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Refractory magnesia-carbon scrap as a valuable secondary raw material

Introduction

Magnesia-carbon scrap is used in the refractories industry particularly in countries without resources of natural graphite and magnesite. The scrap was obtained during the demolition of the lining of oxygen converters that represent the most important installations for the production of steel with a BOF (*Basic Oxygen Furnaces*) method. Graphite deposits do not occur in Poland and there are no perspectives whatsoever to find them. Although this raw material can be partly replaced by synthetic graphite manufactured in our country, it is unsuitable for producing refractory materials because of its very fine granulation. In turn, the magnesite raw materials occur in Lower Silesia but represent only the a very fine-grained (aphanitic) and compact variety. This kind of magnesite is most often also unsuitable for manufacturing basic refractories since it contains variable, most often elevated quantities of silica, a component undesirable in the technology. Thus, the entire demand for magnesia must be covered by the import which is brought to Poland in the form of thermally processed

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materials, i.e. either dead burned magnesia (DBM) or, recently more often, fused magnesia (FM). Considering the almost monopolistic position of China, much strengthened in the last years on the international magnesite market, it is the country which fulfils the demands of the Polish industry of refractories. Chinese deposits provide 67% of the world mine production of raw magnesite while its thermally processed products cover 75% of the world demand for total magnesia: in 44% for the burned magnesia DBM and in 80% for fused magnesia FM (Flook and Wilson 2018). It is the latter product that is more and more widely used by the Polish industry of refractories. The monopolistic position of China on the international market of magnesite and magnesia caused an enormous growth in their prices in 2017, especially in the case of the fused magnesia. The FM variety containing 96% MgO, priced in the first half of 2017 at about USD 400/t, reached around USD 1000/t at the end of that year, while the price of the FM variety containing 98% MgO jumped from around USD 1000 to 2000/t (Anonym 2018). An economic aspect must have stood behind a decision of Polish producers of the magnesia-carbon refractory materials to initiate investigations on their manufacturing from the caustic magnesia obtainable from domestic, alternative sources. They represented the brines processed on a pilot line (Skalska et al. 2016), moreover that such a possibility had been suggested even earlier (Piątkowski 1991; Kloska and Piech 1991). However, this idea needs some obstacles, as these brines contain elevated quantities of some trace elements, for instance of boron, undesirable by technological reasons. Boron considerably lowers the properties of magnesia refractories, in which it forms low-fusible phases of magnesium and calcium borides. This problem does not exist if thermally treated, traditional magnesite raw materials are used in the manufacturing of most of magnesia-carbon refractories. Therefore, the recycling of such no longer serviceable refractory scrap is fully justified in Poland if only this scrap could be processed to obtain its required properties.

The other component needed for the process, however in minor quantities of about 10 wt.%, is natural graphite. It is fully imported by Poland, firstly from China, but as of late also from Brazil. The market situation of graphite is the same as in the case of the magnesia raw materials: China is an unquestionable leader and provides 60–70% graphite on the world scale (Smakowski et al. 2015). The industry of refractories is based mainly on coarse-flake varieties of graphite, which are by far more resistant to oxidation than the finer varieties of natural graphite. A gradual growth of the utilization of flake graphite in the technologies of various industries, including the manufacturing of refractories, have resulted in putting this deficit natural raw material on the list of the so-called raw materials critical for the economy of the European Union (Radwanek-Bąk 2016). On the other hand, a deficit of graphite has obviously resulted in a considerable increase of its prices: for instance, in 2013 they reached USD 1300/t for the coarse-flake graphite containing a high contents (94–97 wt.%) of elemental carbon (Smakowski et al. 2015).

The high prices of the magnesia and graphite raw materials are a reason that the utilization of the adequately processed magnesia-carbon scrap becomes an urgent economic and technological challenge in Poland that should secure – to some extent – the needs of the industry of refractories.

The adequate management of the waste scrap not only saves natural mineral raw materials but also protects the natural environment. It limits the industrial use of energy and cuts on emissions of industrial gases into the atmosphere, for instance those of CO₂ generated in the process of firing the magnesia clinker, and also lowers the space needed for the storage and disposal of waste.

The problem of utilizing the refractory scrap is gaining more and more interest, which is manifested by the growing number of respective publications. For instance, at the 14th Biennale Worldwide Congress UNITECR 2015 in Vienna, a special section was devoted to recycling of refractories, the proper management and utilization of which were then considered to be insufficient. According to the estimates of the European Refractory Producers Federation PRE, only 20% of the scrap was utilized by the industry of refractories, 27% by other industries, 35% was totally lost during technological processes, and 18% landed on municipal landfills (Roberts 2015). One of the papers (Ducastel et al. 2015) presented an interesting concept of sorting the refractory scrap according to its chemical composition. This solution was given a follow-up and a prototype installation “Refrasort” presented at the ECREF 59th International Colloquium on Refractories in Aachen by Hartenstein et al. (2016).

The ArcelorMittal Refractories Ltd. Krakow, Poland, have been dealing with the recycling of the refractory scrap for many years and some of the results were shown at the Congress UNITECR 2011 in Toronto (Kielski et al. 2013). The authors mainly discussed the sorting of the converter and ladle basic scrap. When the scrap was ground, some deleterious admixtures, such as SiO₂, Al₂O₃ and Fe₂O₃ passed mainly into the fine-grained fractions. This find gave rise to developing adequate procedures, in which the magnesia-carbon scrap could be processed and recycled for manufacturing refractories of a good quality. A follow-up of these investigations provides the data shown below that explain the mechanism of reporting the unwanted admixtures into the finer grain fractions.

1. Methods

The methods applied included the determinations of the following: the phase composition, the microstructural development, i.e. a distribution of the phase components, the chemical composition, and the grain-size distribution.

The phase composition was established using X-ray diffraction (XRD) and standard powder samples analyzed with a RIGAKU SmartLab diffractometer under the following conditions: CuK_α radiation, graphite reflexive monochromator, lamp voltage 45 kV, lamp current 200 mA, measuring step 0.05° 2θ, counting time 1 sec/step.

Hand specimen and microscope observations provided microstructural data on the grain size and the mutual relation of the grains. They were carried out using an Olympus SZX-9 stereoscope and a universal Olympus BX51 polarizing microscope at magnifications of 10 and 125, respectively. The samples were prepared as standard polished specimens for

reflected light. Prior to cutting and polishing, the brittle specimens were hardened by impregnating them in epoxy resin.

The chemical composition was analyzed using X-ray fluorescence (XRF) with an ARL Advant' XP spectrometer at the accredited Laboratory Research Facility FERROCARBO Ltd in Krakow.

The starting samples were disintegrated using a cone crusher. The grain size analyses were conducted with the sieve method following Polish and other European standards.

2. Results

The yields of the major grain fractions of the magnesia-carbon scrap obtained after crushing the starting sample indicate that the fraction 1–4 mm usually prevails and makes about 50 wt.%, while the other two fractions occur in lower and comparable amounts: grains 0–1 mm make 20–35% and 4–6 mm – 20–30%. The chemical compositions (Table 1) of these fractions were supplemented by calculating two significant ratios for each sample: C/S and A/F, where C is the CaO content, S the SiO₂ content, A the Al₂O₃ content, and F the Fe₂O₃ content; both indexes have been important in further considerations.

Table 1. Chemical composition of the major grain fractions of the disintegrated magnesia-carbon scrap

Tabela 1. Składy chemiczne podstawowych frakcji ziarnowych rozdrobnionego złomu magnezjowo-węglowego

Composition, wt.% Grain size, mm	Loss on ignition	C _e	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	C/S	A/F
0–1	11.82	9.90	1.40	1.60	1.08	1.91	93.60	1.36	1.48
1–4	8.85	7.92	0.86	1.13	0.71	1.71	95.60	1.99	0.98
4–6	10.23	9.20	1.15	0.58	0.59	1.65	95.70	1.43	0.98

C_e – elemental carbon, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃.

As the fine-grained material contains higher contents of admixtures, the fraction 0–1 mm was further sieved into seven sub-fractions, whose chemical compositions were also analyzed and the C/S and A/F ratios calculated (Table 2). The data given in this table show that a decrease of the grain size is accompanied by increases of the contents of admixtures and the carbonaceous substance and a decrease of MgO. They corroborate that the further beneficiation of the magnesia-carbon scrap is advisable and confirm the former results obtained by the authors (Kielski et al. 2013).

The C/S ratio is a technological index related to the phase composition of the magnesia refractories. In the magnesia clinkers of a good quality it takes values exceeding 2.0. The lower values, particularly those in the range between 1.0 and 2.0, point to an adverse composition of charge materials which results in the formation of easily fusible silicate phases: monticellite and merwinite. The data (Tables 1 and 2) indicate that the C/S ratio decreases with a decrease of grain sizes. Also significant are the values of the A/F ratio, although their impact is more complicated and will be discussed at the end this Chapter.

The ratios C/S and A/F have also been calculated for the data previously obtained by Kielski et al. (2013) and presented in Table 3. The C/S ratio values decrease with the

Table 2. Chemical composition of the grain fractions below 1 mm obtained after sieving

Tabela 2. Składy chemiczne złomu frakcji 0–1 mm po przesianiu

Composition, wt.% Grain size, mm	Loss on ignition	C _e	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	C/S	A/F
0.0–0.06	13.19	9.68	2.04	1.62	1.38	2.40	92.2	1.18	1.17
0.06–0.09	13.24	12.75	1.77	1.60	1.34	1.99	92.9	1.12	1.19
0.09–0.12	14.54	11.64	1.67	1.67	1.33	1.98	93.0	1.19	1.26
0.12–0.20	14.51	11.92	1.66	1.65	1.24	1.99	93.2	1.20	1.33
0.20–0.50	12.13	9.97	1.40	1.57	0.99	1.82	94.2	1.30	1.59
0.50–1.00	9.45	7.92	1.15	1.53	0.82	1.75	94.7	1.52	1.87
>1.00 (residue)	8.81	7.53	1.14	1.50	0.77	1.75	94.6	1.54	1.95

C_e – elemental carbon, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃.

Table 3. Chemical composition of the grain fractions of the magnesia-carbon scrap (Kielski et al. 2013)

Tabela 3. Składy chemiczne frakcji ziarnowych złomu

Composition, wt.% Grain size, mm	Loss on ignition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	C/S	A/F
0.0–0.5	22.79	1.55	4.17	2.51	1.96	87.90	1.26	1.66
0.0–1.0	18.16	1.33	2.94	1.90	1.91	90.70	1.44	1.54
0.5–1.0	10.20	1.04	1.35	1.63	1.83	93.70	1.76	0.82
1.0–1.5	9.38	1.02	1.16	1.25	1.95	1.95	1.91	0.80
1.5–6.0	8.41	0.85	0.56	0.82	1.75	95.80	2.05	0.68

C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃.

decrease of grain sizes. It was also established for the scrap generated several years ago. Therefore, the connection of lower C/S values with finer grain fractions may be considered a regularity and proves the technological stability.

Lowering the C/S ratio values is a sign of the presence of admixtures in the fine-grained fractions of the scrap. To find the reason of this dependence, the authors tested it on two selected magnesia-carbon scrap, i.e. the scraps with a relatively high and low Al_2O_3 contents (Tables 4 and 5). Both types of scrap were disintegrated in industrial cone crushers.

Table 4. Chemical composition of the bulk sample of the magnesia-carbon scrap with a low Al_2O_3 content and of its grain fractions

Tabela 4. Składy chemiczne wyjściowej próbki złomu magnezjowo-węglowego o małej zawartości Al_2O_3 i jej frakcji ziarnowych

Composition, wt.% Grain size, mm	Loss on ignition	C _e	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	C/S	A/F
0.0–6.0	13.84	n.d.	0.93	0.29	0.73	1.46	96.4	1.57	0.40
0.0–0.5	18.51	17.92	1.05	0.36	0.72	1.43	96.3	1.36	0.50
0.5–1.0	12.44	12.10	0.85	0.23	0.66	1.34	96.7	1.57	0.35
1.0–4.0	10.64	12.51	0.88	0.20	0.69	1.42	96.7	1.61	0.30
4.0–6.0	8.80	11.80	0.94	0.17	0.66	1.46	96.7	1.55	0.26

C_e – elemental carbon, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, n.d. – not determined.

Table 5. Chemical composition of the bulk sample of the magnesia-carbon scrap with a high Al_2O_3 content and of its grain fractions

Tabela 5. Składy chemiczne wyjściowej próbki złomu magnezjowo-węglowego o dużej zawartości Al_2O_3 i jej frakcji ziarnowych

Composition, wt.% Grain size, mm	Loss on ignition	C _e	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	C/S	A/F
0.0–6.0	14.19	n.d.	0.76	5.16	0.33	1.58	91.8	2.07	15.68
0.0–0.5	24.44	24.12	1.32	9.88	0.50	1.83	86.1	1.38	19.76
0.5–1.0	15.22	15.08	0.77	5.51	0.34	1.47	91.6	1.90	16.21
1.0–4.0	13.05	10.14	0.81	3.89	0.34	1.57	93.5	1.93	11.44
4.0–6.0	12.30	8.44	0.81	3.68	0.33	1.62	93.3	2.00	11.15

C_e – elemental carbon, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, n.d. – not determined.

The data (Tables 4 and 5) fully confirms previous observations. In the finer grain fractions the contents of admixtures gradually increase, which is indicated by the decreasing MgO contents and the values of the C/S ratios, despite the high chemical diversification of the two magnesia-carbon scraps. The increasing contents of the carbonaceous matter in the finer grain fractions are consistent with the losses on ignition that result from oxidation of carbon at 1000°C in the ambient atmosphere. The details of the process were discussed previously (Kielski et al. 2013), when the scraps were analyzed using the thermo-gravimetric method combined with the analyses of evolving gases.

Some conclusions on the diversification of the chemical composition of the grain fractions were drawn on the basis of the qualitative XRD analysis and microscopic observations. In addition, the qualitative composition of the grain fractions was determined based on their chemical analyses following the method of Nadachowski (1995), proving a full equilibration of the samples, but not considering their presence of carbon in the form of graphite (Tables 6 and 7). The phase composition analyzed with the XRD method (Fig. 1) have identified

Table 6. Phase composition of the magnesia-carbon scrap with a low Al₂O₃ content

Tabela 6. Skład fazowy złomu magnezjowo-węglowego o małej zawartości Al₂O₃

Grain size, mm	On the basis of XRD analyses	On the basis of the chemical composition
0.0–1.0	M, MA, CMS, C ₂ MS ₂	M, CMS, MA, MF
0.5–1.0	M, G, MA, CMS, C ₂ MS ₂	M, C ₃ MS ₂ , C ₂ S, MA, MF
1.0–4.0	M, G, MA, CMS	M, C ₃ MS ₂ , C ₂ S, MA, MF
4.0–6.0	M, G, CMS, C ₂ MS ₂	M, C ₃ MS ₂ , C ₂ S, MA, MF

See below Table 7.

Table 7. Phase composition of the magnesia-carbon scrap with a high Al₂O₃ content

Tabela 7. Skład fazowy złomu magnezjowo-węglowego o dużej zawartości Al₂O₃

Grain size, mm	On the basis of XRD analyses	On the basis of the chemical composition
0.0–1.0	M, G, MA, CMS, C ₂ S	M, CMS, MA, MF
0.5–1.0	M, G, MA, CMS, C ₂ S	M, C ₂ S, C ₄ AF, MA, MF
1.0–4.0	M, G, MA, C ₂ S	M, C ₂ S, C ₄ AF, MA, MF
4.0–6.0	M, G, MA, C ₂ S, CAS ₂	M, C ₂ S, C ₄ AF, MA, MF

Refer to both Table 6 and Table 7.

M = MgO – periclase; G = C_e – graphite; MA = MgO · Al₂O₃ – magnesium-aluminium spinel; MF = MgO · Fe₂O₃ – magnesioferrite; CMS = CaO · MgO · SiO₂ – monticellite; C₃MS₂ = 3CaO · MgO · 2SiO₂ – merwinite; C₂S = 2CaO · SiO₂ – dicalcium silicate; C₄AF = 4CaO · Al₂O₃ · Fe₂O₃ – brownmillerite; C₂MS₂ = 2CaO · MgO · 2SiO₂ – åkermanite; CAS₂ = CaO · Al₂O₃ · 2SiO₂ – anorthite.

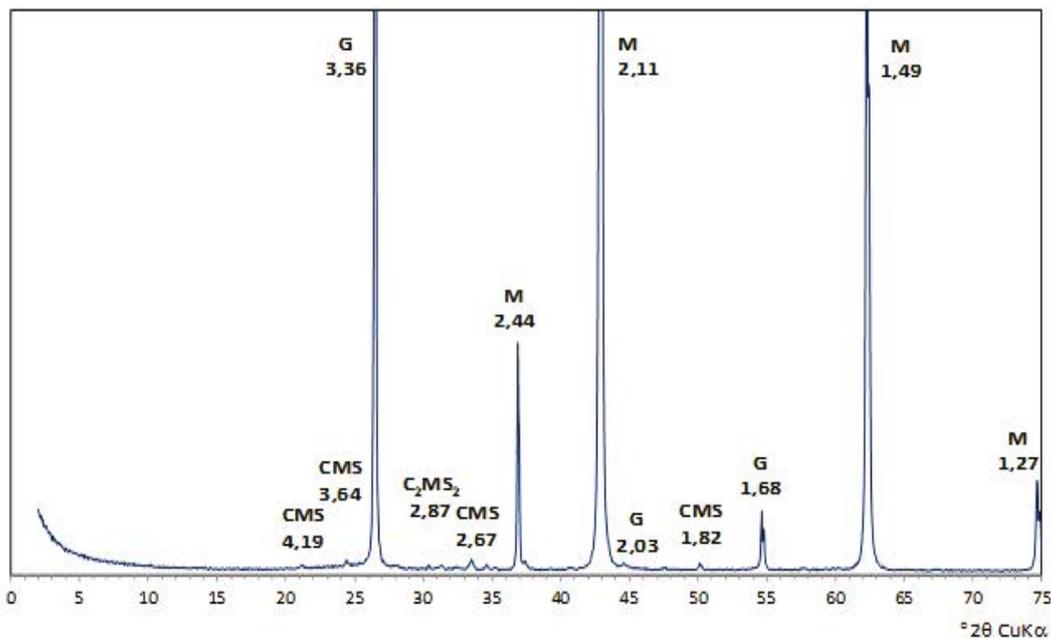


Fig. 1. An example of an XRD pattern of the magnesia-carbon scrap with a low Al_2O_3 content used in ArcelorMittal Refractories, Krakow, for the production of basic refractories
 CMS – monticellite, C_2MS_2 – åkermanite, G – graphite, M – periclase. Interplanar distances d_{hkl} are given in Å

Rys. 1. Przykładowy dyfraktogram rentgenowski złomu magnezjowo-węglowego o małej zawartości Al_2O_3 , stosowanego w ArcelorMittal Refractories w Krakowie do produkcji zasadowych wyrobów ogniotrwałych
 CMS – monticellit, C_2MS_2 – åkermanit, G – grafit, M – peryklaz.
 Wartości odległości między płaszczyznami sieciowymi d_{hkl} podano w Å

small amounts of silicates with low values of the C/S ratio, i.e. of monticellite with the ratio C/S = 1.0, and even of åkermanite and anorthite whose C/S ratios are lower. The presence of dicalcium silicate in the scrap with the high content of Al_2O_3 is an exception. Most probably this phase already occurred in the magnesia clinker which had been used to manufacture a high-aluminum lining. However, another possibility is the formation of the dicalcium silicate in the lining because among the calcium silicates the first to crystallize is always the Ca-orthosilicate, i.e. the dicalcium phase.

There is a significant difference between the presence of the phases inferred from the chemical composition and those identified with the XRD method. It must be a result of both the lack of equilibration and the heterogeneity of refractory materials. The latter is also visible when observing the distribution of phase components in microscopic images.

Major materials used for manufacturing magnesia-carbon refractories are magnesia clinker and graphite. In their typical compositions (Table 8) turns the attention a high silica content in the graphite-derived ash, which is consistent with the data of Galos and Wyszomirski (2001). The silica contents of the magnesia clinker are low and, accordingly,

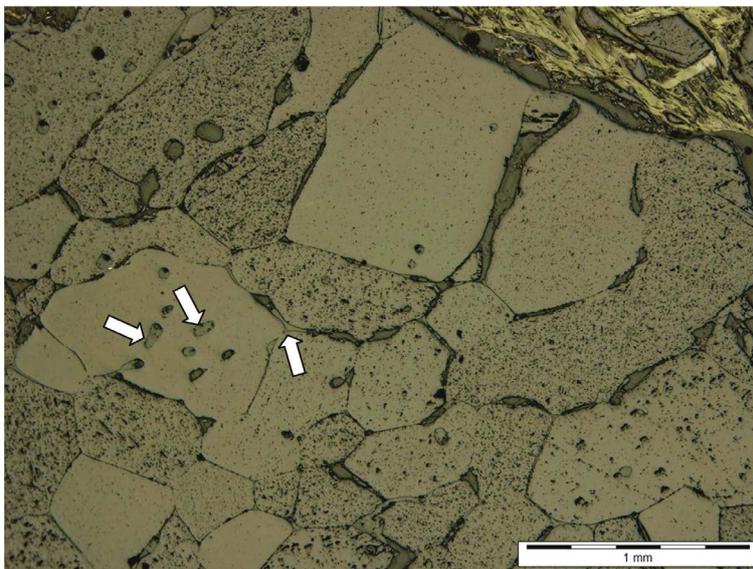
Table 8. Chemical composition of a typical magnesia clinker, raw graphite and the ash of the burned graphite

Tabela 8. Składy chemiczne typowego klinkieru magnezowego, surowca grafitowego i popiołu otrzymanego po spalaniu grafitu

Composition, wt.% Grain size, mm	Loss on ignition	C _e	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	C/S	A/F
Magnesia clinker	–	–	0.54	0.25	0.46	1.11	97.60	2.05	0.54
Raw graphite	95.85	95.40	–	–	–	–	–	–	–
Ash of a burned graphite	–	–	51.30	25.70	15.00	2.81	2.09	0.05	1.71

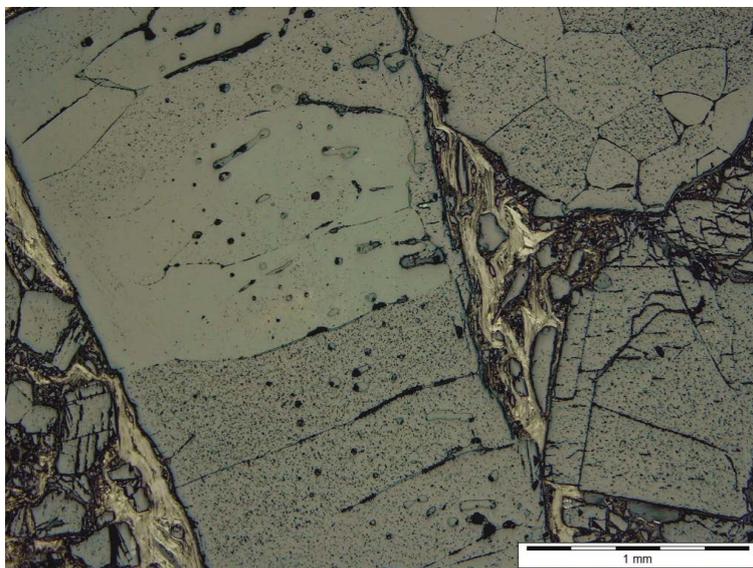
C_e – elemental carbon, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃.

the silicate phases developed on the borders of the periclase grains and those developed as microinclusions within such grains occur only sparsely (Table 8, Photos 1 and 2). The matrix among the periclase grains is occupied by large accumulations of graphite (Phot. 3), which after oxidation forms ash and becomes a source of easily fusible silicate phases with low values of their C/S ratios.



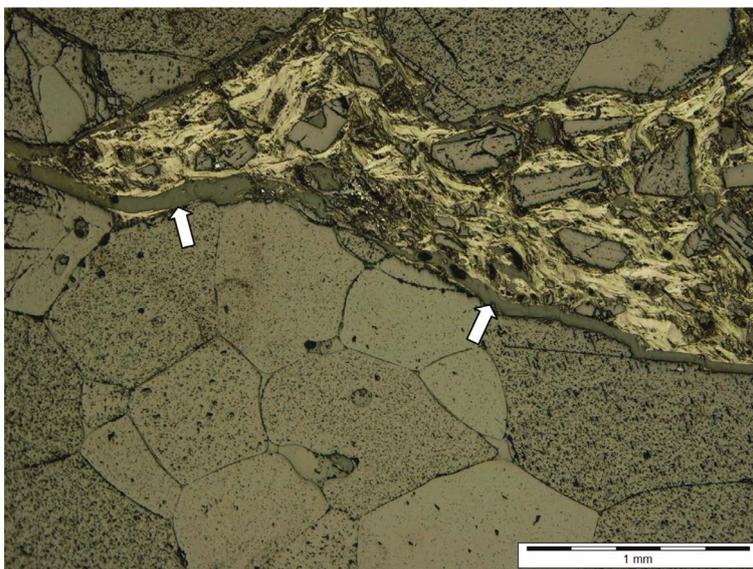
Phot. 1. Polycrystalline grain of periclase with small accumulations of a silicate phase (arrows).
Photomicrograph, one polarizer

Fot. 1. Polikrystaliczne ziarno peryklazu z niewielkimi skupieniami fazy krzemianowej (strzałki).
Mikrofotografia, jeden polaryzator



Phot. 2. Monocrystalline grain of periclase with fine inclusions of a silicate phase.
Photomicrograph, one polarizer

Fot. 2. Monokrystaliczne ziarno peryklazu z drobnymi wrostkami fazy krzemianowej.
Mikrofotografia, jeden polaryzator



Phot. 3. Matrix composed of fine grains of periclase and flake graphite (light) among large grains of periclase.
The fracture in the middle is filled with the epoxy resin (arrows). Photomicrograph, one polarizer

Fot. 3. Osnowa złożona z drobnych ziaren peryklazu oraz łuskowego grafitu (jasny) pomiędzy dużymi ziarnami peryklazu. W środku widoczna szczelina wypełniona żywicą (strzałki). Mikrofotografia, jeden polaryzator

The silicate phases of the scrap are characterized by low hardness, cleavage and brittleness, particularly revealed after their crystallization. For these reasons they accumulate mainly in the fine-grained fractions of the disintegrated scrap. Also the non-oxidized graphite reports to the fine grain fractions because of its very low hardness. Since the graphite of the polytype 2H is relatively resistant to oxidation, the non-oxidized flakes of graphite most probably represent just this variety. As such, they are a component much looked for in manufacturing the magnesia-carbon refractories.

Looking at the A/F ratio, two processes must be considered. The magnesium-aluminum spinel is one of the hardest phases of the magnesia-carbon refractory materials. Accordingly, any increase of the A/F ratio must be accompanied by lowering the Al_2O_3 contents in the fine-grained fractions of the scrap. However, if the metallic aluminum is applied as an anti-oxidant, the scrap often undergoes hydration. If this happens, the increase of the A/F ratio is accompanied not by a decrease but an increase of the Al_2O_3 contents in the fine-grained fractions.

3. Discussion of results and conclusions

The investigations have shown that after the disintegration of the magnesia-carbon scrap, the decreasing size of the scrap grain fractions is accompanied by the following: the increasing contents of their chemical admixtures, i.e. SiO_2 , CaO , Fe_2O_3 and Al_2O_3 ; the decreasing values of the C/S ratio; and variations of the values of the A/F ratio. In addition, the content of elemental carbon C_e increases and, simultaneously, the losses on ignition increase. The changes of the C/S ratio are caused by the changes of the phase composition, i.e. the increase of silicate phases with lower temperatures of fusing and, consequently, inferior refractory properties. The XRD analyses have corroborated this conclusion and even revealed the presence of low-fusible silicate phases with their C/S ratios even lower than those predicted on the basis of the calculation that provided the equilibrium conditions. To be precise, instead of the expected monticellite and merwinite, the presence of åkermanite and anorthite has sometimes been identified.

The easily fusible silicate phases are characterized not only by lower hardness but, firstly, better cleavage and higher brittleness in comparison with periclase, these properties being manifested mainly directly after their formation. Therefore, these are phases undergoing easier disintegration when crushed and milled. Graphite is the softest phase and it reports to and concentrates in the fine-grained fractions. The magnesia clinker of the good quality, which is the major component for manufacturing the magnesia-carbon refractory materials, is characterized by low silica contents and, simultaneously, high C/S ratios. The microscopic observations have revealed that the silicate phases, initially occurring in the clinker, are developed as fine accumulations along the borders of the periclase grains and/or as inclusions within them (Photos 1 and 2). On the other hand, the flakes of graphite represent a much higher source of silica, as they form relatively large accumulations. Nevertheless, the ash

remaining after oxidation of carbon in graphite contains about 50 wt.% SiO_2 (Table 8) and is responsible for the formation of low-fusible silicate phases. In the matrix of the magnesia-carbon materials, graphite forms accumulations among the grains of periclase (Phot. 3) and due to this, contributes to generating fine-grained fractions when the scrap is comminuted. It is one of the reasons of the higher contents of admixtures in such fractions. The A/F ratio is also linked to the phase composition of the scrap and its tendency to hydration.

The conclusion drawn on the admixtures reporting to the fine-grained fractions of the disintegrated magnesia-carbon scrap is an important clue to scrap recycling. The processing must be based on removing the finest grain fractions with unfavorable chemical compositions applying carefully designed sieving procedures. As the investigations have shown, the magnesia-carbon scraps are highly diversified considering their chemical and phase compositions. Therefore, each batch of the scrap going to be utilized must be chemically analyzed with the determination of the C/S ratio and a scrap tendency towards hydration established. The scrap prone to hydration should have this tendency tested following the procedures specified by Kielski et al. (2013). Concluding, the non-hydrating scrap varieties after being processed includes two steps: 1. the removal of the finest grain fractions with a chemical composition unfavorable from the viewpoint of production of magnesia-carbon refractories, and 2. the homogenization of the remainder, can be directly applied to producing the magnesia-carbon refractory materials of advisable properties. The finest grain fractions may be used as a component of gunite mixes (also known as shotcreting or torcreting masses), in which the presence of some amounts of low-fusible phases is simply required.

The ArcelorMittal Refractories Ltd., Krakow, Poland, has been utilizing base refractory scraps as secondary materials to manufacture high quality products for many years as any lowering of the production costs is an obvious economic advantage. This is particularly important in the case of the magnesia-carbon refractories, because graphite deposits do not occur in Poland at all, while domestic deposits of magnesite provide the raw material not meeting the technological criteria of the production of refractories. The results indicate that the utilizations of the scraps cannot be limited to their sorting only but should also include their processing and homogenization. The condition to have the scrap homogenized is its well-planned disintegration. Since the ArcelorMittal projects aim at a full utilization of the waste materials, some attempts have been made to other uses for the magnesia-carbon scrap. For instance, the company is involved in manufacturing the gunite mixes considering the presence of valuable graphite, most probably of the 2H polytype, in the sieved grain fractions of this scrap.

The following conclusions referred to the methods of manufacturing the magnesia-carbon products from the recycled refractory scrap can be finally summarized:

1. The graphite component, and particularly the ash formed after its oxidation, contains considerably more undesired oxides (mainly SiO_2) than the magnesia clinker.
2. Graphite directed to the process should be characterized by possibly low contents of ash since at the ash expense may form the low-fusible silicate phases.
3. The content of graphite should be limited to a necessary minimum.

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REFERENCES

- Anonym, 2018. Out of the melting pot: A year of change in refractories. *Industrial Minerals* September 2018, pp. 28–31.
- Ducastel et al. 2015 – Ducastel, A., Gueguen, E., Horckmans, L., Bouillot, F., Fricke-Begemann, C., Knapp, H., Makowe, J. and Stark, A. 2015. Innovative separation technologies for refractory waste. *Materials Unitecr 2015*, abstr. No. 141.
- Flook, R. and Wilson, I. 2018. Demanding supply. *Industrial Minerals* September 2018, pp. 47–51.
- Galos, K. and Wyszomirski, P. 2001. Some refractory raw materials– mineralogical and technological characteristics (*Niektóre surowce przemysłu materiałów ogniotrwałych – charakterystyka mineralogiczno-technologiczna*). *Ceramika/Ceramics* 64, pp. 59–68 (in Polish).
- Hartenstein et al. 2016 – Hartenstein, J., Ducastel, A., Gueguen, E., Horckmans, C., Fricke-Begemann, C., Knapp, H., Bouillot, F., Makowe, J. and Stark, A. 2016. Enhanced recycling of refractories by automated sorting. *Materials 59th International Colloquium on Refractories 2016*, Aachen, Eurogress, pp. 34–37.
- Kielski et al. 2013 – Kielski, A., Obszyńska, L., Sułkowski, M., Wyszomirski, P. and Blumenfeld, Ph. 2013. The issue of use basic refractory scrap. *Materials Unitecr 2011*, Toronto, pp. 1250–1255.
- Kłoska, A. and Piech, J., 1991. Magnesia clinkers obtained from mine brines (*Klinkiery magnezjowe z solanek kopalnianych*). *Polskie Towarzystwo Mineralogiczne – Prace Specjalne* 1, pp. 111–115 (in Polish).
- Nadachowski, F., 1995. Outline of refractories technology (*Zarys technologii materiałów ogniotrwałych*). Second edition. Katowice: Śląsk Publishing House, pp. 283–300 (in Polish).
- Piątkowski, W., 1991. Mine brines as a source of magnesia (*Solanki z wód kopalnianych jako źródło otrzymywania magnezji*). *Polskie Towarzystwo Mineralogiczne – Prace Specjalne* 1, pp. 147–153 (in Polish).
- Radwanek-Bąk B., 2016. Designation of key raw materials for the Polish economy (*Określenie surowców kluczowych dla polskiej gospodarki*). *Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią PAN* No. 96, pp. 241–256 (in Polish).
- Roberts, J., 2015. European refractories recycling – current trends and prospects. *Materials Unitecr 2015*, abstr. No. 73.
- Skalska et al. 2016 – Skalska, M., Darlak, M., Śnieżek, E., Madej, D. and Szczerba, J. 2016. Magnesia-carbon products made from raw materials originated from alternative resources – properties and application (*Wyroby magnezjowo-węglowe z zastosowaniem surowców magnezjowych z alternatywnych źródeł – właściwości i zastosowanie*). *Materiały Ceramiczne/Ceramic Materials* 68(4), pp. 355–361 (in Polish).
- Smakowski et al. 2015 – Smakowski, T., Galos, K. and Lewicka, E. (eds) 2015. Mineral Yearbook of Poland 2013 (*Bilans gospodarki surowcami mineralnymi Polski i świata 2013*). ISBN 978-83-7863-467-6. Warszawa: PIG-PIB (in Polish).

REFRACTORY MAGNESIA-CARBON SCRAP AS A VALUABLE SECONDARY RAW MATERIAL**Keywords**

refractories, magnesia-carbon scrap, secondary raw materials

Abstract

The authors established the chemical and phase compositions of grain fractions of the magnesia carbon scrap disintegrated using industrial cone crushers. The investigations included chemical and XRD analyses and optical investigations. The contents of admixtures: SiO_2 , CaO , Fe_2O_3 and Al_2O_3 increase with the decreasing size of the scrap grain fractions, whereas the C/S ratio decreases in finer and finer fractions due to changes of the phase composition. These relations are caused by the presence of low-fusible silicate phases, characterized by their cleavage and brittleness. Such phases were mainly derived from the graphite ash containing a high silica content. The scrap after removing its finest grain fractions can be recycled and utilized for producing the magnesia-carbon refractory materials. However, the finest grain fractions may be used, e.g. as a component of gunite mixes. Many years of experience collected by the ArcelorMittal Refractories Ltd., Krakow, Poland in the field of refractory scrap utilization has also been presented.

**ZŁOMY MAGNEZJOWO-WĘGLOWYCH WYROBÓW OGNIOTRWALYCH
JAKO WARTOŚCIOWY SUROWIEC WTÓRNY****Słowa kluczowe**

wyroby ogniotrwałe, złomy magnezjowo-węgłowe, surowiec wtórny

Streszczenie

Badano składy chemiczne i fazowe frakcji ziarnowych złomów magnezjowo-węglowych po rozdrobnieniu w kruszarkach przemysłowych. W badaniach posłużono się oznaczeniami składu chemicznego, rentgenowskimi i mikroskopowymi. Stwierdzono, że ze zmniejszaniem się rozmiarów ziaren wzrasta zawartość domieszek w postaci SiO_2 , CaO , Fe_2O_3 i Al_2O_3 oraz maleje wartość stosunku C/S wskutek zmian składu fazowego. Przyczynę stanowią łatwo topliwe fazy krzemianowe odznaczające się łupliwością i kruchością pochodzące głównie z popiołu grafitowego o dużej zawartości krzemionki. Omówiono sposoby uzdatniania złomów na drodze eliminacji frakcji drobnoziarnistych. Te ostatnie mogą być jednak wykorzystane, np. do sporządzenia mas do torkretowania. Przedstawiono wieloletnie doświadczenia firmy ArcelorMittal Kraków, Poland w zakresie wykorzystania złomów ogniotrwałych.