 http://dx.doi.org/10.1590/0366-69132022683883357

Influence of the addition of niobium oxide on the properties of fused aluminum oxide used in abrasive tools

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Abstract

Fused alumina is a material used in the manufacturing of abrasive tools, due to its high fusion point, great hardness, and mechanical toughness. In this context, this study addressed the influence of niobium addition on the properties of fused alumina for abrasive applications. A comparison was also made between this oxide and the brown fused alumina and the white fused alumina traditionally applied in this market, using different characterization techniques, such as particle size characterization, scanning electron microscopy, real and bulk density, chemical analysis, fracture resistance, and abrasiveness indexes. Among the main findings of this study, it was possible to observe that the addition of niobium to fused alumina significantly increased the fracture resistance and abrasiveness indexes compared to the brown and white fused alumina.

Keywords: abrasives, alumina, niobium, titania.

INTRODUCTION

The industry of sandpapers and grinding wheels strongly depends on the quality of its raw materials, among which the abrasive grits, especially the grits of fused alumina: brown, white, pink (below 0.5% of chromia), ruby (above 1.5% of chromia), and blue fired (heat-treated brown fused alumina). Aside from fused alumina, the abrasive market also uses silicon carbide, natural and synthetic diamonds, and cubic boron nitride (cBN). Considering that the manufacturing process of these abrasives requires a large amount of energy and that the sustainability concept is unquestionably essential in manufacturing processes, the search for new compositions and/or additives aimed at improving the properties of the abrasive grits becomes relevant [1, 2]. Synthetic abrasive grits have two major classifications, which can be divided into chemical and physical. The first indicates the chemical composition of the material, once modifying the impurity content and the fused material type, the mechanical properties are influenced [3]. The other classification refers to comminution, depending on the process to which the material is submitted the abrasive properties are modified. After fusion and cooling, the ingots are initially crushed and routed to rolling mills, for further sieving. As these are high-impact processes and the materials are fused ceramics, the comminution process generates large fractures, resulting in sharp, imperfect, and anisotropic particles.

Among the most common types of abrasive grits, due to their properties, availability, and cost-benefit, the white and brown fused alumina assume special prominence [4]. The white fused alumina is basically composed of 93 to 99 wt% of α-alumina or corundum and approximately 1 to 7 wt% of impurities [4]. The amount of such impurities determines the application characteristics for the different types of fused alumina. In general, the major influence of these impurities is related to the abrasiveness of the materials; this matter is addressed in the next items of this study [4]. To produce the white fused alumina, bauxite is submitted to the Bayer process and purified electrochemically, reaching levels greater than 99.5 wt% of Al_2O_3, thereafter the material is calcined and submitted to a fusion process [5]. In contrast, the brown fused alumina is obtained through the fusion directly from the blend of the following raw materials: bauxite, source of titania, reducing agent, and iron chips. Basically, this oxide is graded by its titania (TiO_2) level: low titania or high purity (approximately 1.2 wt% of TiO_2) and high titania or low purity (approximately 3.0 wt% of TiO_2) [5]. A technical reason for the such distinction is that the higher purity material (low TiO_2) reports inferior abrasiveness compared to the white fused alumina and superior abrasiveness compared to the high titania aluminum oxide. Another relevant property of the low-level TiO_2 is its marked capacity in replacing edges as the grit suffers fractures, indispensable for abrasives [2].

Once it is technical-scientific knowledge that the impurities in this kind of oxides are responsible for affecting the properties of such oxides, the addition of components intentionally inserted can modify the properties and cause effects that shall be points for investigation [2]. It is worth highlighting that the presence of Cr_2O_3 and TiO_2, for example, increases toughness, while the presence of Na_2O is disadvantageous since it results in the formation of β-$11Al_2O_3.Na_2O$ compound responsible for reducing the hardness of the white fused alumina [6]. As in the conventional sintering process, the addition of niobium in

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the calcined aluminum oxide reduces the alumina sintering temperature due to the activation of the presence of the liquid phase [7], and densification happens as the temperature and the concentration of niobium increase. However, the effect resulting from adding niobium to fused alumina grits has not been explored yet and may generate technical-scientific contributions to the abrasive sector.

Influence of niobium oxide on aluminum oxide properties: alumina is widely used in the advanced ceramics industry, mainly for mechanical and electronic applications [8]. For such applications, electrical resistivity, mechanical resistance, and hardness are fundamental properties, however, alumina's high fusion point (2050 °C) demands a high sintering temperature estimated at 1650 °C. Several additives such as silica, manganese, and titania have been used with the objective to reduce the sintering temperature, in the production of electronic substrates [9]. Sintering temperature reduction generally stems from the formation of a vitreous phase in the alumina. In the same context, there are various studies regarding the use of niobium oxide as an additive, and the preliminary findings indicate that high densities and good mechanical resistance may be obtained after sintering in temperatures nearly 1450 °C [10]. The equilibrium phase diagram Al_2O_3-Nb_2O_5 (Fig. 1) has a eutectic reaction at 1425 °C. In this way, the increase in density may arise from the formation of a transitory liquid phase [10]. Although small amounts of niobium oxide (1 to 6 wt%) may improve both the density and the mechanical properties of sintered alumina at temperatures as low as 1177 °C, the thermal properties may, thus, be affected by the introduction of this additive. As all studies concerning the addition of niobium oxide to alumina are associated with a sintering process, the objective of this study is to investigate the effects of niobium oxide additives in alumina during a fusion process.

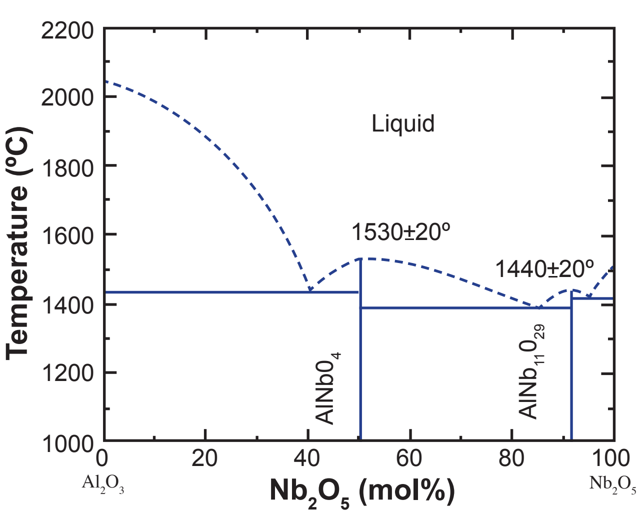

Figure 1: Equilibrium phase diagram of Al_2O_3-Nb_2O_5 [10].

Production system: in the production of fused alumina using the Higgins electric furnace, bauxite is the raw material for the production of alumina-based abrasive grits. The Higgins electric arc furnace consists of a steel or aluminum shell with a wall of water running outside of the shell that is responsible for cooling and maintaining the integrity of the shell. Inside the shell a layer of aluminum oxide that forms on the surface help this integrity because of the high fusion point of alumina. Three carbon electrodes then touch the bottom of the furnace with a high current applied. The process starts connecting the three electrodes using a conductive material on the bottom that is consumed fast but the heat generated melts the bauxite, which then becomes an electrolyte liquid. After amperage stabilization, the feed material is added continuously over the next several hours to build up the volume of melt. The current is controlled by adjusting the height of the electrodes which are eventually consumed in the process [11].

In the case of white fused alumina, bauxite is purified electrochemically through the Bayer process, reaching levels greater than 99.5% of Al_2O_3. Thereafter alumina is calcined and submitted to a melting [1]. Such type of fused alumina has pores originating from the volatilization of a small amount of Na_2O, incorporated during the Bayer process. Sometimes, small amounts of chromium oxide are added during the fusion process of the white fused alumina, spawning the pink or ruby fused alumina. Likewise, the addition of a small amount of vanadium oxide results in greenish alumina [12]. For the brown fused alumina, bauxite, along with the reducer and the iron chip, are raw materials, generating an abrasive product family which contains controlled limits of up to 4% of titanium dioxide [13]. The process of transforming the mineral into a product requires a chemical control of some oxide percentages, once such oxides influence directly the physical properties of the material. This control is determined by the addition of reducing agents during the fusion, through a pre-defined stoichiometry of the load to be fused. The consequent responses to this correction are reduction reactions (gain of electrons), which reduce the present oxide to metal for further separation [13]. The most significant reduction reactions during the fusion of brown electro-fused alumina are [12]:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \quad (A)$$

$$SiO_2 + 2C \rightarrow Si + 2CO \quad (B)$$

$$TiO_2 + 2C \rightarrow Ti + 2CO \quad (C)$$

After the fusion process, the material is submitted to a comminution process. The blocks are opened, pre-selected according to the different qualities of the stones, and crushed. After this stage, the material is routed to rolling mills to be reduced subsequently. Thereunder, once the effect of adding niobium oxide to fused alumina grits has not been explored yet, this study aims, within the same production methodology used for grits of fused white and brown alumina, to generate technical-scientific contributions to the sector of abrasives, observing some of the key points for the functionality of these materials, especially the fracture resistance and abrasiveness indexes. Thus, the main purpose was to study the influence of niobium oxide addition on the properties of the fused alumina for abrasive applications compared to brown and white fused alumina already used industrially.

MATERIALS AND METHODS

The fused alumina used in the market has not only differences in chemical composition but also considerable particle size diversity. For this study, the samples were prepared from grits with particle sizes P60 (average particle diameter of 0.212 mm) and obtained in compliance with the ANSI B7412 standard [14]. This study was carried out using white fused alumina (WFA), semi-friable brown fused alumina (BFA), and white fused alumina with the addition of niobium oxide (WFA-Nb). For the brown fused alumina (BFA), calcined alumina and ilmenite were used as raw materials, whose results of chemical analysis are presented in Table I. For the electrofusion of white fused alumina (WFA), it was used as raw material only calcined alumina. Finally, for the electrofusion of white fused alumina adding niobium oxide (WFA-Nb), calcined alumina, and niobium oxide were used as raw materials, whose chemical composition is shown in Table II.

Table I - Results of chemical analysis (wt%) of the APF calcined alumina and ilmenite used in the production of the samples.

Oxide	APF calcined alumina	Ilmenite
Al_2O_3	99.55	1.03
TiO_2	0.01	60.43
SiO_2	0.02	0.33
Na_2O	0.37	0.00
Fe_2O_3	0.01	-
FeO	-	37.11
CaO	0.04	0.15
ZrO_2	-	0.95

Table II - Results of chemical analysis (ppm) of the impurities in niobium oxide used in the production of the samples.

Ta	Fe	Si	Al	Cr	Mn	Co	Cu
960	2.8	23	0.6	0.5	0.6	0.3	0.8

Samples preparation: the materials were fused and sieved into specific particle sizes in the Research Center of Elfusa Geral de Eletrofusão. The samples were analyzed using X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD) for the determination of impurities and identification of the phases, respectively, in the three types of fused alumina. Moreover, the samples were submitted to

Table III - Results of chemical analysis (wt%) of white fused alumina (WFA), brown fused alumina (BFA), and white fused alumina with the addition of niobium oxide (WFA-Nb).

Material	Al_2O_3	TiO_2	Na_2O	Fe_2O_3	Nb_2O_5
WFA	99.65	-	0.35	-	-
BFA	97.64	1.30	0.10	0.10	-
WFA-Nb	95.69	-	0.30	0.05	1.30

scanning electron microscopy (SEM) coupled with an energy dispersive spectroscopy (EDS) to observe the surface of the particles and to identify chemical elements, respectively. The evaluation criteria considered in this study were the fracture resistance and abrasiveness indexes comparing the three types of oxides: white fused alumina (WFA), brown fused alumina (BFA), and white fused alumina with niobium oxide (WFA-Nb) and their chemical compositions are shown in Table III.

Standard fracture resistance index: the fracture resistance index (FRI) trial aims to show the percentage of particles that resist breakage after being submitted to a milling process. For determining this property, the sieved grits were milled for 10 min in a ball mill. After some time in the milling process, the grits were sieved and the amount of material retained in a pre-defined standard sieve was verified as per the size of the analyzed particle. Thus, the FRI was calculated by:

$$FRI = \frac{W_{RAM}}{W_T}.100 \quad (D)$$

where W_{RAM} is the weight of the sample retained in the sieve after milling and W_T is the total weight of the initial sample. It is known that the shape of the particles has a direct influence on the material's FRI, consequently, the sha rp particles have a lower FRI if compared to the blocky particles, of the same granulometry. In order to mitigate the effect of the particle shape concerning the FRI, the standard fracture resistance index (SFRI) was calculated by:

$$SFRI = \frac{FRI.D_r}{D_b.100} \quad (E)$$

where D_b refers to bulk or volumetric density and is defined by the relationship between the particle mass necessary to fulfill a recipient of known volume (g/cm^3), and D_r corresponds to the real specific mass of the grits. This volume includes the solid part of the aggregate and the volume of impermeable pores (here considered as an integral part of the volume of solids).

Abrasiveness trial: a rubber wheel tribometer, in compliance with ASTM G65 standard [15] was used, and a layout of the equipment can be seen in Fig. 2. In this trial, the specimen was pressed against a rubber wheel for 10 min with a constant load applied through dead weight, with fixed rotation and continued abrasive flow. To evaluate

Table IV - Trial parameters used in the rubber wheel tribometer.

Duration (min)	Load (N)	Rotation speed of the wheel (rpm)	Hardness of the wheel (Shore A)	Diameter of the wheel (mm)	Sliding distance (m)
10	130	202	62	225	~1523

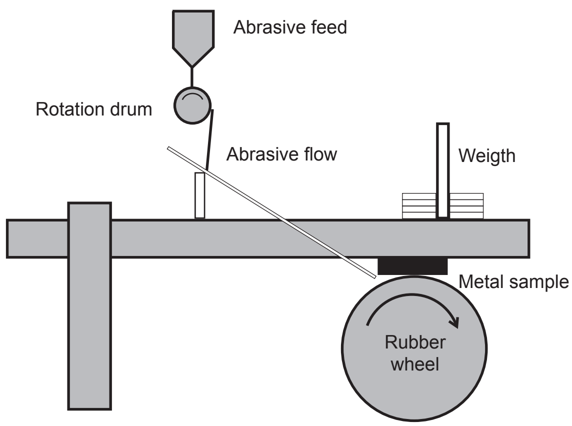

Figure 2: Layout drawing of horizontal rubber wheel equipment.

abrasiveness, AISI D2 steel was adopted as a specimen, with quenched martensitic microstructure and hardness of 62±2 HRc (~740 HV). Such material is considered as reference material in ASTM G65 standard. The trials were carried out in triplicate for each sample. Procedure B of the mentioned standard was adopted, and the parameters are featured in Table IV.

RESULTS AND DISCUSSION

Regarding the analysis of the standard fracture resistance index (SFRI) of each of the three types of material carried out in triplicate, it could be observed that the white fused alumina with niobium oxide SFRI showed superiority when compared to the brown and to the white fused alumina, as exposed in Table V. To complement the fracture resistance index trial findings, an abrasiveness trial was adopted. As aluminum oxide abrasives had the same theoretical size distribution, the measurement was carried out with white fused alumina [15]. The obtained result was an average flow of 613±13 g/min, whose value was greater than the value achieved when the standard abrasive silica sand #50 was used, with theoretical granulometry of +0.30/-0.60 mm and an average flow of 430 g/min. Such results provided an indication of a greater flow of alumina abrasive in wear trials. Table VI illustrates the particle size distribution data of alumina abrasive (WFA), white fused alumina with niobium oxide (WFA-Nb), brown fused alumina (BFA), and the standard sand-SS #50 used. The reliability of wear results was ensured by the calibration of the tribometer in trials that used a standard material (AISI D2 steel tempered and quenched with a hardness of 740 HV_{30kgf}), medium sand (normal Brazilian sand with granulometry #50) and the same trial parameters (procedure B of the standard) [15]. The result of specimen mass loss was 0.21 g, a characteristic value of mass loss in such trial conditions. The results of the mass material removal for different types of abrasives are shown in Fig. 3. Results showed that the greatest mass loss in AISI D2 steel specimen occurred in white fused alumina with the addition of niobium oxide (WFA-Nb) trials, followed by white fused alumina oxide (WFA) trials and brown fused alumina (BFA) trials, proving the result obtained in the standard fracture resistance index (SFRI).

As a contribution to the characterization studies of samples, the X-ray diffraction (XRD) technique was applied to quantify the phases in all types of abrasives (Fig. 4). The quantification of the phases was hampered once the main phase α-Al_2O_3 was greater than 95%. However, in the white fused alumina (WFA) sample, since it was a fusion of calcined alumina, as expected [5], it was possible to identify the main phases of α-alumina (Al_2O_3) and β-alumina ($Al_2O_3.xNa_2O$). In the brown fused alumina (BFA) sample, it was not possible to identify a phase with the titanium oxide through X-ray diffraction once it had a content below 1.5 wt% and probably was in a solid solution. In the white fused alumina with niobium oxide (WFA-Nb) sample, it was possible to identify the main phase of α-alumina (Al_2O_3) and sodium niobate ($NaNbO_3$), with the sodium introduced from the calcined alumina (from caustic soda, NaOH, used in Bayer process) [4].

To help in the identification of the phases, the scanning electron microscopy (SEM) technique with energy

Table V - Results of the P60 grit standard fracture resistance index of brown fused alumina (BFA), white fused alumina (WFA), and white fused alumina with the addition of niobium oxide (WFA-Nb).

Property	BFA	WFA	WFA-Nb
Real density (g/cm^3)	3.95±0.01	3.94±0.01	3.98±0.01
Bulk density (g/cm^3)	1.68±0.01	1.62±0.01	1.65±0.01
FRI (%)	58.50±0.01	56.10±0.01	59.40±0.02
SFRI	1.38±0.01	1.36±0.01	1.43±0.02

FRI: fracture resistance index; SFRI: standard fracture resistance index.

Table VI - Data of particle size distribution of the aluminum oxides and the standard silica sand #50 after abrasiveness trials.

Sample	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
BFA	303	409	796
WFA	300	415	800
WFA-Nb	305	410	808
Standard sand #50	302	402	803

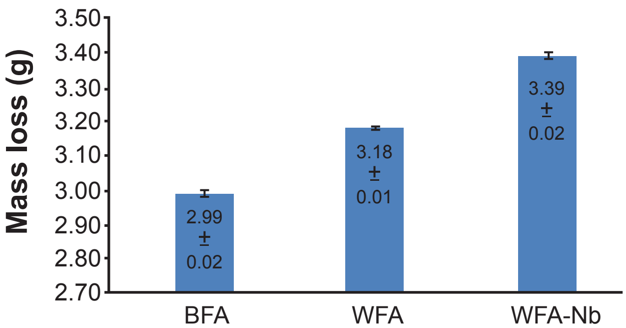

Figure 3: Results of mass loss of AISI D2 steel specimen after abrasiveness trials with brown fused alumina (BFA), white fused alumina (WFA), and white fused alumina with niobium oxide (WFA-Nb).

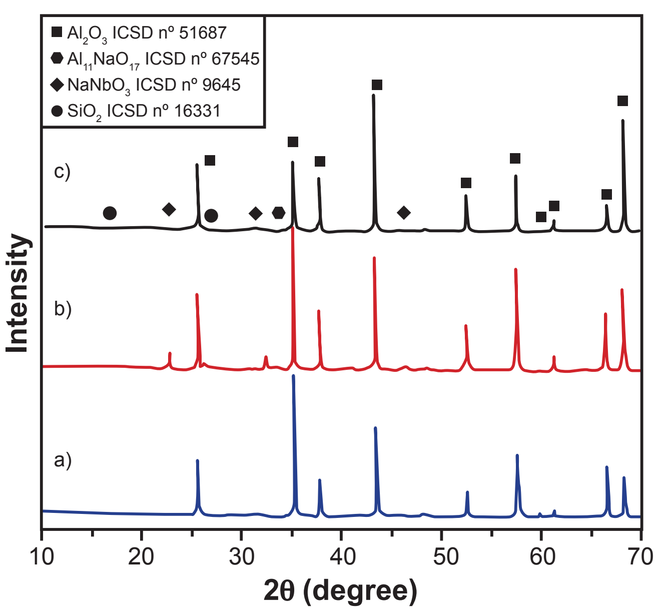

Figure 4: XRD patterns of the samples of grits of: a) brown fused alumina (BFA); b) white fused alumina with niobium oxide (WFA-Nb); and c) white fused alumina (WFA).

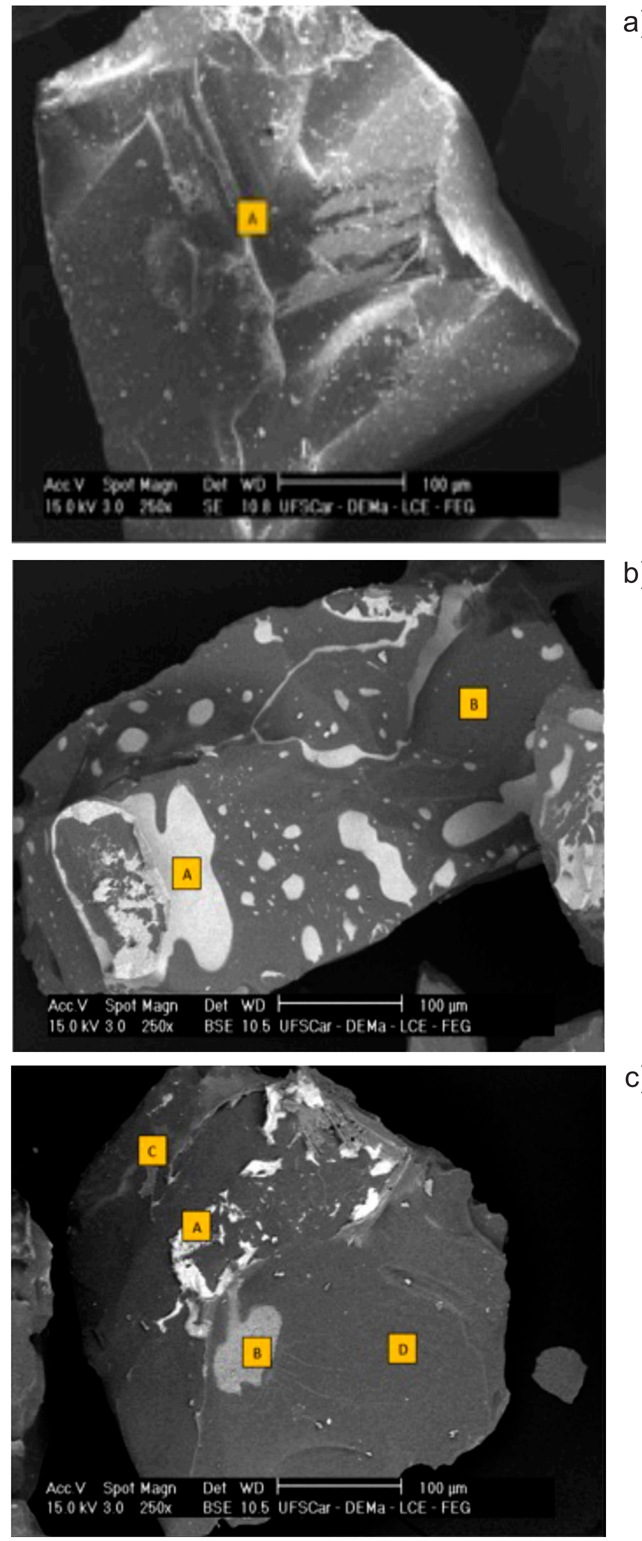

Figure 5: SEM micrographs of P60 grits of: a) white fused alumina (WFA); b) white fused alumina with the addition of niobium oxide (WFA-Nb); and c) brown aluminum oxide (BFA).

dispersive spectroscopy (EDS) was used. The sequence of images provided corresponded to: white fused alumina (Fig. 5a), white fused alumina with niobium oxide (Fig. 5b), and brown fused alumina (Fig. 5c). In Fig. 5a, the SEM-EDS of the white fused alumina (WFA) confirmed the presence of the major phase composed by the chemical element Al (Table VII) [13]. In Fig. 5b, the SEM-EDS of the white fused alumina with the addition of niobium oxide (WFA-Nb) confirmed the presence of two phases: the dark phase (point B) composed mainly by alumina and the light phase

Table VII - Results of EDS (wt%) from the points indicated in the SEM micrographs in Fig. 5.

Element	WFA	WFA-Nb		BFA			
	Point A	Point A	Point B	Point A	Point B	Point C	Point D
O	57.82	30.22	54.92	42.27	52.71	51.18	52.20
Al	42.18	4.04	42.01	3.20	5.56	9.71	43.80
Na	-	4.57	1.80	-	16.07	6.07	0.15
Nb	-	32.08	1.15	-	-	-	-
Ti	-	-	-	13.09	3.92	13.84	0.90
B	-	16.18	-	-	-	-	-
C	-	11.59	-	4.57	12.91	7.88	0.30
Ca	-	1.02	-	4.40	2.51	1.42	0.23
K	-	-	-	-	0.27	0.38	-
Mg	-	-	-	-	1.10	0.79	-
Mn	-	-	-	0.35	0.28	1.22	-
Si	-	0.30	0.12	-	4.60	6.68	2.40
Zr	-	-	-	32.12	0.07	0.84	0.02

(point A) showing the presence of a higher proportion of niobium oxide. In Fig. 5c, the SEM-EDS of the brown fused alumina (BFA) identified 3 phases, despite only 2 phases being identified by XRD, as well as their distribution. The main elements proved the composition, having major elements Al, Na, and Ti (Table VII).

SEM and EDS analyses are reported considering that all samples were submitted to the same fusion, milling, and sieving route. It is possible to observe in the micrographs in Fig. 5 marked differences in morphology. The white fused alumina (WFA) showed a homogeneous phase, while the white fused alumina with the addition of niobium oxide (WFA-Nb) featured a biphasic structure composed of Nb and Na, proving the existence of the sodium niobate phase identified by the X-ray diffraction. Lastly, in Fig. 5c, it is possible to verify the microstructure of the brown fused alumina (BFA) with a heterogeneous structure. It is also possible to observe in Fig. 5c and Table VII that point D is a major phase and is composed basically of Al, Ti and Si derived from raw materials. The phases identified as A, B and C were present in minor proportion if compared to phase D and had a lower level of Al and consequently higher levels of other elements, such as C, Na, Ca, Ti and Zr. Thus, the greatest abrasiveness value found in the white fused alumina with niobium oxide (WFA-Nb) was justified by the distribution and proportion of the $AlNbO_4$ phase observed in the microstructure (Fig. 5b) [3].

CONCLUSIONS

With the purpose of evaluating a new composition of fused alumina grits for application in abrasive devices, after the analyses of results, it was possible to conclude that the white fused alumina with niobium oxide (WFA-Nb) reached the greatest abrasiveness and the highest standard fracture resistance index (SFRI) among all tested materials, followed by the white fused alumina (WFA) and by the brown fused alumina (BFA). The greatest abrasiveness in the white fused alumina with the addition of niobium oxide (WFA-Nb) was related to the distribution and proportion of the $AlNbO_4$ phase identified by SEM and EDS. Therefore, due to its great abrasiveness, the white fused alumina with niobium oxide (WFA-Nb) demonstrated to have promising abrasive properties for application in sandpapers, resinoid grinding wheels, cut-off wheels, and blasting.

ACKNOWLEDGMENTS

This study was financed partly by the Coordination for the Improvement of Higher Education Personnel - Brazil (CAPES) - Finance Code 001. The authors acknowledge the company Elfusa Geral de Eletrofusão Ltda. for all the support in the provision of samples and guidance in analyses, and to the Surface Phenomenon Laboratory (SFL), Department of Mechanics of the Polytechnic School of the University of São Paulo.

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(Rec. 02/06/2022, Ac. 04/07/2022)