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ABRASIVE ARTICLES

Samuel S. Kistler, Salt Lake City, Utah, and Charles V. Rue, Tiffin, Ohio, assignors to Wakefield Corporation, Detroit, Mich., a corporation of Michigan

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The present invention relates to abrasive articles and more particularly to solid abrasive articles such as grinding wheels adapted for snag grinding of hard steel such as stainless steel.

In the abrasive industry is has been the usual practice to make grinding wheels for high stock removal from steel or difficult to grind alloys such as the numerous stainless steels or high speed steels, by bonding together grains of aluminum oxide with a resin or a ceramic material. Much art has been developed around the process of making such grinding wheels and around bond compositions. This is especially true of the resin bonded wheels in which the addition of fillers of various types to the bonding resin has imparted valuable properties to the resulting wheels, such as improved rate of cut and higher stock removal per wheel.

In spite of the expenditure of large sums of money on research in abrasive compisitions, it is surprising that during the last half centry, very litte has been achieved with respect to the abrasive grains themselves. While manufacturing processes have been improved, for example, the development of continuous melting and casting of alumina, it is nevertheless true that the grains in commercial use today in a large proportion of grinding wheels employed for dry grinding of the hard metals, range between about 92% and 100% alumina. For the most part, the alumina grains are fragments of single crystals or fragments of a commercially pure fused alumina that has been induced to crystallize into a polycrystalline mass. The only other material which has demonstrated good performance on stainless steels is zirconia, but this material has not become commercial because it is too expensive to manufacture and use as long as alumina is available.

In accordance with the present invention, it has been discovered that zirconia can be commercially employed as the abrasive grain in solid abrasive articles when the zirconia is in the form of fine crystallites suspended in a glassy phase, which is preferably high in silica.

The primary object of this invention is to provide superior abrasive products, and particularly grinding wheels, which are capable of more efficient and more economical grinding of various types of materials.

Another object of this invention is to provide a low cost superior snagging wheel.

Another object of this invention is to provide resin-bonded grinding wheels of superior quality which are capable of grinding both soft and the hardest materials which are ground commercially, and specifically including the stainless steels.

Another important object of this invention is to provide grinding wheels including fused zircon as the abrasive grain.

Another object of this invention is to provide improved grinding wheels containing zirconia and alumina particles intimately mixed and embedded in a high silica glassy phase, and which wheels are superior in snag-grinding characteristics to the polycrystalline alumina wheels which are currently available.

Other objects and advantageous features of the invention will become apparent from a full consideration of the description of the invention which follows.

As above indicated, this invention is based on the discovery that zirconia particles embedded in a glass matrix constitutes a new and useful abrasive grain, which, when fabricated into resin-bonded grinding wheels, forms wheels having unusual and unexpected grinding ability. Moreover, the quantity of the glass phase is relatively high and this makes the grains commercially competitive with fused alumina and much less expensive than the heretofore known fused zirconia materials. Fused zirconia has been proposed for use in abrasive articles in U.S. Patent 2,769,699, issued November 6, 1956, and a particular recommendation for such use is made therein of the stabilized fused zirconia made in accordance with U.S. Patent 2,535,526. The fused zirconia of each of these patents is a zirconia which is over about 97% pure ZrO_2, or one which may contain up to about 6% by weight of the ZrO_2 of an alkali or alkaline earth metal oxide. In either event the zirconia is substantially free of silica or SiO_2. It is well known that glassy materials are fragile and readily susceptible to fracture and disintegration and at least partially for this reason, the abrasive industry has intentionally avoided glassy components in abrasive grains up to the present time. It was, therefore, surprising and unexpected to find that zirconia particles embedded in a glass matrix, when reduced to over-all particles in the range of about No. 8 to No. 250 grit size, formed resin-bonded grinding wheels of superior grinding ability.

The abrasive grain which is suitable for use in forming the abrasive articles of this invention comprises about 15% to about 60% glass, by volume, having embedded therein particles which are entirely zirconia, as hereinafter defined, or a mixture of zirconia and alumina. The zirconia may constitute the balance of the grain, that is, from about 40% to about 85% by volume, or, when alumina is also present, may constitute as low as about 7% by volume of the total grain, the alumina and glass forming the balance. Stated in another way, the hard particle portion of the grain may be from about 10% to 100% by weight of zirconia, and from about 90% to 0% by weight of alumina. Especially good results are obtained when alumina is present in a ratio to the zirconia in the range of about 1:1 to about 2:1. The term "zirconia" as used herein, and in the appended claims, refers to the material which is known in the trade as zirconia, that is, the material which is in reality $x(ZrO_2)+y(HfO_2)$, wherein y is usually about 0.5%–1.5% hafnium and which may include up to about 3% of other metal oxides. The term "alumina" as used herein, and in the appended claims, refers to the material known to the trade as crystalline alumina or corundum as well as fused alumina.

The glass or glassy phase of the abrasive grains of this invention may be any of the commonly known glasses, but preferably is a glass which is high in silica, tough and resistant to heat shock. A large number of specific glass compositions have been used successfully, typical compositions of which are given, in percent by weight, in Table I, but based on this broad experience there is no evidence at hand which indicates that any specific glass component is determinative of success. When the ultimate use is a snag grinding wheel for stainless steel grinding, certain glass formulations have been found to be better than others and these superior formulations, for

this purpose, are indicated in Table I by being marked with an asterisk.

TABLE I

	SiO_2	Al_2O_3	B_2O_3	CaO	MgO	BaO	Na_2O	K_2O	B_2O_5	PbO	TiO_2	Fe_2O_3
1	*55.3	22.9	7.4	4.7	8.5	------	0.6	0.4	------	------	------	--------
2	5.8	39.8	------	49.4	5.0	------	------	------	------	------	------	--------
3	*61.4	18.3	------	------	20.3	------	------	------	------	------	------	--------
4	*53.7	22.0	------	13.5	------	5.8	------	------	5.0	------	------	--------
5	*72	2	------	------	12	------	12	2	------	------	------	--------
6	*63.6	3.8	6.7	14.0	2.6	------	8.7	0.4	------	------	------	--------
7	37.2	8.2	27.6	20.7	------	------	2.1	4.2	------	------	------	--------
8	*54.3	--------	1.5	------	------	------	3.0	8.0	------	33	------	--------
9	*70	--------	------	------	19	------	------	------	------	------	11	--------
10	25.0	17.7	------	------	------	------	------	------	------	------	19.3	39.0

Although glass Formulas 1–8 do not contain Fe_2O_3 or TiO_2, it has been found that glass Formulas 9 and 10 which contain no alkalis but contain high proportions of Fe_2O_3 and TiO_2 function very satisfactorily. The Fe_2O_3 and TiO_2 provide good fluxing characteristics and are advantageous components in any of the glass Formulas 1–8, as a substitute for a part of the silica or the alkalis, and may be present in an amount of up to about 15% Fe_2O_3 and/or 15% TiO_2. For the purposes of this invention it is unnecessary that the glass contain the well known fluxing ingredients B_2O_3, Na_2O or K_2O since it has been found that high proportions of MgO, CaO, BaO or other oxides such as Fe_2O_3 or TiO_2 function in lieu thereof, with at least one of the Fe_2O_3 and TiO_2 being preferred for this purpose.

The glass containing abrasive grains which are suitable for use in the manufacture of the abrasive articles of this invention, may be formed by simply fusing zircon under conditions which do not vaporize the silica. Particles containing alumina and zirconia may be formed by intermixing zircon and alumina, crystalline or fused, and fusing the batch under conditions which will not drive off the silica, or by admixing zirconia, alumina and a selected glass and fusing the batch under conditions which will not drive off the silica. The preferred material for forming snag grinding wheels for use in connection with grinding stainless steels are compositions which include alumina as a part of the hard particle portion of the glass containing abrasive grain. A particularly satisfactory composition is one having the following composition:

	Percent by weight
ZrO_2	33–35
Al_2O_3	50–55
SiO_2	11–12
Na_2O	0.7
B_2O_3	0.8

Particularly good results for snag grinding wheels have been obtained from the use of abrasive grains containing a zirconia-alumina-silica eutectic composition, having the approximate formula of about 53% alumina, 17% silica and 30% zirconia, when that eutectic is formed in the presence of sufficient quantities of boric oxide or alkali or alkaline earth oxides to form a glassy phase, such as a borosilicate-type glass, with the basic eutectic composition of zirconia-alumina-silica. The final grain in this case contains between about ½ and 1% of boric oxide and may contain up to about 2% of alkali or alkaline earth metal oxides. This preferred form of material is formed by fusing raw ores containing appropriate quantities of zirconia, and silica, together with boric oxide and the alkali or alkaline earth metal oxide by fusing the admixture in an oxidizing atmosphere. The fusion temperature of such a composition is approximately 3200–3300° F. The fusion of such a composition may be made in an electric arc furnace with a water cooled shell, the batch to be fused acting as a lining for the inside of the furnace shell. Examples of compositions of raw batches which are suitable for making this preferred form of the abrasive grain of this invention is as set forth in tabular form in Table II in parts, by weight:

TABLE II

Constituent	1	2	3	4	5	6
Alumina	50	53	46	47	52	46
Zircon sand	35	30	47	43	46	47
Electric furnace zirconia	13	15	7	8.4	------	7
Boric acid	1½	2	1	2	2	1½
Dead burned lime	1	----	1½	------	------	1½
Soda ash	--------	----	1	1½	------	------
Silica flour	--------	----	------	------	1	------

In forming an abrasive grain from zircon sand, it is simply necessary to raise the zircon to its fusing temperature and thereafter cool the fused mass preferably relatively quickly. The cooling may be effected for example, by pouring the fused mass on a cold steel plate, by using an air blast or by water cooling. It is undesirable to employ an extended or slow cooling technique when using zircon sand because such a slow cooling has a tendency to cause reassociation of the zirconia and silica which is present and the resulting product contains an undesirable quantity of reformed zircon. In forming mixed batches for fusion, it is preferred to employ relatively small particle size starting materials, which are preferably thoroughly and uniformly intermixed prior to the fusion operation. This preliminary intermixing enhances the uniform distribution of the zirconia and alumina particles which are present in the fusion product, which even after crushing have a tendency to retain the relationship established in the fused form. Subsequent to the fusion and cooling of the fused mass, the fused mass is crushed and sized to form the abrasive particles useful for the formation of the end product abrasive article. In addition to the process whereby abrasive grains are made by fusion and subsequent crushing of the cooled mass, heterogeneous abrasive grains of alumina, zirconia and glass may be made by firing the intimately mixed and compacted components to a temperature high enough to melt the glass phase. Compaction of the components may be by pressing, extrusion or slip casting. For grinding wheels, the sized particles may be in the range of about No. 8 to about No. 250 grit size and preferably are about 12 to about 16 grit size. It is also desirable to use a variety of grit sizes, as is conventional in the art, for example, a mixture of equal quantities of No. 12, No. 14, No. 16 grit sizes.

The abrasive articles of this invention may be formed by using the conventional cold or hot pressing techniques or by the displacement molding method described in U.S. Patent No. 2,860,961 and may contain, satisfactorily, from about 40 to about 64% by volume of the abrasive grains of this invention, and from about 36% to about 60% by volume of a suitable bonding material including various amounts of resins fillers, plasticizers, pores and other additives. Suitable filler materials which may be satisfactorily employed include, for example,

cryolite, metallic sulfides, and others which are inert or which improve the cutting efficiency of the resultant abrasive grinding wheel. If desired, the bond composition may also contain lime and where furfuraldehyde is employed for wetting the surface of the abrasive grains, the presence of lime is recommended.

The binder resins which may be satisfactorily used in forming the abrasive article of this invention, and particularly grinding wheels, include resins of the thermosetting type, for example, phenolaldehyde resins, cresolaldehyde resins, resorcinol aldehyde resins, urea aldehyde resins, melamine formaldehyde resins, furfuryl alcohol resins, and mixtures thereof, etc. The phenolformaldehyde condensation product is the preferred binder for grinding wheel use. In order to provide improved adhesion of the abrasive grains to the bonding agent, it is preferred to preliminarily wet the surfaces of the abrasive grains with a solvent for the thermosetting resin to be employed, such as furfuraldehyde, for example. It is also contemplated that the thermosetting bonding resin can be modified with small quantities of other resinous materials such as epoxy resin, vinyl resins including polyvinyl chloride, polyvinyl butyral, polyvinyl formal, polyvinyl acetate and others, and may contain cross linking aids such as hexamethylene tetramine or paraformaldehyde, and suitable solvents or plasticizers such as furfural and propylene sulfite. Other plasticizers such as cresol, furfuryl alcohol or the like can be employed if desired.

The following examples are intended to more clearly illustrate typically useful compositions and procedures for making the improved abrasive articles of this invention, but it is to be understood that they do not contain the proportions or conditions which define the limits of this invention since they have been set forth hereinabove; the examples are intended for illustrative purposes only.

Example I

Zircon sand was melted in an electric furnace, open air, and poured onto a cool steel plate to effect rapid cooling of the molten zircon. The solidified zircon was removed from the plate, crushed and sized to pass through an 8 mesh screen and be retained on a 16 mesh screen.

Test grinding wheels 12" x 1½" x 2" were made with the particles retained on the 16 mesh screen by admixing the following materials in parts by volume:

	Parts by volume
Powdered B-stage phenol formaldehyde resin	21.60
Potassium sulfate, powdered	5.54
Zinc sulfide, powdered	2.38
Lime, powdered	2.88
Geon 202	3.60
Furfuraldehyde	5.64
Trichlorobenzene	1.77
Zirconia-glass grain	56.00

The furfuraldehyde is first added to the abrasive grain followed by the resin and filler ingredients and trichlorobenzene. Mixing was continued until uniformity was obtained and thereafter the wheels were cold pressed to a density of 0.129 pound per cubic inch.

Using identical volumes of materials and similar procedures, standard alumina grinding wheels were made containing comparably sized crystalline alumina abrasive grit for comparative test purposes. These wheels were pressed to 0.106 pound per cubic inch as required by the difference in density of the abrasive.

A series of the standard and zirconia-glassy grit wheels were tested in a standard snagging machine in the snag grinding of 302 type stainless steel and the following results were obtained:

Abrasive	Wheel Wear, cu. in./hr.	Steel Removed, lbs./hr.	Ratio, Steel/ Wheel
Standard Alumina	91.92	117.28	1.28
Zirconia-glassy grain	48.12	87.7	1.82

Example II

Zircon sand was admixed with sodium bicarbonate in the amount of 0.04 mols of sodium bicarbonate per mol of zircon sand. The mixture was then ball milled to a particle size less than 10 microns and the fine particle sized material was then moistened with water, pressed into blocks and fired for ½ hour at 3000° F. At this temperature a dense hard mass of zirconium oxide crystals in glass was produced. The mass was crushed and fired to pass through an 8 mesh screen and be retained on a 16 mesh screen, and these crushed grit were employed in the making of a series of 12" x 1½" x 2" snagging wheels. In making these wheels, a composition comparable to that set forth in Example I was employed and in a similar fashion, standard crystalline alumina wheels were made for comparison purposes. Both sets of wheels were tested in the standard snagging machine for grinding 302 type stainless steel and the following results were obtained:

Abrasive	Wheel Wear, cu. in./hr.	Steel Removed, lbs./hr.	Ratio, Steel/ Wheel
Alumina	61.9	90.1	1.45
Zirconia-glassy grain	76.0	82.9	1.09

An analysis of the zirconia-glassy grain used in this test showed that the grains contained about 45% by volume of glass and 55% zirconia in the form of microscopic crystals.

Example III

An abrasive grain comprising a mixture of zirconia, alumina, silica, boric acid and soda ash was prepared by melting together a mixture of zircon sand, Bayer alumina, borax and soda ash in an electric furnace. The materials were melted and cast into blocks which were thereafter crushed in size to produce grit passing through an 8 mesh screen and be retained on a 16 mesh screen. Upon analysis the grit was found to have the following composition:

	Percent
ZrO_2	34
Al_2O_3	52.5
SiO_2	11.5
Na_2O	.7
B_2O_3	0.8

This grit was employed in making a series of 12" x 1½" x 2" wheels using the procedures and similar bond compositions to that described above in Example I. For comparison purposes, a series of test wheels were made employing polycrystalline alumina which is available to the trade under the designation "44 Alundum," and specifically recommended for heavy snagging operations. When the wheels were comparatively tested on the standard snagging machine in grinding 302 type stainless steel, the following results were obtained:

Abrasive	Wheel Wear, cu. in./hr.	Steel Removed, lbs./hr.	Ratio, Steel/ Wheel
Polycrystalline Alumina	92	122	1.32
Zirconia-Alumina Whl. 1	41.5	86.8	2.09
Zirconia-Alumina Whl. 2	42.1	95.2	2.26

The zirconia alumina-glassy grain contained 23% by volume of zirconia and 30% by volume of glass.

Example IV

A portion of the abrasive grit described in Example III was modified to confer less slivery characteristics to each of the particles and to convert them into a somewhat blockier shape by mulling. A portion of this modified grain was then employed in making a series of wheels using the materials and procedures described in Example

I, and after testing these wheels in comparison to standard crystal and alumina wheels, the following results were obtained:

Abrasive	Wheel Wear, cu. in./hr.	Steel Removed, lbs./hr.	Ratio, Steel/ Wheel
Alumina	92	122	1.32
Zirconia-Alumina #3	66.5	133	2.0
Zirconia-Alumina #4	49.8	121	2.43

What is claimed is:

1. A solid abrasive article comprising abrasive grains having a grit size in the range of No. 8 to No. 250 bonded with at least one thermosetting resin, said abrasive grains consisting essentially of about 15% to about 60% by volume of glass, about 7% to about 85% by volume of zirconia particles and about 78% to 0% by volume of alumina particle, said zirconia and alumina particles being embedded in and distributed throughout said glass.

2. An abrasive article comprising abrasive grains having a grain size in the range of No. 8 to No. 250 bonded with at least one thermosetting resin, said abrasive grains consisting essentially of about 15% to about 60% by volume of glass having embedded therein and distributed throughout said glass crystalline particles of zirconia and alumina, said zirconia particles being present in an amount in the range of about 7% to about 85% by volume, and said alumina particles being present in an amount in the range of about 78% to 0% by volume.

3. An abrasive article comprising about 40% to about 64% by volume of abrasive grains having a grit size in the range of No. 8 to No. 250 and about 36% to about 60% by volume of thermosetting bonding material, said abrasive grains consisting essentially of about 15% to about 60% by volume of glass, about 7% to about 85% by volume of zirconia particles and about 78% to 0% by volume of alumina particles embedded in and distributed throughout said glass.

4. An abrasive article comprising about 40% to about 64% by volume of abrasive grains having a grit size in the range of No. 8 to No. 250 and about 36% to about 60% by volume of thermosetting bonding material, said abrasive grains consisting essentially of about 15% to about 60% by volume of glass having embedded therein and distributed therethrough crystalline particles of zirconia and alumina, said zirconia particles being present in an amount in the range of about 7% to about 85% by volume, and said alumina particles being present in an amount in the range of about 78% to 0% by volume.

5. A solid abrasive article in accordance with claim 4 wherein alumina is present in a ratio to said zirconia in the range of about 1:1 to about 2:1.

6. A solid abrasive article in accordance with claim 4 wherein said glass includes at least one oxide selected from the group consisting of ferric oxide and titanium dioxide in an amount up to about 15% by weight.

7. A solid abrasive article in accordance with claim 4 wherein said glass is substantially free of alkali earth metal oxides.

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MORRIS LIEBMAN, *Primary Examiner.*