Role of Ceramics in a
Self-sustaining Environment
R. Pampuch and K. Haberko (Editors)

ELECTROFUSED CERAMICS AND INNOVATION

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To review in a few lines 37 years of my professionnal life and to share with you the main facts both from a technical and an emotional point of view is quite a difficult exercise.

My award being for the Section « Industry and Innovation » I have chosen to talk about Fused Cast Ceramics which the main part of my working life has been devoted to and probably one of the lesser known classes of Ceramics. Concerning Innovation, as everything has already been said by distinguished experts, I'll limit myself to presenting my approach through my own experience and 3 examples of my contribution.

My first contact with refractories was in 1958 when, after my second year in the Engineering School d'Electrochimie et d'Electrométallurgie in Grenoble, I did a summer job with Société Electroréfractaire. At that time, the word « ceramic » had an artistic connotation but from the end of the 19th Century refractories were so vital in the development of high temperature industries like metallurgy, glass, cement or petrochemistry... that they had a certain nobility. Today « refractory » means commodity and often needs to be upgraded as in the name : High Performance Refractories, or better still : Thermal Ceramics. From that time, it is true that ceramic properties other than refractoriness have been developed. Marketing has appeared and you know the importance of words in marketing.

To really make the most of my training period, before I started I tried to acquire some knowledge on Fused Cast Refractories.

I was very disappointed because in the plentiful litterature I read, only 3 lines mentionned the special technology used to manufacture refractories for the glass industry. Fortunately the on the job experience was more rewarding and for two months I discovered the exciting and unfamiliar world of melting and casting oxides.

My unsatisfied curiosity caused me to come back one year later, then, after my engineering degree, to do research into this specific area, in other words a thesis on « Electrolysis of fused chromites and bauxites.

Still working in this field I have the same feeling that a lot of exciting questions remain to be answered.

FUSED CAST REFRACTORIES

History :

After this quick outline of my career, a few words on the history of Fused Cast Refractories.

Electrical melting of oxides has been used since the 19th century to produce bulks which are crushed into grains and used as abrasives or raw materials for refractories manufactured in the classical way (bonded refractories).

Around 1925 Corning Glass Works researchers had the idea of manufacturing refractories directly in their final shape by melting adequate mixtures in an electric furnace then pouring the melt into an adapted mold. The idea seems exciting but not simple even 70 years later, because technologies must be mastered at temperatures above 1750°C and especially for molding and annealing. So, it was only in 1928 that Corning set up his subsidiary Corhart Refractories to manufacture the first fused cast blocks in his Louisville (Kentucky) plant. This invention would revolutionize all glass production.

Incidently I am very happy to emphasize the fact that Corning has made many great innovations in his particular field right up to the present day.

The Company of SAINT-GOBAIN, aware of the importance of this invention for glass production, decided to develop this technique in a joint venture with Corning called Electroréfractaire and started manufacturing as early as 1929 in his Modane plant (Savoie). The plant was bombed during the 2nd World War and Electroréfractaire moved to Le Pontet near Avignon in 1947.

Before 1952, all the process and product specifications came from Corning and chemical analyses and other measurements were carried out in the SAINT-GOBAIN Central Lab. In 1952 a Control Lab was set up in Le Pontet. This led to improvements and finally to a crucial worldwide process and product patent, culminating in todays products.

The Lab became in less than 10 years an R & D Center, and has played a great role in the development of fused cast refractories and in the constant growth of Electrorefractaire called Société Européenne des Produits Réfractaires (S.E.P.R.) since 1974.

I don't think it would be out of place to say that, over the last 10 years, the fact that S.E.P.R. is a world leader in Fused Cast Ceramics has influenced SAINT-GOBAIN's decision to invest in industrial ceramics.

The R & D Le Pontet Center employs today 110 people, 20 of whom are engineers. Our basic skills are concerned with high temperature, oxide melting physico-chemistry and product-process knowledge but our research has led to a greater diversity of applications that is to say mechanical, tribological, electrical and chemical applications where the term « ceramic » is more appropriate.

Today, there are several companies around the world which manufacture fused cast refractories. SAINT-GOBAIN is without a doubt the leader, with its production coming from 5 plants :

Le Pontet (France) : S.E.P.R.
Mezzocorona (Italy) :Refradige
Louisville (U.S.A.) :Corhart
Brisbane (Australia) :SEPR Australia
Beijing (China) :Z.P.E.R.

Before going into more detail on fused casting which was my main research area, a few words about all the ceramics operations that Saint-Gobain built up around SEPR and which constitute today «Branche Céramiques Industrielles». Among the more significant acquisations are :

Corhart : the inventor of fused casting
Ceramiques Stettner - Ceramiques Desmarquet (Spécial Céramics)
TSL (fused silica)
Bicron - Harshaw- Crismatec (Crystals and detectors)
Norton : Abrasives - Special ceramics - Refractories - Performance Plastics
Carborundum : Refractories - Fiber ceramics - Special ceramics.

Today, the Industrial Ceramics Branch of Saint-Gobain consists of 6 Divisions:
- Electrofused Ceramics
- High Performance Refractories
- Advanced Ceramics
- Silicon Carbide
- Specialty Crystals and Process Systems
- Performance Plastics

with 32 Companies employing 11000 people in 87 plants in 19 countries.

The total sales are expected to be around 9.3 Billions Francs for 1996.

Manufacturing : (Fig. 1)

Well, let's come back to the Electrofused Ceramics and first of all the manufacturing process. We have already characterized them globally when we said that it is a foundry of oxides starting by the technical study of the piece to be produced and the definition and preparation of the mix to be melted. But, compared to metal foundry, the difficulties are increased by the higher temperatures and the less favorables thermomechanical properties of the oxides.

Melting is one of the most critical steps done in a three electrodes arc furnace and leading to a homogeneous liquid, without unmelted parts and suitably refined. The oxido-reduction level for example changes porosity, color and more generally behavior in contact with melted glass like corrosion, resistance and defect generation like bubbles, cords and stones.
In this area the contribution of SEPR has been vital and its expertise has been recognized all over the world.

The pouring temperatures vary from 1800°C to 2500°C and the molds are adapted to the liquid with technical and economic considerations (size and number of pieces). 3 types of **molds** are used :
- sand bonded with adequate resins : used just one time
- graphite mold : used several times
- watercooled metal mold :more expensive but usable for big series.

Annealing is specific to the foundry of oxides. It is a slow cooling from 1 to 18 days and monitored to avoid cracks. After pouring it is necessary to homogenize the temperature at the high level of the plastic zone of the ceramic, then the cooling has to be adapted to get a low gradient in the typical fragile and elastic zone, until it reaches room temperature.

FUSED-CAST PROCESS

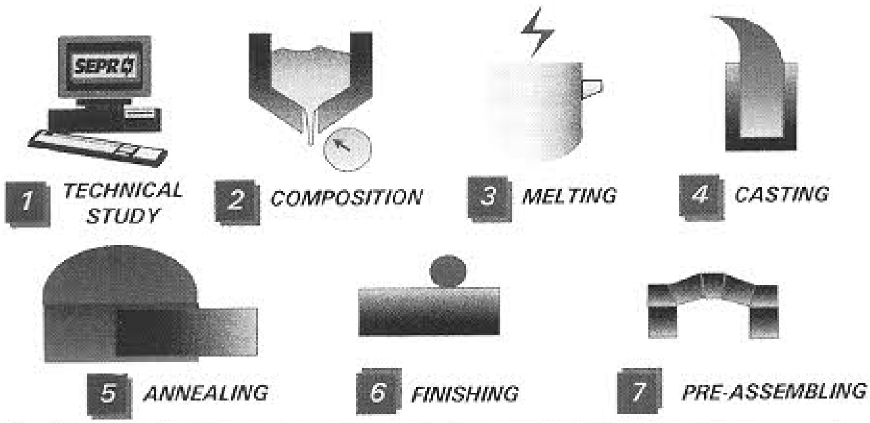

Figure 1

CONTAINER GLASS FURNACE

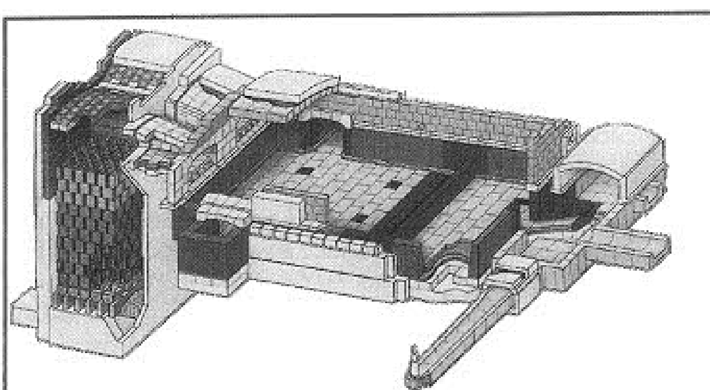

Photo 1

One characteristic of the foundry is the change in density from liquid to solid. For oxides the contraction is around 15% in volume after solidification, leading to voids.

Either we tolerate this and place the void outside the working part of the piece or finely disperse it (closed porosity) in the complete piece or, we remove the void totally or partially by sawing.

Finishing is sometimes a simple cleaning operation but more often includes sawing, machining and polishing with diamond tools.

Preassembly is done in almost all cases to check the mass coherence and then it is submitted to the Customer's approval .

So - here I have described very briefly the main steps of the manufacture of electrofused cast ceramics. Obviously each step is subject to appropriate controls and often needs specific adjustments to improve feasability or to adapt it better to final use.

We are still working on molding, melting, refining, solidification and annealing problems with special sizes and shapes as well as new compositions.

The industrial fused cast ceramics can be classified in 5 families :

- Alumina-Zirconia-Silica (AZS)
- Alumina-Chromium oxide-Silica
- High Alumina (>94%)
- High Zirconia (>94%)
- Magnesia-Chromite

Application fields :

The main field of application is the glass melting furnace **(Photo 1)** where all the advantages of this process can be seen :

- no porosity
- high corrosion resistance
- big blocks
- special shapes

The AZS family is by far the most used but Alumina-Chromic oxide or high zirconia refractories can also be used in some parts of the tank or for special glasses.

The high alumina refractories are generally found in the end part (lower temperatures) of the furnace.

Although conditions in different parts of the furnace vary, fused cast refractories are also used outside the glass contact (superstructures) for the same reasons. In addition, in this field we have developed an extended use of the AZS inside the checkers for glass tank regenerators with our patented Cruciform solution but I'll come to this later.

Fused cast ceramics respond well to thermochemical stresses at high temperature (corrosion) but less to thermomechanical stresses at low temperature (thermal cracks). So they are well adapted to continuous hot processes, in the case of glass furnaces running several years without stopping.

Apart from glass furnaces there are however other typical uses. Some metallurgical applications can be mentionned even though they are less developed than traditional bonded refractories :

- Magnesia-Chromite in steel electric arc furnaces , on copper , nickel and tin refining vessels
- High alumina in the processing of magnesium, aluminium and titanium. As furnace lining in the nuclear industry and bottom paving of reheating steel furnaces.

Besides these main applications where the fused casts are used at high temperature we find some at room temperature. More especially AZS are used for their :

- Hardness
- Low porosity
- Possibilities in different sizes and special shapes.

The antiabrasion applications are the most developed in :

- the steel industry
- coal power plants
- chemical and petrochemical applications
- mining

RESEARCH AND INNOVATION

Besides the list of achievements cited by the nomination committee I would like to emphasize the importance of the innovation process rather than the result itself.

The Innovation process is not a linear one with well defined and linked steps. It is essentially a system of interactions, exchanges between different functions and players whose experience, knowledge and expertise grow, and are mutually beneficial. Several surveys have shown that most innovation ideas come from problems arising from the general running of the business, and only a few from the research lab.

The relationship with users, taking into account demand and market needs anticipation, is at least as important as the mastering of technology.

I am not trying to give general rules, but I am simply describing my long experience in the very specific field of fused cast ceramics and a more recent involvement with the rest of the ceramic industry.

It is true that some people are more creative than others. But, from experience, I am convinced that in a community like a Research Center, creativity comes essentially from how R&D works in practice, how it is organized and how it is managed on a daily basis bearing in mind the long term viewpoint.

For all the above reasons I pay maximum attention to :

- profile of research people when hired
- a stable core of senior staff who reinforce knowhow , knowledge and experience

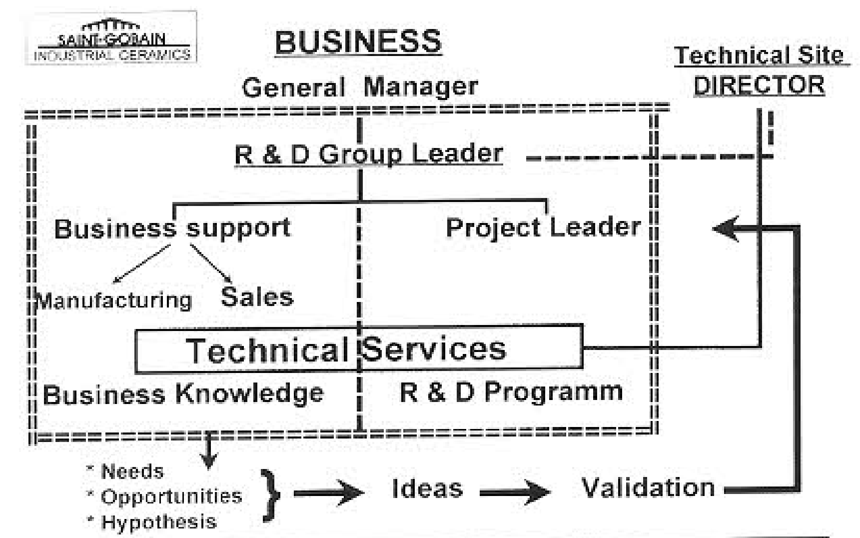

Figure 2

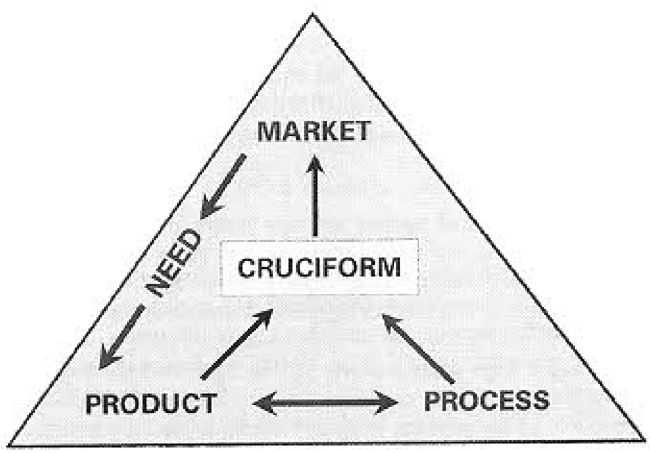

Figure 3

- daily management
- some mobility towards technical functions and marketing
- organisation

As a result our research is fed by a real knowledge of the business. That is to say :
- product knowledge
- process knowledge
- applications (market) knowledge.

More precisely, our organization chart is clearly business focused with each specific activity having its own R & D Group. **(Fig. 2)**

The R & D Group structure is crossed by Technical Services which include several human and material elements with different experts and specialists to solve specific problems who serve as real bridges and synergies between the different research teams within the Research Center.

I should need more time to show you how this approach has resulted in a large number of innovations which extend the range of our existing products but the 3 examples I present now are more radical, one in the field of an existing market, the others opening up new markets.

CRUCIFORMS : (Fig. 3)

A GOOD KNOWLEDGE OF MARKET NEEDS
A PRODUCT - PROCESS FUSED CAST ANSWER

The **Cruciform** solution is a perfect illustration of how such a structure works and how knowledge of the business leads to innovation.

All the big glass tanks heated by fuel or gas are equipped to recover the heat of the fumes. The regenerative system is the most developed **(Photo 2)**. They use big chambers (1 per burner) filled by a packing of refractory bricks and where fumes are alternatively cooled then, combustion air heated.

The thermomechanical and chemical stresses are very severe and although the checkers (the other name of the chambers) do not play a direct role in glass manufacturing they cause problems and often stop the furnace. So obviously the normal life-span of the checkers needed to be improved and designing a better refractory came naturally from this.

The refractories used had a high open porosity (15 to 27%) and therefor poor mechanical resistance lowered by penetration by corrosive products carried by fumes . The advantage was a low price especially as the payback is always questionable for a non productive part of the furnace.

It was obvious that standard fused cast AZS bricks with their high corrosion resistance and no open porosity were good candidates. But the expected manufacturing cost was too high to be accepted if a longer life-span was the only criterion.

The Marketing reaction was clear : « no chance at all ». But our knowledge of the glass

REGENERATORS

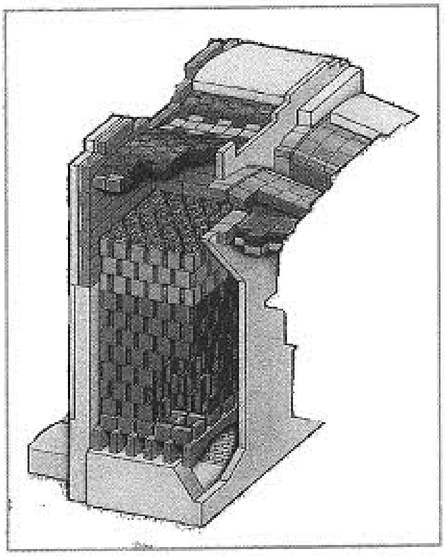

Photo 2

market gave us a greater understanding.

Examining the checkers problems more closely we learnt that they differ considerably depending on the type of glass, the type of furnaces and running conditions. In addition to refractory weaknesses we found clogging problems arising from a large carryover by the fumes, or packing collapse due to a loss of stability.

So to these refractory problems we added a need to improve stability and to maintain better open channels.

Although the thermal function of the checkers was not called into question we looked at how the calories were recovered from the fumes and transferred to the combustion air by the bricks. We found that in the working conditions the optimum thickness of the bricks was between 25 and 30 mm instead of the 75 to 120 mm commonly used, for stability and sometimes corrosion reasons.

As we were learning our innovation process was making headway : roughly the same thermal efficiency and life span could be obtained with 3 times less fused AZS than traditional refractories if we were able to provide the right packing stability.

Based on these conclusions the important final step from an industrial point of view was to try to find a competitive solution which would take advantage of our experience with fused casting.

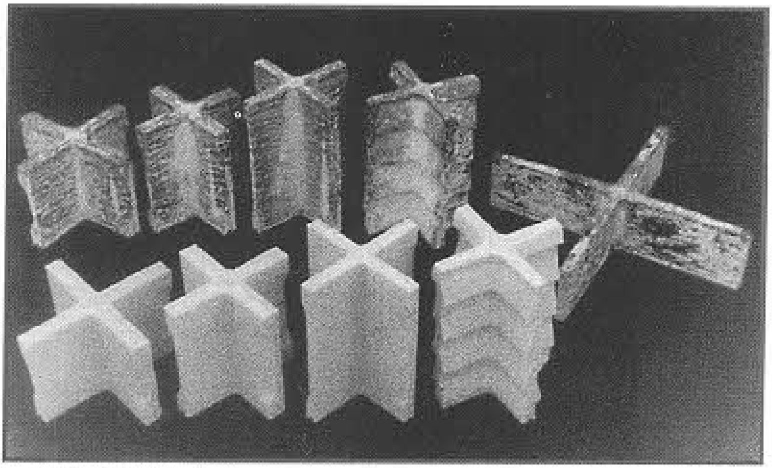

Photo 3

The cruciform concept results from three requirements linked to : the regeneration function, a desire to make the packing more stable and manufacturing cost considerations.
From that point we started dealing with the problems of economic feasability where we had to solve certain problems like :

- Permanent water cooled metal mold (cost and feasability)
- Adjustment of AZS composition and refining (feasability)
- Adapting pouring conditions : several kilogrammes per 20 seconds instead of several tons per hour
- Annealing conditions (feasability and cost)

The first generation of cruciform was an AZS composition 40 mm thick to be safe in the event of corrosion on the first applications. Since that time we have developped a high alumina composition better adapted in many cases, we have reduced the thickness to 30 mm and developed new corrugated shapes increasing dramatically the heat exchange. **(Photo 3)**

Today, the cruciform solution is used in hundreds of furnaces and is the worldwide reference for regenerative packing.

BEADS : (Fig . 4) (Photo 4)

During the seventies we were asked for anti-abrasion linings for a new concept of carbonate micronisers or homogenisers for paints and inks.

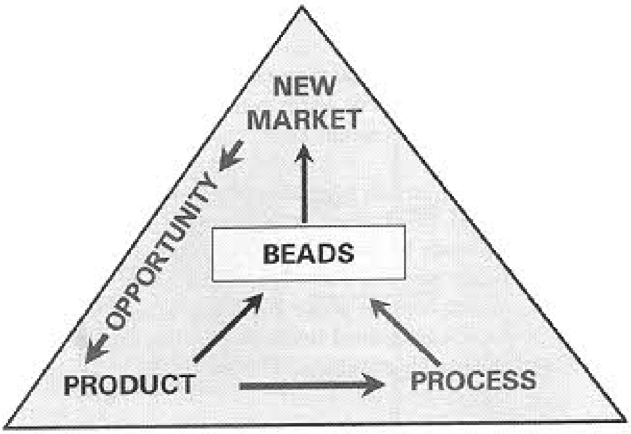

Figure 4

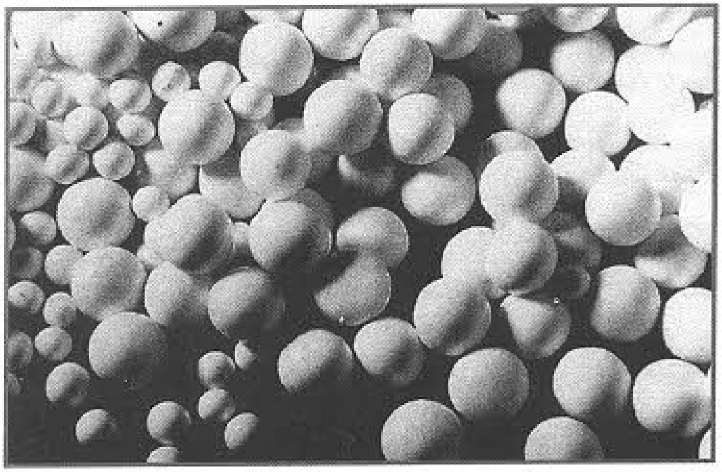

Photo 4

We learnt they use very special sand or 1 to 2mm glass beads as milling media.These milling media were extremely cheap and not a problem in spite of their fragility and insufficient abrasion resistance. But it appeared that the extension of that new technique was limited by the pollution caused by the milling media.

Some ceramic beads prepared by traditional processes were tried out without success because improvement was generally insufficient or prices were prohibitive when performances were good. Again it was obvious that fused ceramic beads could be a tremendous improvement.

The milling media had to be : spherical, high strength, and abrasion and corrosion resistant. Each of these properties could be obtained both from the chemical composition and the process. We decide to make beads by dispersing a suitable liquid in adapted conditions and treating the droplets. Apparently easy but a lot of problems would have to be solved. Melting, pouring, dispersing being at temperatures above 2000°C it is easy to imagine the difficulties. Obviously without all the knowledge gained from our previous experience with fused casting, it would have been almost impossible to solve all the difficulties.

We succeeded with a Zirconia-Silica based composition which rapidly gave full satisfaction - on most mineral micronisation and slip dispersions :

- better efficiency,
- beads consumption divided by ten at least,
- linings less abrased.

All of that at a competitive price.

We learnt from the users themselves that fused ceramic beads enabled these emerging techniques to develop.

From that first success we tried to take advantage of our most recent discoveries on dispersing fused oxides, adapting again both composition and process to make beads for other applications.

Our biggest operations today include cleaning, finishing and mechanical treatment of metallic surfaces by adapted fused ceramic beads. **(Fig. 5).**

Starting by a market opportunity we come to an unique worldwide product through the melting process ending in an unexpected development in micronisation techniques .

ZIRCONIA POWDERS : (Fig. 6)

A PROCESS IDEA that SINGLED US OUT FROM COMPETITORS
A NEW LINE OF BUSINESS FOR US

The first idea came from the technology we used on fused cast AZS. It enables **Zirconia powder** to be manufactured through a completely new and simple process and results in a dramatic cost down (2 to 3 times less).

This was also in the seventies and at that time the market for zirconia was very low, the price relatively high and limited to a lot of little niches with no development forecast. This was the conclusion of a Marketing survey by a Team of Consultants. The merit of our researchers was

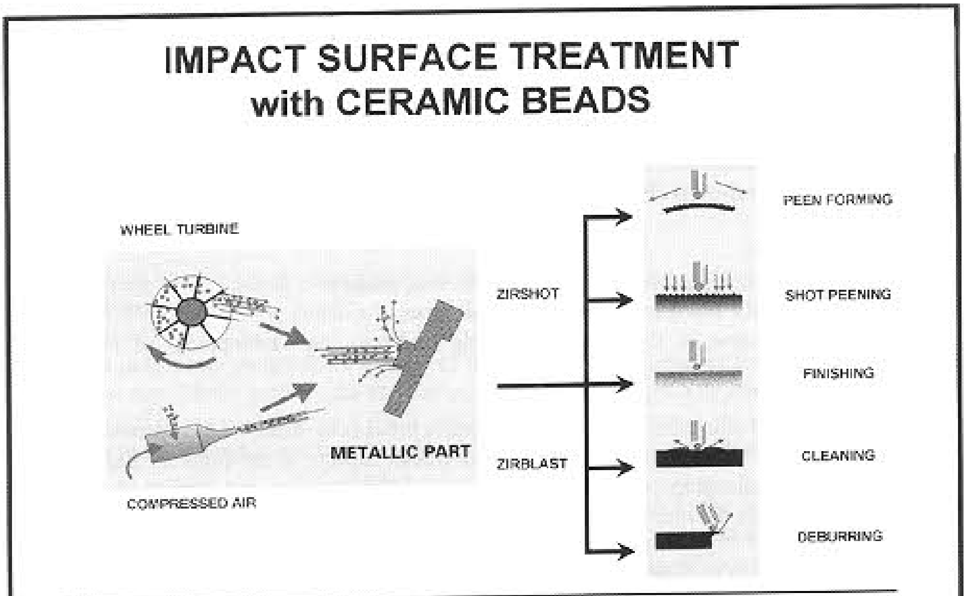

Figure 5

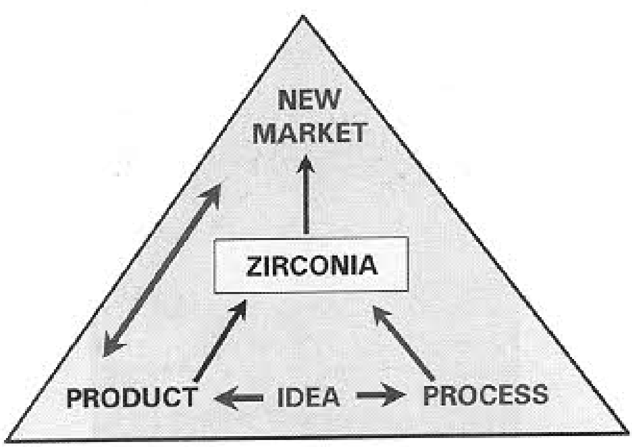

Figure 6

that they tried to understand why a material with such interesting properties was not developed more extensively and what the brakes were.

We carried out an extensive survey on the processes used at that time to find out where the qualities of zirconia came from and the main applications. First, all the available samples were characterized. Then this was complemented by contacts and exchanges between our researchers and the end-users.

Our conclusions were :

- Compared to the existing one, our process idea was, without a doubt, more simple and should be less costly but it could not produce all types of zirconia.
- The price of zirconia at that time was a big brake to the development of existing applications and potentially new one.

Because we strongly believed in our potential to reduce the cost by half or more we decided to go forward into a new area of business. But, two crucial aspects of the problem had to be considered : the relationship between the product and the process, and finding the right potential market within the limitations we have already mentionned.

We managed to find the answers by constantly getting feed-back from the end-users, from the first grams prepared in the lab, right through to the more significant later sampling. Having got these results, we finally decided to go ahead with the process which meant producing the quality suitable for the emerging market of colour ceramics. This market had not been spotted by the marketing consultants I previously mentionned.

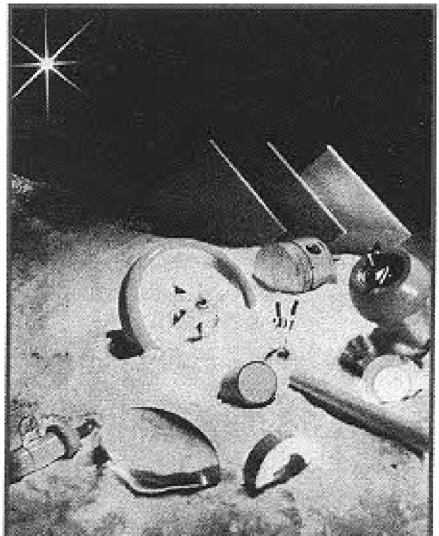

Photo 5

We had to learn a lot about this new area of business. It took a long time, needing much effort and perseverance but what an exciting challenge it was for the people involved.

Twenty years later we can say our confidence in the material is justified. The little niches we found have been developed but more interestingly the lower prices have opened completely new markets like color ceramics for enamels **(Photo 5).** Learning more and working around the original process we produce to-day all types of zirconias for special ceramics and other zirconium compounds.

I hope you know more now about fused cast ceramics, their history, their technology and how they have evolved.

You have judged my contribution worthy of the Academy of Ceramics Prize and I am very grateful for that. I hope you feel the same after my lecture and especially after the presentation of 3 examples of my contribution. I don't need to tell you that I wasn't alone in my research. I have been lucky enough to manage a wonderfull team who also deserve your full recognition.

But all that is in the past, and as a Research Manager I have to look to the future. I don't know what the future of ceramics will be and especially that of fused cast ceramics but from experience I know that the safest way to plan for the future is to constantly prepare and maintain favourable ground for creativity, nourished by a deeper knowledge of the business.