

# **FROM MONOMETALLIC TO COMPOSITES AND CERAMIC WEAR RESISTANT MATERIALS: AN INDUSTRIAL CHALLENGE**

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## **Abstract**

The methodology adopted by Magotteaux for the development of wear resistant materials is described based on the wear mechanisms observed. This approach consists of six steps from identification of wear mechanisms and mechanical constraints to continuous improvement of the industrial supply chain.

This method is currently used for monometallic balls and liners for grinding mills and allows the optimal selection of steel or iron composition and heat treatment. Based on a large database of marked ball and liner tests, application-specific products and wear models have been established for tube mills.

The same basic approach is also used for the mining industry based on slurry chemistry, recovery, grinding efficiency and wear reduction.

The development of composite and ceramic materials is reviewed. The metal matrix composite (MMC) parts are based on two families, namely oxides and carbides. Manufacturing challenges to produce these new wear resistant materials are described regarding the required properties and size of the castings.

Some examples and wear results for vertical roller mills and crushers are also presented. Finally, ceramic beads are discussed for ultrafine grinding applications.

## **Introduction**

Magotteaux International, a Sigdo Koppers Group company, started in Belgium in 1918 as a small foundry producing grinding media for the cement industry. Shortly after it was established, an 'in-house' R&D laboratory and a pilot foundry were created to study and test wear resistant materials. After a few years, Magotteaux started to develop castings for cement mills' internal components, and then also to develop products for the mining industry, with balls and liners for grinding tube mills using high chromium steels and irons. Magotteaux then pursued development in other grinding and crushing equipment, as well as in other markets (aggregates, dredging and power stations, etc.). Magotteaux now supplies a wide range of optimized solutions to industries involved in comminution, including high carbon forged balls for tube mills and Semi Autogenous Grinding (SAG) mills, ceramic beads for ultrafine grinding and Metal Matrix Composites (MMC) for wear parts.

This paper describes the development of wear resistant products in the Magotteaux Group. General wear mechanisms literature is also reviewed and listed in references [1-11].

### Background on Wear Mechanisms

Wear is a complex synergistic mechanism that removes pieces of an equipment part and affects its efficiency [4,5]. One cannot construe wear as an intrinsic characteristic of a material, mainly because wear also depends upon the environment. According to Zum Gahr [1], four different wear mechanisms can be identified, namely: adhesion, abrasion, tribochemical reaction and surface fatigue, Figure 1.

In crushing and grinding activities, we disregard adhesion as irrelevant to the comminution process.

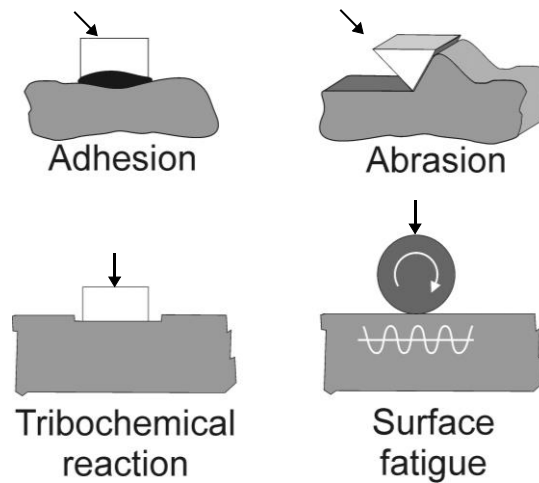


Figure 1. The four wear mechanisms [1]. Arrow refers to applied load.

#### Abrasion

Abrasion is defined as ‘displacement of material caused by the presence of hard particles, between or embedded in one or both of the surfaces in relative motion, or by the presence of hard protuberances on one or both relatively moving surfaces’. Abrasion includes four mechanisms: microploughing, microcutting, microfatigue and microcracking [1], Figure 2.

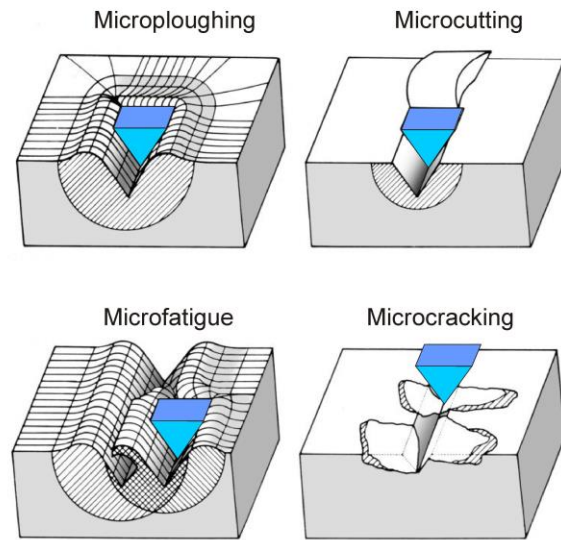


Figure 2. The four abrasion mechanisms [1].

As an example, SEM views of microcutting on a wear part of a crusher are shown in Figures 3 and 4.

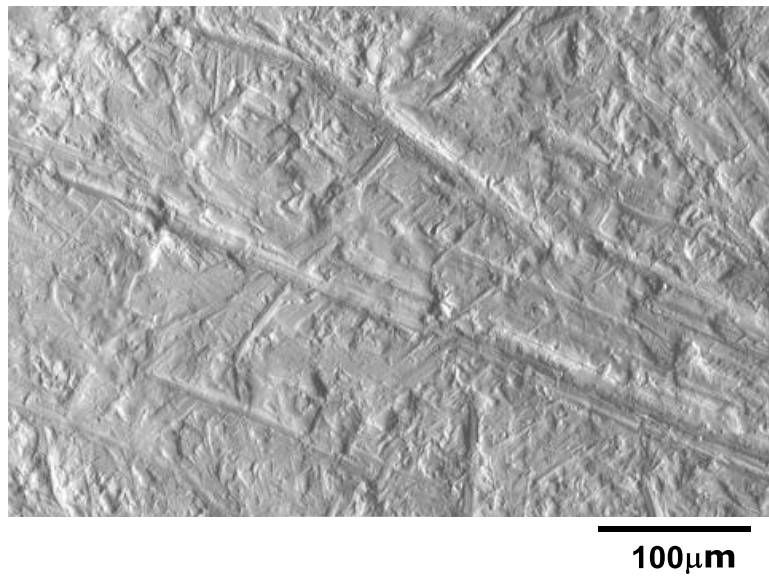


Figure 3. SEM image of microcutting surface (BEI).

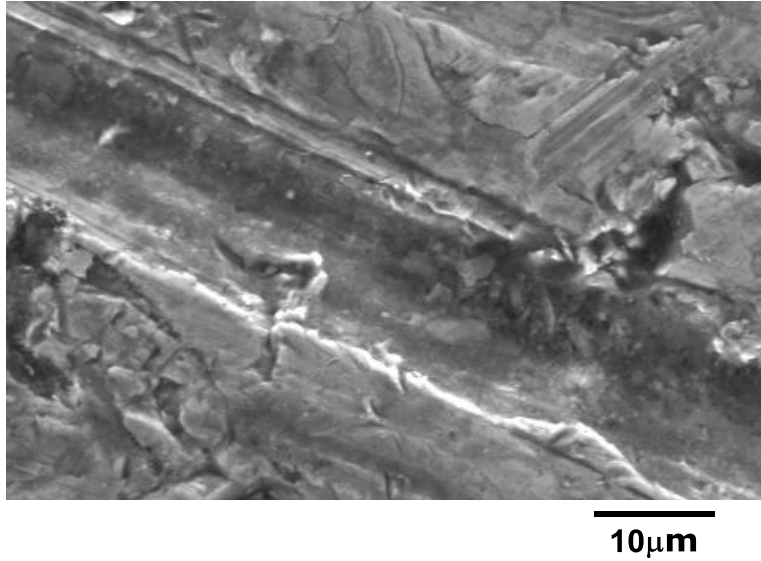


Figure 4. SEM image of microcutting surface (SEI).

### Surface Fatigue

This mechanism is defined by ‘crack formation and flaking of material caused by repeated alternating loading of solid surfaces’ [1]. As an example, SEM views of microfatigue on a first chamber cement grinding ball are shown in Figures 5 and 6.

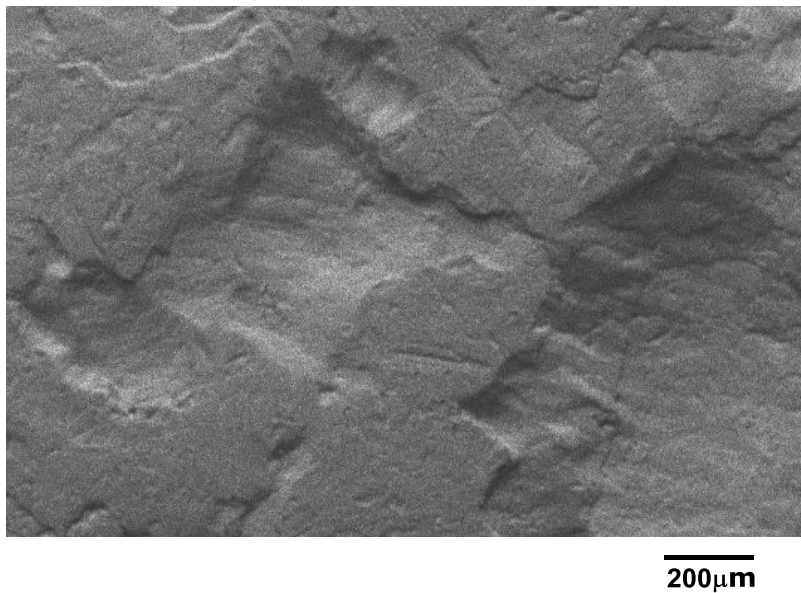


Figure 5. SEM image of microfatigue (BEI).

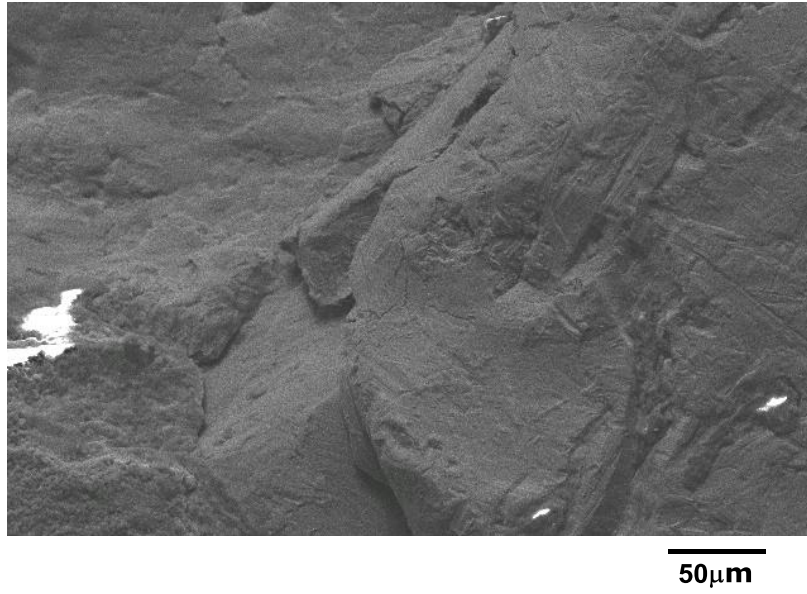


Figure 6. SEM image of microfatigue, detail (BEI).

### Tribochemical Reaction

The tribochemical reaction (tribocorrosion) is defined by the same author [1] as the ‘rubbing contact between two solid surfaces that react with the environment’. The corrosive environment can be gaseous or liquid. The wear process proceeds by continual removal and new formation of reaction layers on the contacting surfaces [1]. As an example, SEM views of tribocorrosion on an iron ore secondary mill grinding ball are shown in Figures 7 and 8.

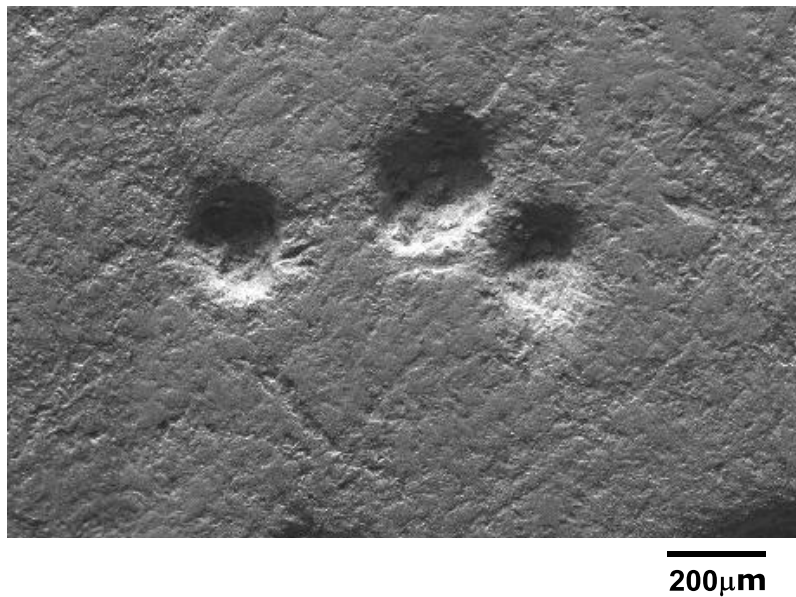


Figure 7. SEM image of tribocorrosion (BEI).

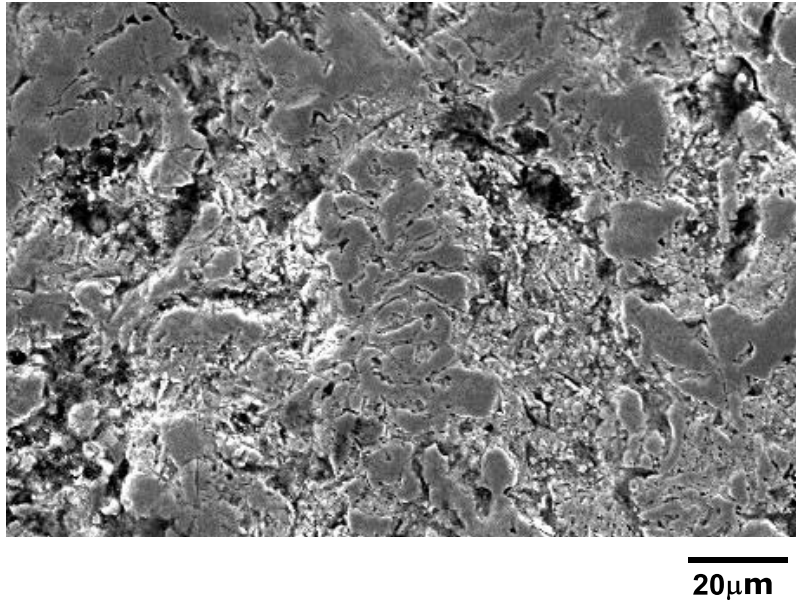


Figure 8. SEM image of tribocorrosion, detail (BEI).

In practice, it is generally difficult to identify just one acting wear mechanism in industrial processes.

### **Methodology for Material Selection**

We employ a very similar scheme for any wear part under development:

- Identify and understand the wear mechanism and mechanical constraints on existing parts;
- Select some potential solutions;
- Test the solutions in the laboratory;
- On site testing;
- Validation and agreement;
- Continuous improvement.

We can easily and directly test some potential solutions in the field for equipment, such as grinding balls or vertical shaft crusher parts which have short lifetimes. For long-lasting parts, modelling and simulation have to be used.

Selection of material with optimal mechanical characteristics will be described here. As parts can be fixed to the equipment, we have to reconcile mechanical (machinability, formability) and wear aspects. Due to the large expansion of the possible range of materials available and thanks to the development of new simulation tools, as well as of new measuring equipment, it is now important to apply a rigorous methodology such as the one described by Ashby [6] to select and design the optimum material based on the customer application. Empiricism is no longer sufficient and we need a methodology to reduce time to market of new products.

The first step consists of the characterization of our current materials.

The second step is to measure or calculate the level of micro-stresses induced in the material during service. These stresses will then be simulated using laboratory equipment. From the analysis of the failure modes it should be possible to make a link between the observed wear mechanism and the material properties and microstructure.

### **White Irons and Steels**

Through the years, many ‘in-house’ compositions for chromium irons and steels have been developed and patented by Magotteaux for balls and internals in tube mills. We revealed that the advantage of these alloys lies in the ability to fine tune the final properties by various heat treatments. The microstructure of the irons usually consists of a natural composite with a variable amount of chromium carbides surrounded by a complex matrix comprising martensite, some residual austenite and secondary chromium carbides, Figures 9 and 10.

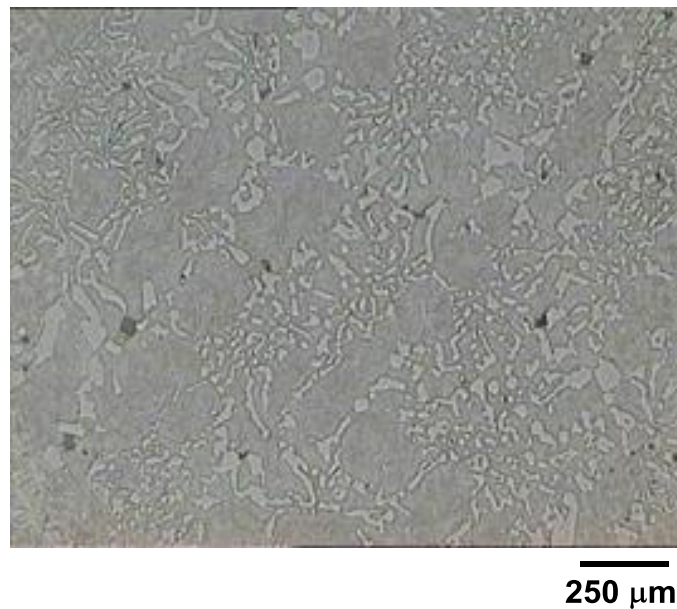


Figure 9. White iron optical micrograph.

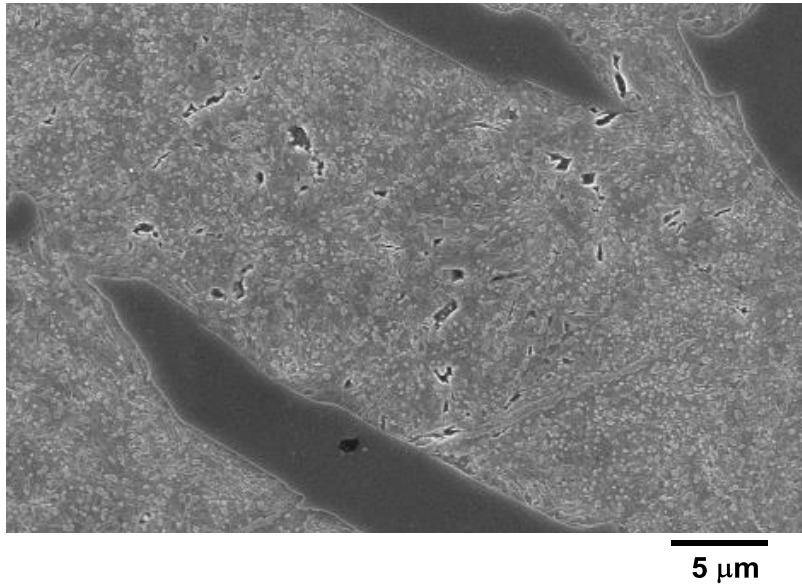


Figure 10. White iron SEM image (SEI).

The microstructure of wear resistant steels usually consists of martensite, some bainite and some residual austenite, Figures 11 and 12.

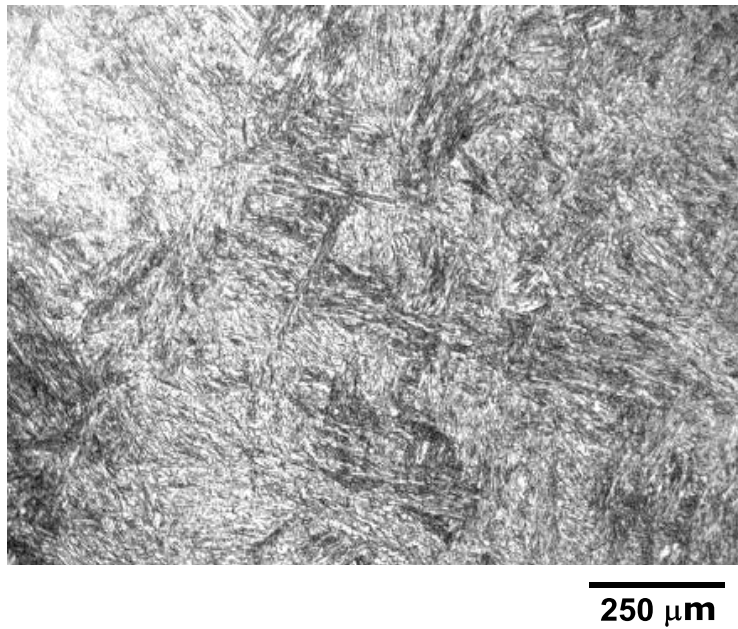


Figure 11. Wear resistant steel showing martensite.



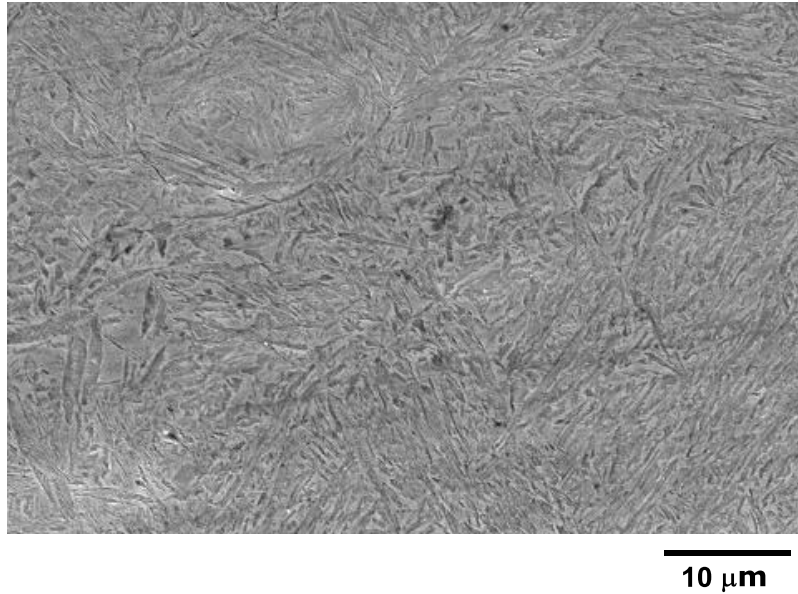


Figure 12. Wear resistant steel showing martensite, SEM image.

### Grinding Media Development

The grinding medium is the historical product of Magotteaux's development for which many alloy compositions and heat treatments were investigated.

Wear mechanism studies are undertaken on used balls. In wet and dry grinding, wear is a result of abrasion; surface fatigue and corrosion being the major players as explained above [2]. It is important to note that the total wear is not a simple summation of each mechanism.

Wet grinding is the most common practice in the mining industry; corrosion is therefore active. The corrosion layer can be protective and does not represent the bulk metal characteristics. The abrasion destroys the existing protecting layer and creates a new corrosion-active surface. The same effect can occur for impact and deformation. Hence, the parameters work in synergy and the total resulting wear can be much higher than that expected from simply combining the individual wear mechanisms.

In comparison, for dry conditions like cement, corrosion is much lower and comes only from the moisture within the raw materials.

Our expertise is based on very long experience and on a very large number of tests made in all grinding environments, from dry cement to any wet ore application. When developing a new application in grinding, the following procedure is used:

- Study of the feed ore and discharge slurry for each mill;
- Discharge-slurry corrosion evaluation;
- Impact level evaluation;
- Marked ball test for fine tuning the properties;

- An industrial test to confirm results on a large time-base.

Feed Ore and Discharge Slurry Characterization. All minerals present are identified and their hardness measured, especially those with a high hardness, Figure 13.

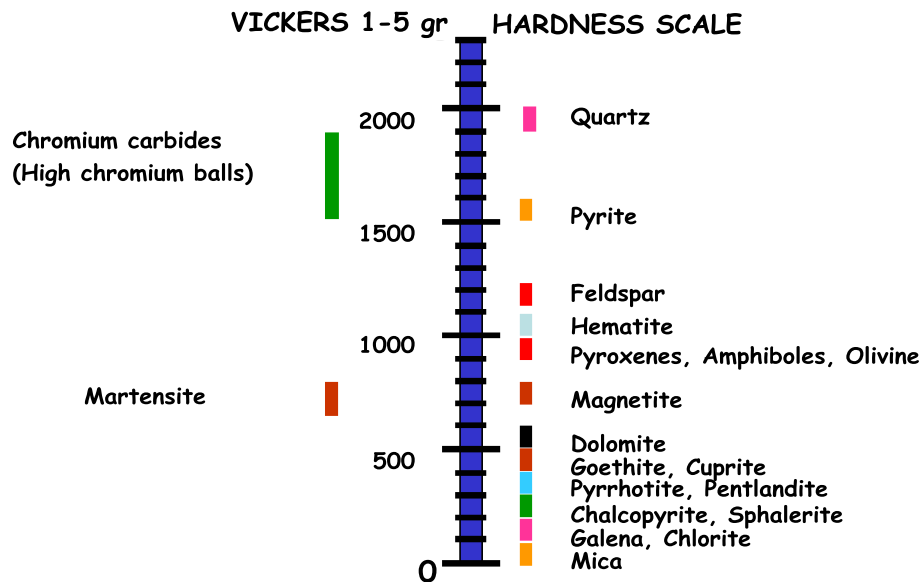


Figure 13. Hardness scale of minerals versus metallic grinding media.

This figure was established by Magotteaux using the Vickers hardness procedure. Those minerals with higher hardness levels will significantly affect the wear rate. Quartz, garnets and feldspar are considered as the most abrasive minerals. Hematite, chromite and pyrite are considered as medium hard minerals.

This study also includes a size and shape evaluation of the abrasive minerals and ore liberation from the gangue.

Discharge Slurry Corrosion Evaluation. Magotteaux has developed a battery of tests to evaluate the corrosiveness of the discharge slurry. It includes a chemical analysis for pH, temperature and ion measurements.

In the case of chromium white irons, Magotteaux are particularly interested in halogens, such as chlorides and fluorides that destroy the corrosive protective layer by pitting.

A comparison of the potentiodynamic response to pitting of the different alloys is performed as in Figure 14, which presents an example for the Duromax grades R, K and G.

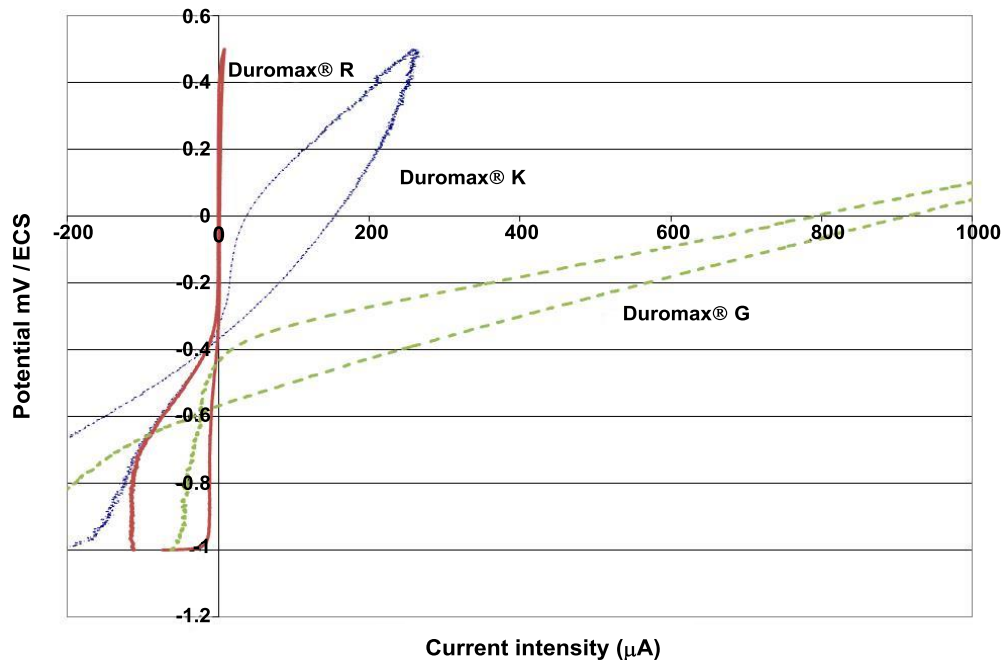


Figure 14. Example potentiodynamic curve comparison of corrosion susceptibility.

In the present example, three different chromium level alloys are compared in the same slurry.

One can see that Duromax®G shows immediate pitting, Duromax®K shows some unstable passivation and Duromax®R shows perfect passivation behavior. This comparison helps evaluation of the ‘safety’ of the proposed solutions. Other ‘in-house’ tests are run to confirm the alloy choice.

Impact Level Evaluation. Impact level assessment is also performed. The parameters controlling this evaluation are geometrical and mechanical rather than chemical. A complete questionnaire is completed, including information on rotation speed, inside diameter, liner and feed end shape. The charge movement is directly fixed by the chosen design. The slurry density is another factor affecting the media motion inside the mill and which Magotteaux controls. Finally, a survey and complete examination of the existing grinding media status completes the picture.

Marked Ball Test Procedure. Magotteaux has decided from the beginning to apply the ‘Norman’ or Marked Ball Test (MBT) procedure to compare the wear of different steels and irons. [7,8,11]. The MBT wear evaluation procedure is a consequence of the difficulty of finding a reliable laboratory test that includes all the parameters existing in a tube mill. Based on ball weights, the millimeters lost on diameter per hundred hours’ wear are calculated for each quality. Absolute comparison between alloys and heat treatment is then possible. Any new result is added to the database and helps to consolidate know-how.

Industrial Test at Medium to Large Scale. On the basis of the MBT results, the optimized alloy and heat treatment can be proposed. Generally, the new alloy is added at regular intervals on to the existing grinding media and not as a complete new charge; therefore, the reduction of wear will not be seen immediately but as a progressive improvement. An 'in house' computer model allows simulation of the wear evolution. Accompanying the supply of new media, regular visits to the mill help assessment of the wear evolution.

Magotteaux's production capabilities enable the supply of forged and cast balls used in mills from fine grinding mills to SAG mills. Ball sizes can vary from 10 mm to 160 mm.

In addition to wear studies, Magotteaux has also developed a multifold approach called Chemillurgy®, including grinding efficiency and slurry chemistry. Nevertheless, this optimization affecting recovery, grade and reagent consumption during ore processing will not be described here [2].

### Tube Mill Internal Development

As the mill internals are linked to the grinding media, the same approach is used, ie.:

- Collection of all the geometrical parameters of the different mills (size, speed, type of discharge, etc.);
- Study of the feed ore and discharge slurry from each mill;
- Comparison to our database.

In addition to the alloy and heat treatment, the design must also be considered. A bad design can increase sliding or ball impacts on the lining and reduce lifetime. Special care has to be taken regarding the maintenance time and the concerns of the customer. As the liner will transmit the energy to the tumbling media charge, a specific approach has to be adopted for obtaining and maintaining the optimum energetic efficiency during the life of the liner. Based on these geometrical parameters, a simulation study is performed to design new internals.

Field tests have been run comparing liner alloys and heat treatment, as has been done for balls, but these are difficult to run.

A large database of confirmed results is used as a help for the designers. Figure 15 shows an example of tube mill internals.

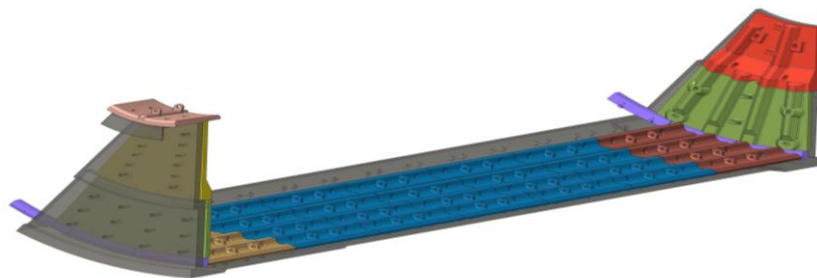


Figure 15. 3D view of tube mill internals. Colors refer to different castings.

## Metal Matrix Composites

During the nineties, Magotteaux started to produce Metal Matrix Composite (MMC) wear parts in the pilot foundry. These parts were tested in some chosen industrial plant. Successful results in some low impact applications encouraged the development of those composites. Two metal matrix composite families have been developed and patented. A similar approach, as already described above, was undertaken for the cast parts of each type of equipment.

The MMC approach allows one to keep the functionality of the casting by reinforcing only those areas which would be subject to wear.

## Oxide Based MMC

Xwin®, neoX® and Recyx® are Metal Matrix Composites based on millimeter-sized oxide particles forming a ceramic core. Different challenges have to be considered to manufacture a successful composite casting.

The Choice of the Ceramic Material. Among all the different tested oxides, the alumina-zirconia system gave the best results. Depending on the zirconia content, the alumina-zirconia system allows one to get a good compromise between toughness and hardness.

Typical mechanical properties of the metal matrix and oxide ceramic grains are given in Table I below.

Table I. Mechanical Properties

<b>Material</b>	<b>HV</b>	<b>K<sub>Ic</sub> (MPa√m)</b>
White iron ( 26%Cr)	800-850	25-30
High alumina	1650	4-6
Low alumina	1350	8-14

Hardness is measured using Vickers indentations.

Toughness is measured using VIF (Vickers Indentation Fracture), Figures 16 and 17.

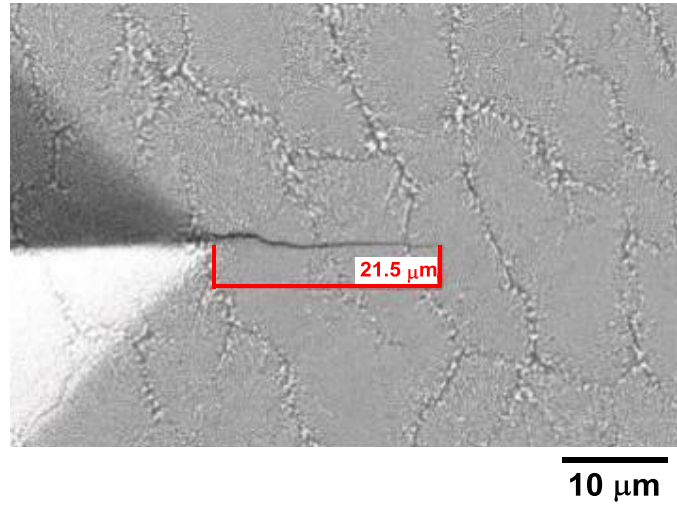


Figure 16. Vickers indentation on MMC with high alumina/zirconia ratio showing a crack from the corner of the indent.

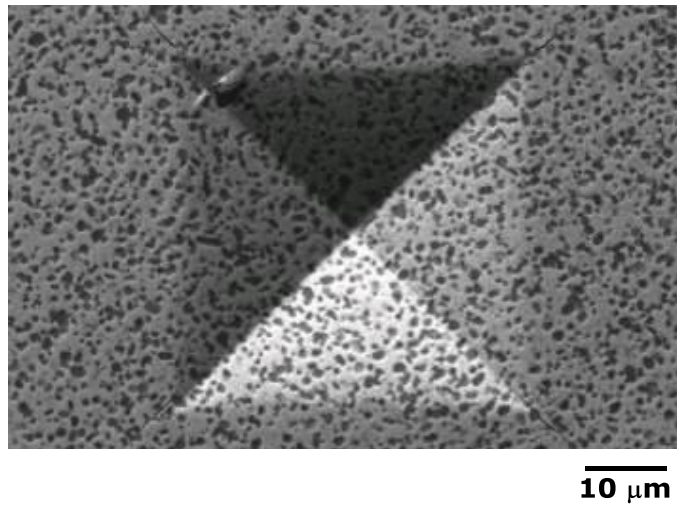


Figure 17. Vickers indentation on MMC with low alumina/zirconia ratio showing no cracking from the corners of the indent.

Values in the table are obtained using the LAWN formula [12]:

$$K_{Ic} = 0.028 \cdot (E/HV)^{0.5} \cdot HV \cdot a^{0.5} \cdot (a/c)^{3/2} \quad (1)$$

$K_{Ic}$ : fracture toughness (MPa.m<sup>1/2</sup>)

HV: Vickers hardness (GPa)

E: elasticity modulus (GPa)

a: half average length of the diagonal of the Vickers marks (microns)

c: average length of the cracks measured from the center of the Vickers marks (microns)

The Size of the Ceramic Grains. A ceramic grain size between 1 to 3 mm is used as a compromise between the manufacturing capability for the casting and wear behavior. Figure 18 shows a 3D view of a worn surface of a composite roller.

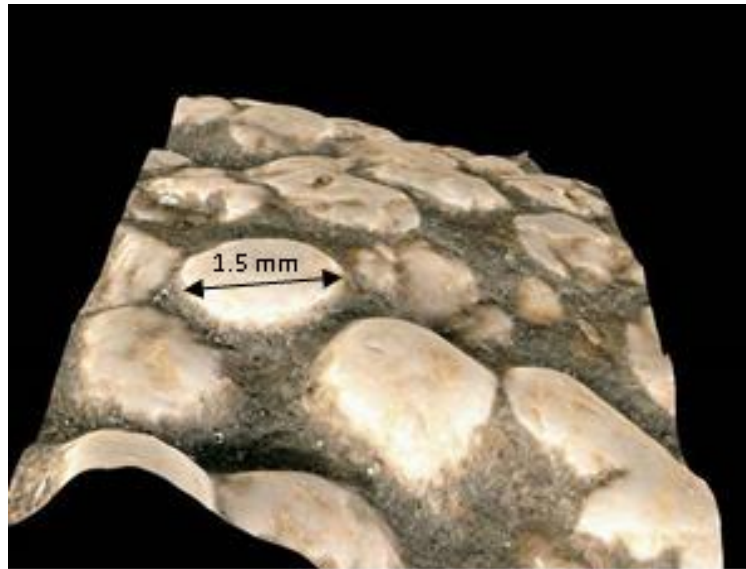


Figure 18. MMC roller detail.

Choice of the Matrix Alloy. As Magotteaux is a steel and iron foundry and manufactures wear resistant castings, the starting point for the matrix chemistry is naturally based on ferrous alloys. White iron or steel is chosen depending on the operating conditions.

Ceramic Core Design. Two main factors drive the design of the porous ceramic core. One is related to manufacturing considerations and the other to wear resistance efficiency.

- Manufacturing considerations.

A good penetration of the ceramic core by the liquid metal, as well as an acceptable stress level in the casting are required. For example, a honeycomb structure is shown in Figure 19.

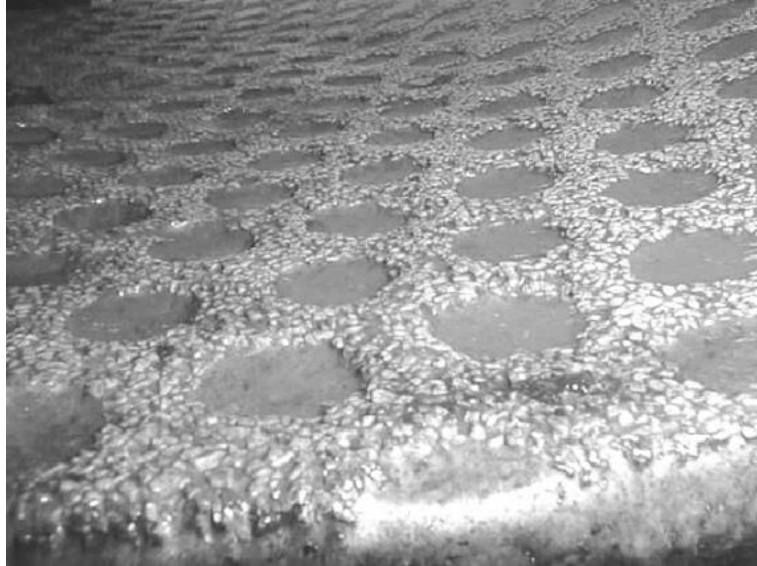


Figure 19. MMC with honeycomb structure.

- Wear resistance efficiency.

The ceramic core is designed based on the observed wear profile of a classical monometallic wear part.

The intrinsic heterogeneity of the composite material properties allows one to get some specific effects on the wear profile and on the customer's process efficiency, if needed. The wear profile during the component's lifetime can be tailored by adjusting the ceramic core design.

Manufacturing Parameters. Different challenges need to be overcome to be able to manufacture castings weighing from a few kilograms to twenty tons. Due to the density difference between metal and ceramic, the concept of the mold has been revised. Even though alumina-zirconia ceramics with a high content of zirconia have a closer thermal expansion coefficient to steel than do the other oxides, there is still a significant difference. In addition to that, both alumina-zirconia and the metallic matrix undergo martensitic transformations with different shrinkage and expansion stages at different temperatures and times. Heat treatments of the castings have been optimised to accommodate these expansion mismatches.

Field Operating Conditions. The wear resistance improvement of the ceramic metal composites can vary over a large range depending on the operating conditions in the different applications (abrasion, impacts). Thus, MMC is not a universal solution but it covers a wide range of applications.

To extend the range of possible application with these materials, Magotteaux has now built its own manufacturing plant to produce ceramic grains. It is now possible to control the final microstructure and properties of the ceramic grains to get the desired composite materials. This composite material based on ceramic oxides is now widely used in crushers for the aggregate and recycling businesses, as well as in vertical roller mills used in power station (coal mills) and cement plants.



A good example can be presented for vertical roller mill wear reduction. Figure 20 shows an industrial vertical mill used in raw milling in the cement industry and coal milling in power stations.



Figure 20. Vertical roller mill.

For the rollers two options are used:

- One option called Duocast® consists of a roller body made in ductile iron to achieve good mechanical properties with white iron inserts, themselves incorporating a ceramic core. The wear resistant inserts are located at the surface of the roller, Figure 21.

Figure 22 shows the wear pattern (1), the white iron insert (2) and ceramic core (3).



Figure 21. Duocast® roller.

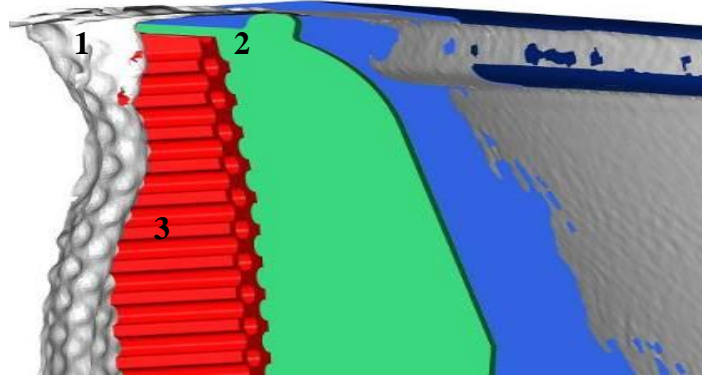


Figure 22. Duocast® roller sketch and wear profile.

- In the second option, the roller is made in white iron with ceramic cores located at the wearing surface. Figure 23 shows MMC rollers and table.

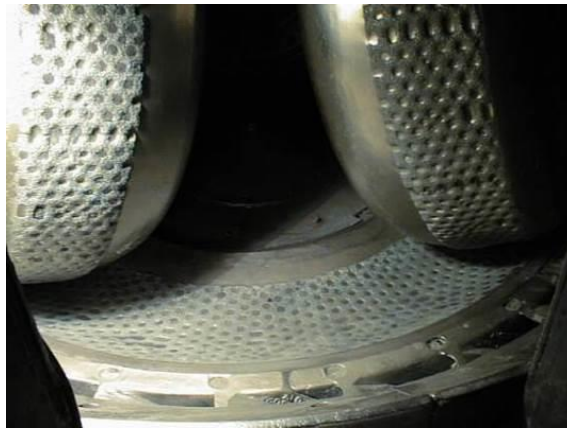


Figure 23. MMC rollers and table.

The wear reduction usually observed in those applications ranges from 1.5 to 5 times the lifetime of white iron rollers.

### **Crushing Mill Wear Reduction**

A vertical shaft impact crusher (VSI) is depicted in Figure 24. Composite impellers and anvils are shown in Figures 25 and 26.

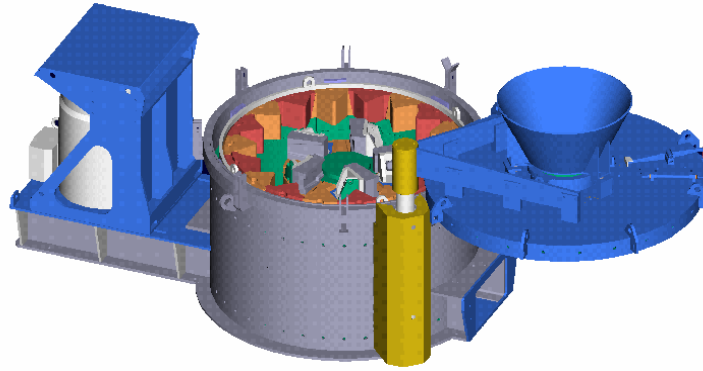


Figure 24. 3D view of VSI crusher.



Figure 25. MMC impeller of VSI crusher.



Figure 26. MMC anvil of VSI crusher.

Another widely used crusher is the horizontal shaft type used in aggregate and recycling applications, Figures 27 and 28.

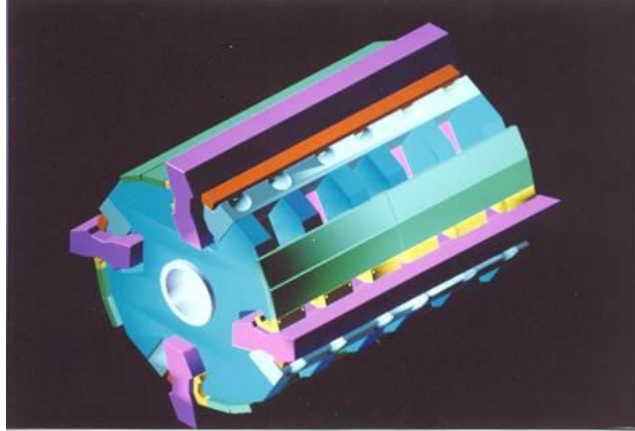


Figure 27. 3D view of a horizontal shaft impact crusher.



Figure 28. MMC blowbar of a horizontal shaft impact crusher.

The total amount of ceramic phase is about 3 to 5% by weight for a total lifetime improvement of about 100%.

#### Carbide Based MMC

Xcc® is another metal matrix composite based on carbide reinforcement. In the oxide based MMC, the reinforcement particles have a size of a few millimeters. In this case, the carbide reinforcement has a rounded shape, with a size of a few microns. One interesting carbide is TiC which has a very high hardness (3000 HV). The carbide reinforcement is surrounded by a ferrous metal matrix, Figure 29.

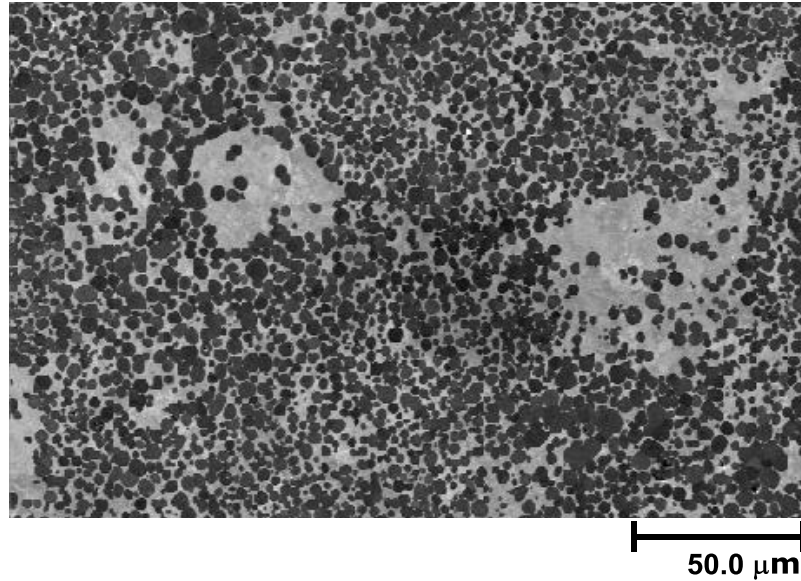


Figure 29. Microstructure of TiC surrounded by the ferrous metal matrix, SEM image.

As for the oxide based MMC, only the wear zone of the casting is reinforced, to maintain the reliability of the casting. The reinforcement could be monolithic, or with a hierarchical structure. In the former case, the wear zone is reinforced with a solid insert, containing about 50% of rounded micron-sized carbides, the remainder being the ferrous metal matrix. In the latter case, the wear zone is reinforced with grains of a few millimeters containing about 50% of rounded micron-sized carbides. The ferrous metal matrix is located between the both the millimeter grains and the micrometric carbides, Figure 30.

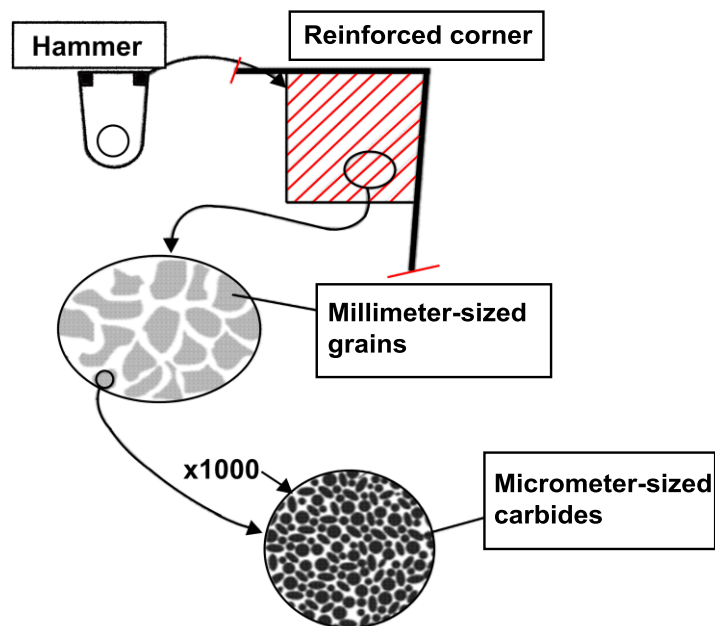


Figure 30. Hierarchical structure of MMC carbide reinforced hammer.

This hierarchical structure combines the wear resistance obtained by the reinforced grains containing around 50% of carbides, and the toughness (due to the ferrous metal which surrounds the grains and the carbides). According to this technique, the volume percentage of carbide reinforcement can vary from around 25% up to 70%.

One of the products developed by Magotteaux using this technology is based on titanium carbide (TiC) reinforcement. The metal matrix could be a martensitic steel or white iron. Typical properties are given in Table II.

Table II. Typical Mechanical Properties of the Metal Matrix and Carbides Grains

<b>Material</b>	<b>HV</b>	<b>K<sub>Ic</sub> (MPa.m<sup>1/2</sup>)</b>
White iron matrix (25% Cr)	800-850	20-30
Martensitic steel (9Cr)	600-700	250-300*
TiC	3000	3.8**
Composite steel/TiC	900-1400	50-60
Composite white iron/TiC	1000-1600	

\*Reference [9]

\*\*Reference [10]

The same challenges exist as for the oxide based composites:

- Choice of the type of carbide reinforcement;
- Monolithic or hierarchical reinforcement, regarding manufacturing and wear;
- Choice of the metallic matrix alloy;
- Ceramic core design;
- Manufacturing parameters;
- Type of application.

Although the challenges are the same for both composites, the ranges used and limits differ.

Some examples of castings using this technology are shown in Figures 31 to 34.



Figure 31. New Xcc® cement hammer.



Figure 32. Xcc® clinker hammer.



Figure 33. Xcc® primary crusher hammer.



Figure 34. Xcc® dredging teeth compared to mono metal.

An increase of the lifetime by a factor of two to four is usually observed in the case of hammers and dredging teeth compared to the classical steel solution.

### Ceramic

About ten years ago Magotteaux started to manufacture Keramax® beads for ultrafine grinding applications, Figure 35. The size of these ceramic beads ranges from about 1 to 5 mm. Fine grinding using stirred mills and ceramic beads is quite new in the mining industry. Such a capability is provided by the IsaMill™, Figure 36.



Figure 35. Ceramic beads used in ultrafine grinding.



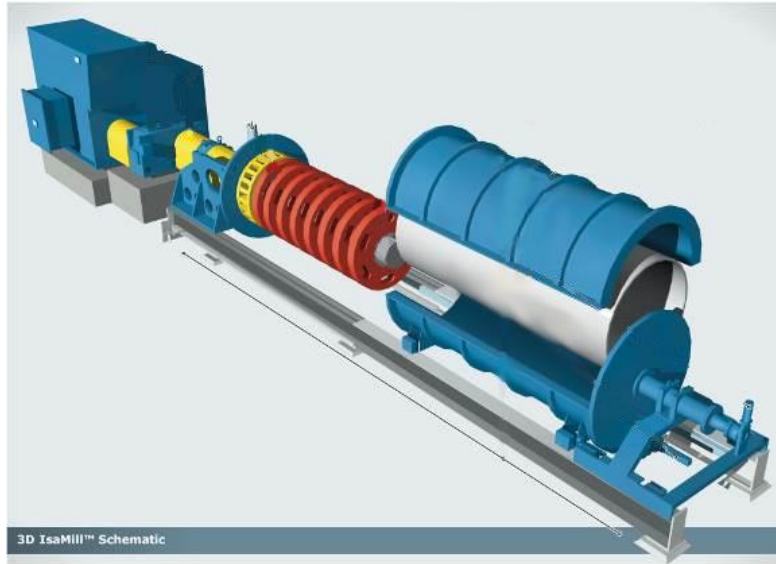


Figure 36. Schematic of an IsaMill™ copyright Xstrata.

Media selection has a major influence on mill parameters such as energy efficiency, internal wear and operating costs.

The wear mechanism of grinding beads is mainly due to a combination of microcutting and surface fatigue processes.

Magotteaux's laboratory is equipped with two IsaMill™ test rigs: LM4 & LM20, Figure 37.



Figure 37. Magotteaux LM20 pilot plant.

These items of equipment are used to evaluate wear and grinding efficiency during fine grinding in conditions close to the industrial ones.

## Conclusions

Based on a large database of marked ball and liner tests, application-specific products were established for tube mills in the cement and mining industries. Chemical composition and heat treatment were selected based on the wear mechanisms involved.

Exploring new markets like aggregate processing, power stations and dredging, for which wear is also an issue, classical materials have proven to be useful but with variable success.

Based on those new challenges Magotteaux R&D developed new materials comprising Metal Matrix Composites (MMCs) and ceramics, which turned out to be a promising response to the new market needs.

An ever increasing and deeper knowledge of the wear mechanisms is now required to develop new materials. This is why Magotteaux now invests in simulation tools, and collaborates with international organizations to make best use of their combined skills.

Whatever are the particular challenges of our customers, these all come down to ensuring maximum cash generation. Our role consists of providing process optimization solutions. Starting with a detailed knowledge of their complete value-chain, we combine expert advice, service, resources, products and equipment, and use all relevant levers to help them make technical specifications meet financial requirements.

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