. Process according to one of Claims 13 to 17, characterized in that an aqueous solution of a salt containing tin, lithium, magnesium or another component is mixed with or sprayed onto a dry intermediate.
- 30 19. Process according to one of Claims 13 to 18, characterized in that sintering is carried out for from



1 to 20 minutes at from 1100°C to 1600°C.

20. Abrasive, consisting essentially of ceramic corundum, characterized by a lithium content.
21. Abrasive according to Claim 20 and one of Claims 1 to 9.
22. Grinding tool, characterized in that a substantial proportion of the abrasive thereof is that according to either Claim 20 or 21.
23. Process for preparing a ceramic corundum abrasive according to Claim 20 or 21, characterized by one or more of the process steps according to one of Claims 13 to 19.

This Sheet Has Been Replaced



* C L M S *