MULTISCALE, COMPUTER AIDED METHOD FOR THE CHARACTERISATION OF REFRACTORY CASTABLES MICROSTRUCTURE.

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ABSTRACT

In this work, different complementary methods were used to describe the microstructure and specially the particle size distribution of bulk refractory castables. A procedure was developed to obtain large size polished samples including a lot of large whole particles (aggregates). Optical and scanning electronic microscopy was used for picture acquisition. A panorama software was used for pictures assembly leading to larger pictures with a high definition. An artifact: ink impregnation was used to enhance the contrast between different phases and to promote grains recognition by image analysis software. A method combining the three procedures was applied to different castables. Results show that it is possible to obtain an assessment of the aggregates size distribution. However, fine grains (matrix) of the materials cannot be assessed by the automatic computer aided method.

KEY WORDS: castable, image analysis, microstructure, spinel, microscopy.

I. INTRODUCTION

Refractory materials (Fig. 1) exhibit very complex microstructures. Classically it is well accepted that they contain two main "physical" phases which are the matrix (bonding phase) and aggregates [1]. Aggregates are large particles ranging from approximately 100 µm to several millimetres. The matrix contains fine particles, generally from 0.1 µm to approximately 100 µm. Generally, they also display several chemical and crystallographic different phases. Today, the description of a refractory material microstructure is very limited. Optical and electronic microscopy are necessary to observe details such as small particles, grain boundaries, porosity,... However, they only allow the observation of small areas with few large particles (aggregates) and a part of them are not fully included in the pictures. Moreover, the figure 1 shows that the contrast between the different phases is often very weak. Contrary to ceramic and metal ([2], [3], [4]) which exhibit fine and narrow size distribution and sufficient contrast between grain and boundaries, refractory features impede microstructure description and quantification. However this parameter could be very interesting for characterising materials, quality control, ...[5]. Some "new" parameters could be quantified: particle size distribution, homogeneity, porosity size and dispersion, phases distribution, particle shape, phase transformation at high temperature,...

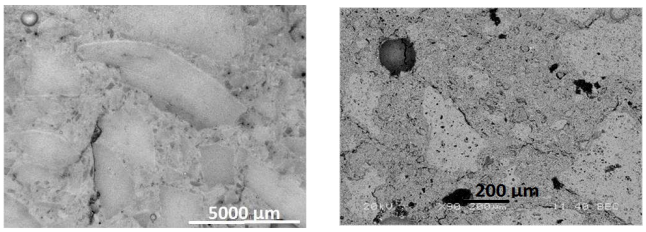

Fig. 1: "Classical" pictures (optical (left) and electronic (right)) of a refractory castable.

The target of this work was to investigate the possibility to develop a new tool which allows describing and/or controlling "the microstructure of refractory materials. The first step was to develop a method allowing a fast description and control of the particle size distribution. Moreover, if possible, the method must be simple and must include the use of "automatic" commercial softwares.

This way of working should lead to minimise the operator influence.

II MATERIALS AND METHODS.

II.1 Materials.

Materials, used in this work, belong to the family of alumina and alumina-spinel castables [6]. Compositions contain alumina (large aggregates, fine and reactive alumina (matrix), either preformed spinel or fine magnesia powder or fine magnesite as magnesia precursor (matrix). In these two last case, spinel is obtained by in situ reaction [7] between alumina and magnesia, at high temperature (>1200°C). Some materials also contain microsilica. At low temperature, they are bonded with calcium aluminate cement or hydratable alumina (5%). Preparation of these materials is described in reference [8]. For microscopy investigation, materials were first heated at 1400°C during one hour to promote sintering and a good cohesion for easy tooling and polishing. Table 1 presents compositions of tested materials.

Tab. 1: Summary of investigated materials compositions (wt %)

REF	PS	MC	Mg	MS	CA	HA	Dmax
1-1	17	-	-	-	5	-	6
1-2	-	-	-	-	5	-	3
1-6	-	5	-	-	5	-	8
3-6	-	4	-	-	5	-	3
3-7	-	8	-	-	5	-	3
3-8	-	-	8	-	5	-	3
3-9	-	-	4	0.5	5	-	3
4-3	-	-	8	-	-	5	3
4-4	-	4	-	-	-	5	3
4-5	-	8	-	-	-	5	3
4-6	-	-	4	0.5	-	5	3
4-7	-	-	8	0.5	-	5	3

PS: preformed spinel, MC: magensite, Mg: magnesia, MS: microsilica, CA: calcium aluminate cement, HA: Hydratable alumina, Dmax: maximum particle size.

The compositions exhibit extensive particle size distributions. Serie 1 materials present different maximum particle size (Dmax). Series 3 and 4 materials are obtained by substituting magnesia or magnesite for alumina of similar particle size. Therefore the particle size distributions (PSD) of these materials are very close. Following experimental results are compared to "theoretical" particle size distribution calculated from raw materials individual particle size distributions.

II.2 Samples preparation

Parallelepipedic samples were obtained by casting in steel moulds at HS Koblenz [8]. After heat treatment one hour at 1400°C, samples were cut in large cylinders (diameter:~36 mm, thickness~ 5 mm) and polished with silicon carbide.

II.3 Microscopy, image processing and analysis.

Polished samples were observed with a scanning electronic microscope associated with an EDS. Optical microscopy consisted of using a different microscope associated to a high resolution camera connected to a computer for pictures recording and treatment.

II.4 Commercial softwares

The work was mainly realized with the help of two softwares. The first one is a panoramic picture editor. Its work consists of assembling lot of individual pictures with minimum picture overlapping to a large panoramic view. Fig. 2 presents the principle of the method.

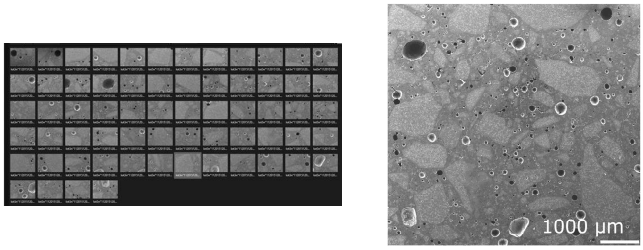

Fig. 2: Principle of the picture assembly with the panoramic picture editor software; left: individual pictures, right: assembly.

The second software is an image analysis software specially including a „grain module“ allowing automatic grain recognition when the contrast is sufficient.

III. RESULTS AND DISCUSSION

III.1 Picture assembly

Fig. 2 (right) presents an example of SEM (SEI) picture obtained from an assembly of individual pictures. This high definition picture presents both an overview of the material, including many large particles and large defects (pores). With help of a computer and observation of high magnification (small areas) on a screen could lead to long distance observation and quantification on the full picture surface. However, attempts to use automatic analysis with the image analysis softwares were not successful. The contrast between the different phases is not sufficient. Manual analysis could be realised but rapidity and the use of an automatic commercial software targeted in this work could not be achieved. Further work will demonstrate the interest of this kind of picture for the detection and the quantification of cracks in materials at high temperatures [10]. In this work, picture assembly was mainly used with optical pictures after using an artefact to enhance phase contrast.

III.2 Contrasting pictures

Image analysis is mainly based on the contrast between different phases. For this, image analysis softwares propose a thresholding function. Thresholding (Fig 3) consist to transform a large range grey shade picture in a binary colour picture. The transformation is gradually realised starting from darker or lighter phase and is stopped when wanted segregation is obtained (Fig 3).

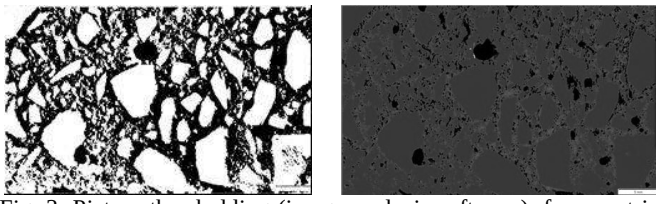

Fig. 3: Picture thresholding (image analysis software), from matrix to aggregates (left) and from aggregates to matrix (right).

Due to the weak contrast observed in the materials, this operation is very difficult. Stopping of the thresholding is submitted to individual appreciation. And results strongly fluctuate when changing operator.

Different methods such as dark field optical microscopy (figure 4) were used to improve the contrast. This last method allows obtaining improved pictures. However, the result does not allow using reproducible thresholding and automatic image analysis. Finally a method based on preferential impregnation was chosen for further analysis. Fig. 5 presents the effect of black ink impregnation on the picture of series 1 materials. Comparison between materials before and after treatment shows a “sufficient” contrast between the phases.

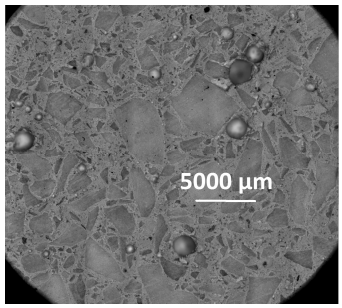

Fig. 4: Assembly of dark field optical microscopy pictures.

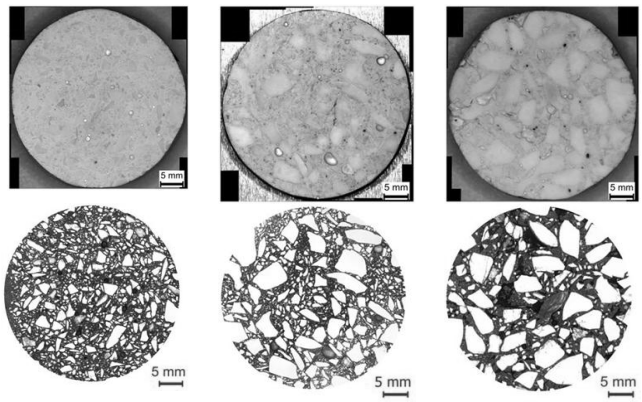

Fig. 5: Effect of black ink impregnation on the contrast.

Pictures of ink impregnated samples were obtained by an assembly of 21 individual pictures obtained with optical microscopy (Fig. 6).

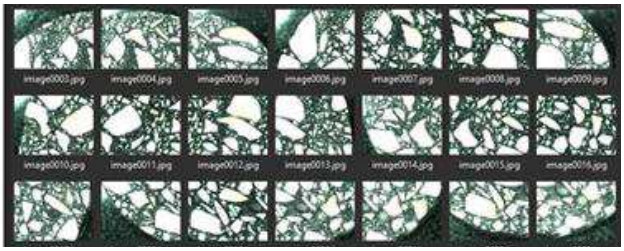

Fig. 6: Individual optical microscopy pictures used image analysis.

III.3 Image analysis

Figure 7 shows the effect of image analysis treatment on picture of two ink impregnated samples. The treatment consists of particle recognition with the automatic “grain module”. The pictures also show that particles which are not fully included in the picture (bright white) are excluded from treatment. The software delivers a file containing a lot of information such as “particle size”, particle surface, shape parameters,...

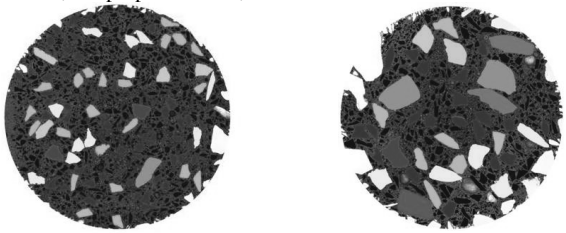

Fig.7: Examples of image analysis (with a commercial software) of an ink impregnated material: particles “recognition” and classification for 2 different particle size distributions.

In this first approach, only the particles surface is considered and only the correlation with particle size distribution is discussed. The operator can also operate a classification based on a specific number

of ranges size. A colour (not visible on the following pictures which are transformed in grey shades) can be attributed to each range. Bright white particles along sample edge are excluded from the treatment.

III.4 Particle size distribution (PSD)

Fig. 8 presents the PSD (2 samples) of series 1 materials, compared to their theoretical volume distribution. The results are presented in surface ratio (% surface) of the total investigated surface, versus the particle higher dimension. This last one was chosen because it is closer of the value obtained from sieving method used for "theoretical" PSD. However, further investigations could use an equivalent circular diameter which is also automatically available from the image analysis treatment. Image analysis demonstrates that it is not possible to detect particles with size lower than 70 µm. Related surface measured under this size could be attributed to the porous, ink colored matrix.

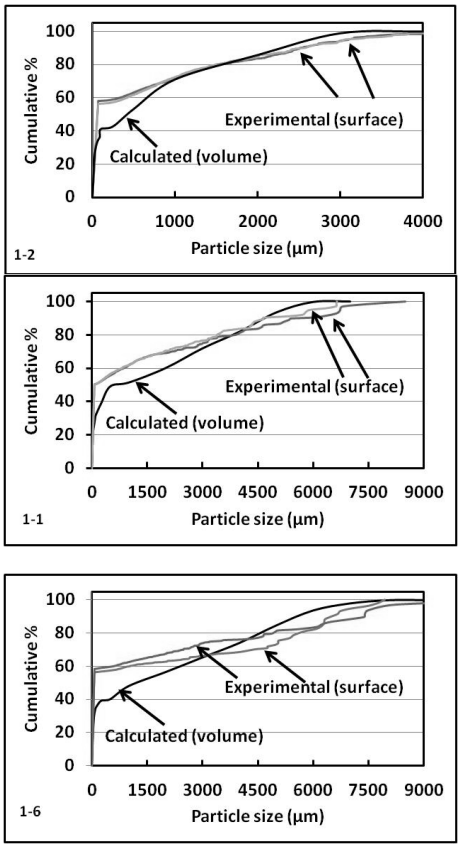

Fig. 8: Calculated and experimental particle size distribution of series 1 materials with different Dmax.

The main difference between calculated (volume) and experimental (surface) curves is the fine particles part which is much higher for surface distribution than for volume distribution. This difference (surfaces between curves) also increases with Dmax. This difference can be explained by the randomly cutting of particles during sample preparation. Figure 9 presents the different possibilities obtained when cutting a large spherical particle. It is obvious that when randomly cutting a spherical particle, a large number of disks with different smaller diameters are generated. Number of different diameter disks increases with the spherical diameter. Only Cutting at the middle of the particles leads to the same diameter. This means that "surface distribution" normally exhibits a larger part of smaller diameters than the equivalent "volume size distribution" and that this difference increases with the average "volume" particle size. However, the maximum size observed is similar for both distributions because it is always the diameter of the larger original particle. In stereology [9], statistical models exist, which allow relating "surface distribution" to "volume distribution". However in this case, it is not possible because small (<70 µm) size distribution is not available.

Fig. 8 also demonstrates that the dispersion between results obtained on two different samples increases with Dmax. For the smaller one (sample 1-2) experimental curves are superimposed, for sample 1-1 (medium Dmax) curves are close, for the larger Dmax difference between curves is significant. This is certainly due to the number of particles which are excluded from the treatment (figure 7) and which therefore modifies the investigated surface. Sampling (sample size and/or sample number) should probably be adapted to Dmax. Fig. 10 and 11 present results obtained for 3 and 4 series materials.

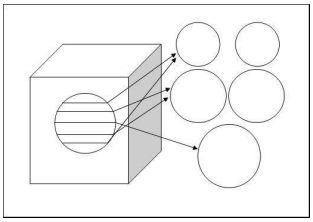

Fig. 9: Effect of randomly cutting of a spherical particle, on the resulting "surface size distribution".

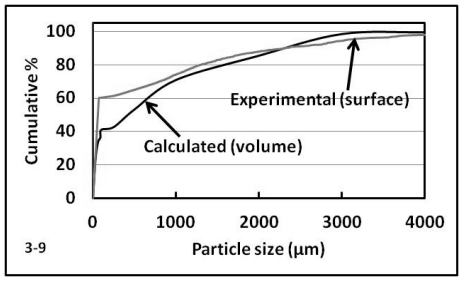

Fig.10: Example of calculated and experimental PSD for 3-9 material, very similar to that one of 3-7, 4-4, 4-5, 4-3, 4-6, 4-7 materials .

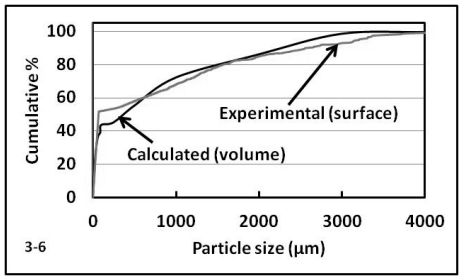

Fig. 11: Example of calculated and experimental particle size distribution for 3-6 material, very similar to that one of 3-8.

As already explained here above, all these materials, including materials 1-2 (Fig. 8) exhibits very close "theoretical" particle distribution. Eight of ten materials (1-2, 3-9, 3-7, 4-4, 4-5, 4-3, 4-6, 4-7) materials exhibit very close results with small variations (Fig. 10). Materials 3-6, 3-8, exhibit a lower fine part and a smaller difference between calculated and experimental curves. These differences cannot be explained in this work. It can be due to sampling method or to the dispersion of the production. Further work is to be done to investigate this kind of variation. From these last observations, it can be concluded that the reproducibility level of this method seems very good but additional (statistical) investigations are necessary.

III.5 Matrix analysis

With the target of a full description of the materials microstructure, the matrix was also investigated. Fig. 12 presents a general overview (electronic microscopy) of a matrix, which is nearly similar for all investigated materials. This picture demonstrates that the limits of different phases are not clear, a lot of different grey shades exist between phases and also in the same phase. The large porosity, in this part of the materials, also interacts with observation. It was not possible to directly apply an automatic image analysis to this kind of

micrograph; and during this work, no artefact was found to improve the pictures and to develop a new method. Therefore, the classical method such as electronic microscopy with help of EDS analysis remains the best method for describing refractory materials matrix. For example, Fig. 12 shows: aggregates (large tabular alumina particles (top left and bottom right, the bonding phase (matrix, from bottom left to top right). This phase contains fine alumina particle (light grey), fine magnesia particles (dark grey) and calcium aluminate cement particles (white).

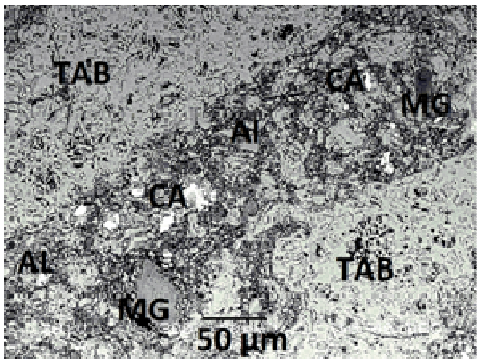

Fig. 12: General overview (electronic microscopy) of a matrix (TAB: tabular alumina, Mg: magnesia, CA: calcium aluminate, Al: alumina).

In the future, matrix investigation with computer aided method could be based on EDS mapping (Fig. 13) which allows exactly locating chemical element and therefore also the different phases.

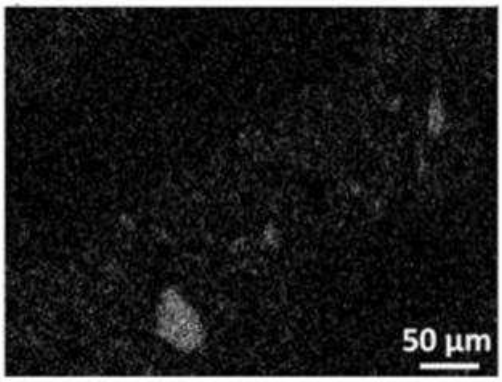

Fig.13: Example of Mg mapping obtained from EDS analysis and showing the location of magnesia or magnesite in the matrix.

IV CONCLUSIONS AND PERSPECTIVES

This work is a contribution to the development of a fast "automatic" method for the characterisation of the microstructure of refractory castable materials. "Classical" microscopy (electronic and optical) high magnification pictures necessary to observe fine part and details of materials, only present few aggregates and a lot of them are cut at the edges. This limitation can be overcome by using "picture assembly" method. As well for electronic microscopy as for optical microscopy, a poor contrast between the different phases doesn't allow the pictures treatment with an image analysis software. Thresholding necessary for phase or grain boundary contrasting is not possible with accuracy and result strongly depends of the operator. An artefact: black ink impregnation of materials was developed to enhance the phase contrast. The result is an effective contrast between the porous matrix and the dense aggregates. This advantage could only be profitable with optical microscopy. The preparation of large samples, ink impregnation, picture assembly and "automatic" image analysis with a commercial software allows obtaining a "surface" particle size distribution. The method is limited to the description of particles higher than 70 µm which means the aggregates. At this stage of the development, statistical method cannot be applied to relate "surface PSD" to origin "volume PSD", because information is not available for small particles. Today, the current method could be applied to control (production, reception, composition development,...) the aggregates particle size distribution and the part of the matrix. In the future, some work can be realised to develop statistical calculation to improve results interpretation. Some other parameters which are available from the image analysis, and which were not described in this work, could also be used to check and quantify the homogeneity, the particle shape,..The method can also be developed to quantify the size, number and dispersion of large defect as observed in figure 3 or smaller ones such as cracking due to mismatch between different phases or induced by a thermal stress. This information could be very interesting to interpret thermomechanical properties. During this work, the method was also applied to detect and to quantify the crack propagation during testing at high temperature in same materials (10). Finally, it would be also interesting to check the possibility to extend the method to shaped and insulating materials.

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ACKNOWLODGEMENT

This work was realized in the framework of a CORNET (network of ministries and funding agencies in Europe) project "HISHOCK" (2015-2017) with participation of BCRC, Forschungsgemeinschasft Feuerfest e.V. and Hochschule Koblenz and was funded by SPW (Belgium-Wallonie) and AiF (Germany).

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