Environment Protection Engineering

Vol. 47 2021 No. 4

DOI:10.37190/epe210403

ANNA NIEMCZYK-WOJDYŁA (ORCID 0000-0001-8568-7478)[1]
AGNIESZKA FORNALCZYK (ORCID 0000-0002-2149-14222)[2]
JOANNA WILLNER (ORCID 0000-0003-3369-3678)[2]
RAFAŁ ZAWISZ (ORCID 0000-0002-1123-5476)[1]

TOWARDS A VIABLE METHOD OF REUSING SILICON CARBIDE. PHYSICOCHEMICAL ANALYSES IN THE STUDIES ON INDUSTRIAL APPLICATION OF THE MATERIAL

The paper presents an investigation on the feasibility of recovery of the highly valuable silicon carbide (SiC) from the slurry waste generated from silicon wafer production in the photovoltaic and semiconductor industry. Compared to the other techniques of recycling, a facile and low-cost method of waste treatment via heat drying followed by low-energy mixing in a shaker mixer was proposed. As the result of the treatment, the slurry waste was converted into a powdered form with dominant content of SiC. Separated SiC material was characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray powder diffraction, and sieve analysis. In addition, analyses of the bulk density, moisture content and melting test were carried out. As was confirmed by the physicochemical analyses, the dominant sieve fraction was in the range of 0.1–0.06 mm, the purity level was a minimum 99% mass of SiC, the moisture content – 0.3%, the bulk density – 1.3 g/cm^3. The physicochemical characteristics of the material were crucial for understanding the material performance, assessment of the material quality and determining the perspective directions of the industrial application. The studies revealed that the material exhibited a high application potential as abrasive, especially in abrasive grinding and waterjet cutting.

1. INTRODUCTION

Silicon carbide (SiC) exhibits a range of unique physical properties that makes it a very attractive and useful material in industrial and engineering applications. It is one

[1]Ad Moto Rafał Zawisz, Aleja Rozdzieńskiego 188B, 40-203 Katowice, Poland.

[2]Silesian University of Technology, Faculty of Materials Engineering, ul. Krasińskiego 8, 40-019 Katowice, Poland, corresponding author A. Fornalczyk, email address: agnieszka.fornalczyk@polsl.pl

of the hardest materials known, second only to diamond. Additionally, it features a relatively low density (approximately the same as aluminium), semiconducting properties, chemical inertness, high-temperature stability and high thermal conductivity [1]. Due to its excellent physical hardness, most of the SiC produced worldwide today is used as an abrasive in machining processes like grinding, honing, sandblasting and waterjet cutting [2]. Other popular areas of its application are refractories, electrical devices, electronics (semiconductors), metallurgy, ceramics, industrial furnaces, diesel particles filters, structural materials [3]. SiC is also applied by the aerospace, automotive, and power generation industries as a reinforcing material in advanced ceramic composites [3].

Only minor quantities of SiC exist in nature. In industrial practice, SiC can be produced by several processes which differ in levels of purity, crystal structure, particle size and shape of received material [1, 4]. Currently, the Acheson process is the main SiC synthesis method, which is started by mixing C-rich and Si-rich materials in an electric resistance furnace and followed by heating the mixture at given temperatures for the desired period [2, 4]. For special applications, SiC is also produced by other advanced processes including physical vapour transport, chemical vapour deposition, vapour–liquid–solid process [4, 5]. Besides these production methods, separating high-purity SiC from industrial wastes can be regarded as the alternative route of obtaining SiC, highly beneficial due to environmental and economic concerns [6].

A large amount of hazardous silicon slurry waste is generated during the slicing of silicon ingots into thin silicon wafers for the fabrication of integrated circuit chips and solar cells [7–10]. The amount of silicon waste slurry is expected to be increasing worldwide, as silicon wafer production increases. For instance, the fast-growing photovoltaic solar cells market achieved a cumulative growth rate of 35% between 2010 and 2019 [11]. As a consequence of this dynamic growth, the amount of the silicon slicing slurry wastes from the production of photovoltaic solar cells was nearly 160 000 Mg in 2017 [11]. Silicon wafer cutting slurry is mainly composed of SiC (as the abrasive), propylene glycol (as the cooling liquid), silicon (residual material after slicing) [12]. Currently, silicon slurry waste is mainly disposed of using incineration or land-filling [10, 12]. It results in serious environmental damage and substantial wasting of resources, therefore, how to treat this waste becomes an important issue. An efficient and low-cost method for obtaining SiC from silicon slurry waste could be a highly desirable step towards sustainable development. It is expected that SiC can be recycled from the slurry waste and reused in the adequate branch of industry (such as abrasive sector, silicon wafer production and steel casting) to reduce the production costs, gain economic benefit, and particularly protect the environment.

Silicon slurry waste can be separated using physical and chemical methods or flotation. In particular, several methods have been developed to recover SiC particles from the silicon slurry waste such as sedimentation, centrifugation, magnetization, filtration, directional solidification, alloying process, phase-transfer separation, electrokinetic separation, froth flotation technologies and carbothermic reduction [5–14]. However, these methods require high-cost apparatus, complex processes and consume substantial amounts of chemicals generating additional wastes. In addition, the problem of complete separation of SiC from the silicon slurry waste remains unsolved. The carbothermic reduction is the most promising method for large scale recycling of SiC, however, most SiC constituents volatilize in the form of SiO(g) and they are wasted [6, 14]. Therefore, further investigations are necessary to optimize the process and raise the recovery efficiency.

In this study, a facile and affordable approach was used for the fast recovery of SiC from silicon wafer cutting slurry. The proposed method exhibited a low complexity of the separation process, no additional wastes generated during the process and low separation cost. The obtained material was characterized by physicochemical analyses which were highly useful in the assessment of the quality of the material and evaluating the potential fields of its industrial application.

2. MATERIALS AND METHODS

Silicon slurry waste was obtained from the silicon wafer fabrication coming from the local market of solar cell production.

In the first step of the waste treatment, the silicon slurry was dried at 200 °C in the muffle furnace with gases extraction. This resulted in complete evaporation of propylene glycol and conversion of the slurry waste into solid in the form of lumps. Subsequently, the solid was cooled down to room temperature and then was subject to low--energy dry milling for 5 min at 50 rpm using a shaker mixer with milling balls (mass ratio of milling balls to mixed sample equalled 0.01:1). The waste treatment method resulted in the powdered material which was characterized by several analyses.

The particle morphology of the sample was analysed using a scanning electron microscope (SEM, Hitachi S 4200) operating at an accelerating voltage of 25 kV. An energy dispersive X-ray spectroscopy (EDS, JEOL JDX-7S) was used for the elemental microanalysis of the sample. The material was characterized by X-ray powder diffraction (XRD) on a JEOL JDX-7S diffractometer with CuK_α radiation under an accelerating voltage of 40 kV and a current of 20 mA. The diffraction patterns were collected at 25 °C and over an angular range of 20–90° with a step size of 0.05° and a dwell time of 12 s per increment. The obtained patterns were matched with references of JCPDS--ICDD database. The sieve analysis was carried out using a shaker (Multiserw-Morek, model LPzE-2e) and a set of sieves with mesh sizes of 0.3, 0.1, 0.08, 0.07, 0.06 mm. The moisture content was determined by the gravimetric method which involved oven drying a sample at 120 °C and reweighing it every hour until the mass of the sample did not change. The bulk density of the material was determined by weighing a known volume of the material that was passed through a graduated cylinder. It was calculated as the ratio of the mass to the volume of the untapped material. The melting test of the material was based on the knowledge of differences in the melting point between pure SiC (2730 °C) and pure silicon (1414 °C). The analysed material was heated in a chamber furnace at 1450 °C for 4 h under observation whether it undergoes melting. Any visible changes in the consistency of the examined material could be related to its contamination with the impurities melting t below 1450 °C.

3. RESULTS AND DISCUSSION

Silicon wafer cutting waste subject to the treatment was in the form of slurry due to the presence of a liquid layer of propylene glycol. In industrial practice, propylene glycol is a commonly used ingredient of the silicon wafer cutting mixture and acts as the cooling fluid [12, 13].

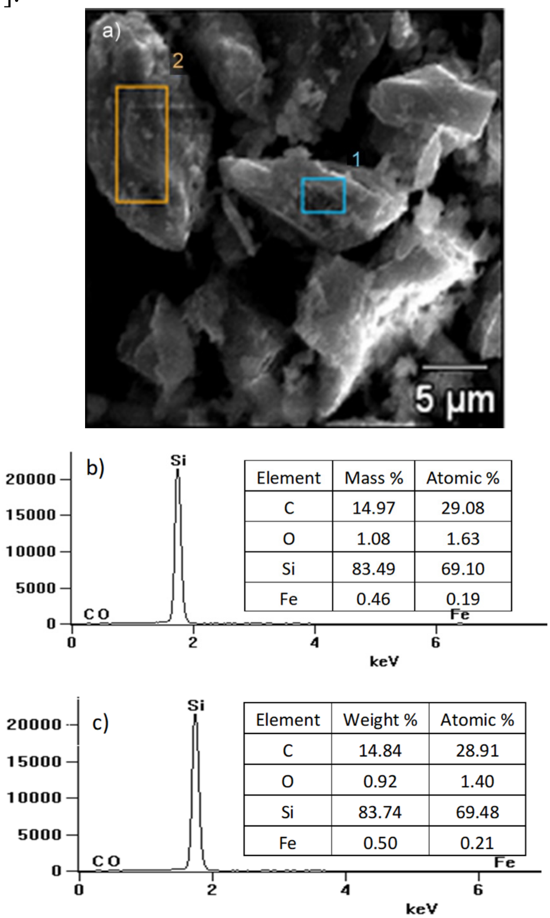

Fig. 1. SEM image with the selected EDS inspection of fields 1 and 2 (a),
SEM-EDS spectra at field 1 (b) and field 2 (c)

First, the slurry waste was treated by high-temperature drying above the boiling point of propylene glycol (200 °C). The obtained solid in the form of lumps was subject to low-energy dry milling using a shaker mixer. The slurry waste was then converted into a dry powdered solid. The colour of the obtained powder was grey without metallic lustre observed.

Further studies were focused on probing the physicochemical properties of the obtained powder. The studies confirmed that the bulk density of the powder was 1.3 g/cm^3. The analysis of the particle morphology (Fig. 1a) confirmed a large number of sharp-edged grains, with numerous vertices and cavities on the surface. However, a precise definition of the grain shape was troublesome due to the diversity of the geometric forms and required the use of a dedicated computer program. As was detected by SEM-EDS analysis (Fig. 1), silicon and carbon were present as the major components. Besides, small amounts of oxygen and iron were detected.

A melting test was performed for a preliminary control of the purity level. The lack of visible changes in the consistency of the material after heating at 1450 °C was a desirable result in terms of preliminary assessment purity level of the material.

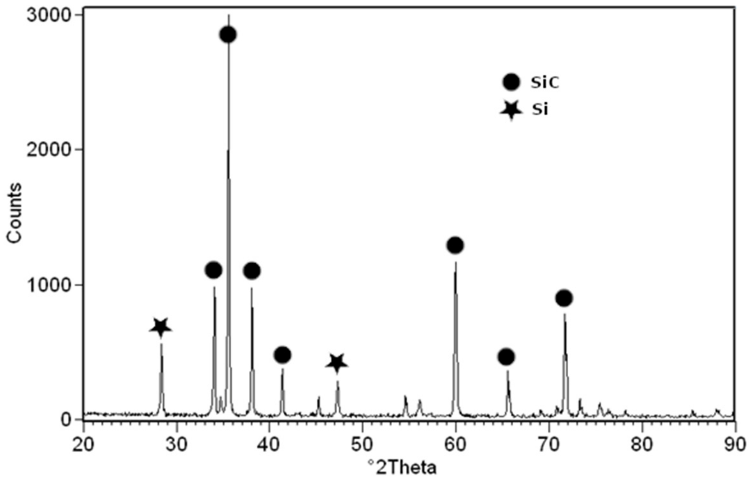

Fig. 2. XRD spectrum of the examined material

As was confirmed by XRD analysis (Fig. 2), the examined material exhibited crystalline form, with a characteristic diffraction pattern assigned to SiC structure, which was the major feature in XRD spectrum. The small diffraction pattern assigned to the silicon structure was detected, thus a minor amounts of silicon were present in the material. The material exhibited a high level of purity at least 99% mass of SiC.

The sieve analysis afforded isolation of six fractions (Table 1). The fraction in the range of 0.1–0.06 mm constituted the dominant share in the particle size distribution, namely 91%. Share of the other fractions was minor.

Table 1

Results of the sieve analysis

Mesh size [mm]	Weight [g]	Share [wt. %]
0.3	28	3.4
0.1	29	3.6
0.08	283	34.4
0.07	187	22.7
0.06	275	33.4
<0.06	20	2.4
Balance		
Input	832	–
Output	822	100
Material loss	10	–

Analysis of the moisture content in the material (Table 2) confirmed the greatest loss of moisture content was merely 0.3% after 2 hours of drying. As it was evident, the examined material has been already properly dried during the stage of the treatment of the slurry waste. The lack of the changes in the mass of the sample after 3 and 4 hours of the drying was evidence that the sample was dried to the constant weight, therefore the analysis was completed.

Table 2

Results of the analysis of moisture content

Time [h]	Weight of the sample [g]	Loss of moisture content	
		[g]	[%]
0	20.00	–	–
1	19.99	0.01	0.05
2	19.94	0.06	0.30
3	19.94	0.06	0.30
4	19.94	0.06	0.30

The analysis of physicochemical properties of the material was a starting point in probing the perspective fields of industrial application. Material needs to fulfil specific standards of quality, durability and performance to be applicable in the industry. The physicochemical properties are a crucial factor in determining the most perspective field of applications. For instance, SiC is a commonly used additive to improve the quality and machinability of steel and cast iron [4]. The standard values for the metallurgical-grade SiC are as follows: the level of the purity from 45% (when integrated into the manufacturing of briquettes) to over 95% (when used as a direct additive in iron and steel foundries), particle size distribution in the range of 5–50 mm; bulk density in the range 1.3–1.7 g/cm^3 [4].

Taking into account the purity grade, the examined material with dominant SiC crystalline phase (minimum 99% mass of SiC) appeared to be high-quality product for metallurgical applications. The bulk density of the examined material which was 1.3 g/cm^3 matched with the standard for metallurgical application. However, the granulometric characteristics confirming the small size of the grains (mainly 0.1–0.06 mm) are disadvantageous for metallurgical processing, which in turn, limit the application of the examined material in metallurgy [4]. Therefore, it could be useful to briquette the material, but it generates additional costs and may affect the final properties of the material.

The perspective area of the industrial application for the examined material could be the abrasive industry. Abrasive-grade SiC has many end-uses. Its specific applications include grinding wheels, honing sticks, waterjet cutting, snagging wheels, lapping and polishing of mechanical components, coated abrasive sheets, surface blasting. The properties of abrasive SiC can be varied to meet specialized needs. Besides hardness and toughness, the other important physical properties are purity grade, particle morphology and granulometric characteristics, moisture content, bulk density. Worldwide, the quality of the abrasive-grade SiC is standardized according to FEPA (The Federation of European Producers of Abrasives), SSPC (The Society for Protective Coatings), ASTM International (American Society for Testing and Materials), ISO (International Organization for Standardization), ANSI (American National Standards Institute) or JIS (Japanese Industrial Standards). Therefore, the industrial utility of the examined material was evaluated taking into account these standards.

For a uniform and predictable performance, the abrasive must be free from impurities. The purity level of the examined material (minimum 99% mass of SiC) matched the industrial requirements (following BS ISO 9286:1997) [15].

The moisture content in the examined material was 0.3% and fulfilled industrial standards (following international ASTM C566-19) [16]. According to the industrial recommendation, the maximum moisture content in SiC material should not exceed 0.5%. Abrasive with moisture content that exceeds the recommended level tends not to have a uniform flow rate.

The quality of abrasive is strongly affected by particle morphology. Namely, the geometric characteristic of a single abrasive grain affects the number and shape of cutting edges and the grain breakage behaviour. Each grain can have one or more cutting edges and grain splintering changes the number and shapes of the cutting edges [17]. In the case of the examined material, the morphology analysis confirmed a large number of sharp-edged grains, with numerous vertices and cavities on the surface. This characteristic can increase the tendency of the grain to self-sharpen which is advantageous in terms of the quality of the abrasive (according to FEPA 45-1:2011; FEPA Standard *Shapes and Dimensions For Precision Super Abrasives*) [18, 19].

The bulk density reflects the geometrical characteristics of abrasive and affects its performance and efficiency. In the case of the examined material, the bulk density was 1.3 g/cm^3 and fulfilled industrial references for abrasive (in accordance to FEPA 44-2:2006; ISO 9136-2:1999) [20, 21].

Another crucial parameter that affects abrasive performance is grain size distribution. The size of the grains and its distribution define the number of cutting edges. For instance, a small grain size commonly achieves smaller surface roughness but also causes higher machining forces and shorter tool life. Oversize particles can have negative effects on part surface quality, so a defined grain size distribution is important. Multiple national and international standards were implemented to define the size range for specific abrasives, for instance: FEPA 42-2:2006; FEPA 43-2:2017; ANSI B74.12 [22–24]. The particle size and its distribution was the criterion limiting the various fields of application of the examined material as abrasive. For instance, the examined material with the dominant fraction in the range of 0.1–0.06 mm could have limited application as the abrasive for polishing and lapping. Herein, commonly used particle sizes are around 0.01 mm and 0.01–0.05 mm, respectively [2].

The further studies aimed to specify which direction of application in the abrasive sector would be suitable for the examined material. The examined material with the dominant fraction in the range of 0.1–0.06 mm complied with the specific standards for the abrasive employed in grinding processes and waterjet cutting [2]. The examined material can be a competitive alternative for garnet which is the natural mineral commonly used as an abrasive in waterjet cutting. The application of the examined material in waterjet cutting can be beneficial from economic concerns. Firstly, the cost of the recovery of the examined material is substantially lower than the cost of garnet mining and processing. Secondly, the SiC dominant phase in the examined material can increase cutting quality by faster cutting, higher precision, less frequent nozzle plugging, which in turn, improve the efficiency of the process of waterjet cutting.

The physicochemical analyses have proven that the most perspective field of application for the examined material is an abrasive sector, in particular abrasive grinding and waterjet cutting. In favour of this conclusion, the selling prices of abrasive-grade SiC are higher than for the metallurgical one, due to more stringent quality standards in the abrasive industry. As the studies exhibited industrial potential, the samples of the examined material together with their physicochemical characteristics were sent to the potential customers from the abrasive sector. Open minds to collaborate and conduct the material testing on industrial apparatus, positive feedback on the quality of the samples, established contacts with customers have proven that facile and low-cost solutions in the field of waste treatment and SiC reuse are highly demanded by entrepreneurs.

4. CONCLUSIONS

Nowadays, the industry faces the following key challenges: continuously increasing requirements regarding environmental protection, increasing material efficiency, outstanding product quality and competitive price. Thus, in response to these challenges, manufacturers must provide innovative and specific solutions. The present studies not only resulted in a facile and feasible route for minimizing the hazardous SiC wastes, contributing to the prevention of environmental contamination but also benefited in the economical method of obtaining highly valuable SiC. The proposed method of the silicon slurry waste treatment can be an alternative method to highly-cost and more complex other methods that require sophisticated apparatus, chemicals toxic for the environment and generate additional wastes. When referring to other methods, the potential benefits of recovering the valuable material from the waste are reduced by the high cost of the treatment, which in turn, can be a limiting factor in scaling up the technology. As studies have proven, the physicochemical analyses of the recovered material were crucial for further material development, understanding its performance and assessment of the quality. The examined material complied with specific quality standards for abrasive-grade SiC. The studies confirmed that the most perspective field of application for the examined material could be abrasive grinding and waterjet cutting.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of Polish Ministry for Science and Higher Education under internal grants 11/010/BK_21/0032 and 11/020/BK_21/0080 for Faculty of Materials Engineering, Silesian University of Technology, Poland.

REFERENCES

[1] BELENKOV E.A., AGALYAMOVA E.N., GRESHNIKOV V.A., *Classification and structure of silicon carbide phases*, Phys. Solid State, 2012, 54, 433–440, DOI: 10.1134/S1063783412020072.

[2] LINKE B., *Life cycle and sustainability of abrasive tools*, Springer International Publishing, RWTH Aachen University, Aachen 2016.

[3] CHOI J., FTHENAKIS V., *Crystalline silicon photovoltaic recycling planning: macro and micro perspectives*, J. Clean. Prod., 2014, 66, 443–449, DOI: 10.1016/J.JCLEPRO.2013.11.022.

[4] COTTRELL A., *An introduction to metallurgy*, Routledge Taylor and Francis Group, New York 2019.

[5] SUN K., WANG T., CHEN Z., LU W., HE X., GONG W., TANG M., LIU F., HUANG Z., TANG J., CHIEN T., TAN G., FAN M., *Clean and low-cost synthesis of high purity beta-silicon carbide with carbon fiber production residual and a sandstone*, J. Clean. Prod., 2019, 238, 117875, DOI: 10.1016/j.jclepro. 2019.117875.

[6] GUO J., LIU Y., LIU L., LIU, J., KONG J., WANG W., JIANG S., XING P., *A low-cost and facile method to recycle silicon carbide particles from the solar grade silicon slicing wastes*, Silicon, 2020, 12, 2405–2412, DOI: 10.1007/s12633-019-00334-y.

[7] DROUICHE N., CUELLAR P., KERKAR F., MEDJAHED S., BOUTOUCHENT-GUERFI N., HAMOU M.O., *Recovery of solar grade silicon from kerf loss slurry waste*, Renew. Sust. Energ. Rev., 2014, 32, 936–943, DOI: 10.1016/j.rser.2014.01.059.

[8] SERGIIENKO S.A., POGORELOV B.V., DANILIUK V.B., *Silicon and silicon carbide powders recycling technology from wire-saw cuttin0510g waste in slicing process of silicon ingots*, Sep. Purif. Technol., 2014, 133 (36), 16–21, DOI: 10.1016/j.seppur.2014.06.036.

[9] HACHICHI K., LAMI A., ZEMMOURI H., CUELLAR P., SONI R., AIT-AMAR, H., DROUICHE N., *Silicon recovery from kerf slurry waste: a review of current status and perspective*, Silicon, 2018, 10, 1579–1589, DOI: 10.1007/s12633-017-9642-x.

[10] SHEN Z.Y., CHEN C.Y., LEE M.T., *Recovery of cutting fluids and silicon carbide from slurry waste*, J. Hazard. Mater., 2019, 362, 115–123, DOI: 10.1016/j.jhazmat.2018.09.014.

[11] HECINIA M., TABLAOUIA M., AOUDJB S., PALAHOUANEA B., BOUCHELAGHEMA O., BEDDEKA S., DROUICHEA N., *Recovery of silicon carbide and synthesis of silica materials from silicon ingot cutting fluid waste*, Sep. Purif. Technol., 2021, 254, 117556, DOI: 10.1016/j.seppur.2020.117556.
[12] DROUICHE N., CUELLAR P., KERKAR F., MEDJAHED S., OUSLIMANE T., HAMOU M.O., *Hidden values in kerf slurry waste recovery of high purity silicon*, Renew. Sustain. Energy Rev., 2015, 52, 393–399, DOI: 10.1016/j.rser.2015.07.114.
[13] KAE-LONG L., KANG-WEI L., TA-WUI CH., WEI-TING L., YA-WEN L., *Utilization of silicon carbide sludge as metakaolin-based geopolymer*, Mater. Sust., 2020, 12, 7333, DOI: 10.3390/su12187333.
[14] KIM Y., MIN K., SHIM J., KIM D.J., *Formation of porous SiC ceramics via recrystallization*, J. Eur. Cer. Soc., 2012, 32, 3611–3615, DOI: 10.1016/j.jeurceramsoc.2012.04.044.
[15] BS ISO 9286:1997, *Abrasive grains and crude. Chemical analysis of silicon carbide*, BS ISO Standards Publication.
[16] ASTM C566-19, *Standard test method for total evaporable moisture content of aggregate by drying,* ASTM International Standards Publication, 2019.
[17] CHEN Y., CHEN X., AIOUARAB L., OPOZ T., XU X.P., YU G., *Morphology analysis and characteristics evaluation of typical super abrasive grits in micron scale*, J. Superhard Mater., 2019, 41, 189–200, DOI: 10.3103/S1063457619030079.
[18] FEPA 45-1:2011, *Chemical analysis of silicon carbide*, FEPA Standards Publication.
[19] FEPA *Standard shapes and dimension for precision superabrasives*, FEPA Standards Publication.
[20] FEPA 44-2:2006, *Grains of fused aluminium oxide and silicon carbide and other abrasive materials. Part 2: Determination of bulk density – Microgrits F and P series*, FEPA Standards Publication.
[21] ISO 9136-2:1999, *Abrasive grains. Determination of bulk density. Part 2: Microgrits*, ISO Standards Publication.
[22] FEPA 42-2:2006, *Grains of fused aluminium oxide, silicon carbide and other abrasive materials for bonded abrasives and for general applications. Microgrits F 230 to F 2000*, FEPA Standards Publication.
[23] FEPA 43-2:2017, *Grains of fused aluminium oxide, silicon carbide and other abrasive materials for coated abrasives. Microgrits P 240 to P 5000*, FEPA Standards Publication.
[24] ANSI B74.12, *Specification for the size of abrasive grain – grinding wheels, polishing and general industrial uses*, Published by Unified Abrasives Manufacturers Association.