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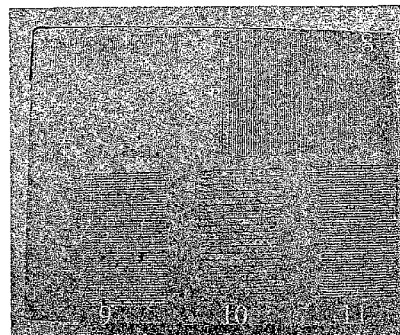
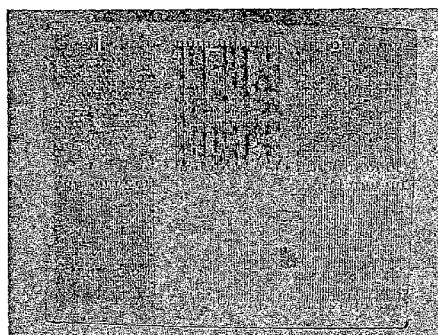
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(54) Title: REFRACTORY METALLIC OXIDE CERAMIC PART HAVING PLATINUM GROUP METAL OR PLATINUM GROUP METAL ALLOY COATING



Showing the patterns drilled in Fusion Cast ceramic using an Electron Beam Gun

MONTRANT LES MOTIFS CRÉÉS DANS UNE CÉRAMIQUE COULÉE PAR FUSION AU MOYEN D'UN PISTOLET À ÉLECTRONS

(57) Abstract: Part of the surface of a metallic-oxide refractory ceramic part, such as a fusion-cast refractory block, is treated using a high energy beam, to remove portions of the surface. A metal film may then be sprayed onto the treated surface of the ceramic part, for example to provide protection against erosion/corrosion in glass furnaces. Excellent adhesion between metal and ceramic can be attained.

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REFRACTORY METALLIC OXIDE CERAMIC PART HAVING PLATINUM GROUP METAL OR PLATINUM GROUP METAL ALLOY COATING

The present invention concerns improvements in coated materials, and more especially concerns platinum group metal-coated ceramics.

Slip-cast and sintered ceramic refractories are used extensively as parts for the handling of aggressive materials such as molten glass. Such sintered ceramic refractories are generally manufactured by forming a dense slurry of the refractory oxide, optionally in the presence of inorganic binding agents, casting the slurry in a mould and sintering the resulting cast item. Such refractories are considered to be of low density, and generally exhibit up to 15-20% of interconnecting porosity. Chemically, such refractories are mixtures of two or more of silica, alumina and zirconia, although other oxide components such as magnesia may be present, plus additives and impurities that may promote sintering etc.

We have shown that such refractories may be given additional protection by coating with platinum using a thermal spraying method (see EP 0 559 330). This technology has met with considerable commercial success. However, there exists another class of refractory materials known as engineering or high density refractories, which includes those made from fine grained ceramic powders made by ramming and iso-static and hydro-static pressing, and fusion-cast refractories. These possess very different physical and physico-chemical properties from the low density slipcast and sintered refractories described above, despite the fact that in chemical composition they may be very closely related. These refractories are characterised by their very high density and possession of at most 3% porosity at low levels of interconnectivity, and exhibition of a hard, smooth external surface.

In the specific case of fusion-cast refractories, the chemical constituents are generally fused by electric arc melting using graphite electrodes, and cast into moulds or flowed onto enclosed surfaces. The fusion-cast refractories find widespread use as furnace lining blocks and channel blocks and in furnace and reaction vessel linings (sometimes called "glass-lined vessels") and generally exhibit improved resistance to corrosion or erosion compared to low density refractories. The same is also true for the less commonly used pressed, engineering refractories mentioned above.

Although fusion-cast refractories and the pressed engineering refractories exhibit high performance in use, under extreme conditions they are still prone to attack and ultimate destruction. For example, in glass-melting furnaces, even these high performance refractories are subject to attack at or below the line of molten glass. The lifetime of such components is determined by temperature, glass-type and the amount of glass processed. Damage to these refractories, because of their use in strategic locations, can lead to the need for partial or even complete shut-down of the furnace and loss of production.

As a result of the smooth, low porosity surface of fusion-cast and pressed refractories, it has generally been found to be very difficult to satisfactorily coat such materials with protective materials such as the noble metals. Methods of keying the surface of low density refractories, such as grit blasting, machining, de-greasing using solvents or etching using mineral acids, are ineffective in providing a suitable surface for bonding noble metal coatings to fusion-cast refractories. The deposition of a plasma-sprayed intermediate layer of ceramic oxide has been suggested as necessary in the coating of hard, high density refractories, prior to plasma flame spraying with platinum, in US 4,159,353. The reason for utilising such an intermediate oxide layer is that neither grit blasting or chemical etching such hard dense refractories has sufficiently roughened the surface to allow an adherent mechanical bonding of the platinum to the refractory. Another characteristic peculiar to the fusion cast refractories, which makes adhesion of any protective coating problematical is their tendency to exude a glassy phase during exposure to high temperatures. To our knowledge, there has never been any successful, commercial, method of platinum coating fusion-cast refractory parts directly, with or without an intermediate oxide coating. The same is also true for the high density iso-statically and hydro-statically pressed engineering refractories.

There has been a demand for many years, therefore, for platinum-coated fusion-cast and engineering refractory parts, which has been impossible to satisfy with known technologies. The Applicants also failed, in their own initial tests, to achieve consistent and adequate adhesion of a flame-sprayed platinum coating.

The surface texturing of some materials such as steel, ceramics such as quartz and alumina, glasses, polymers and composites using a power beam has been disclosed in WO 02/094497. That document suggests adhering another member to a treated workpiece, but

does not consider the application of metal films. Surface texturing prior to applying a coating is also taught in USP 5,435,889, where the substrate is a composite which is termed a "ceramic composite". This document is clearly directed primarily at carbon-carbon composites as the "ceramic". The coating is designed to protect the carbon-carbon composite from oxidation, and accordingly coating thicknesses of 10-50 microns are recommended. The application of coatings to metallic-oxide-based ceramics is neither described nor contemplated.

The present invention is believed to be applicable not just to fusion-cast and engineering ceramics for the glass industry, but to supported or unsupported ceramics and glasses which exhibit the same characteristics of at least a dense, low-porosity surface to which sprayed metals or similarly deposited metal films, show poor adhesion. All such materials are to be considered as metallic-oxide ceramic refractories within the scope of the present invention.

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The present invention provides a refractory metallic-oxide ceramic part suitable for use in the processing of molten glass, said part possessing at least one surface area having a surface drilled to develop an array of slots or closed-end holes, and in which at least a portion of such treated surface carries a platinum group metal or platinum group metal alloy coating pegged thereto by the mechanical interaction between metal pegs formed as part of said coating and positioned within said slots or holes and the ceramic walls and bases of said slots or holes.

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Initial treatment tests have been carried out using a commercial electron beam (EB) gun and vacuum chamber, which was able to produce a wide range of surface profiles and patterns. The specific conditions used for creating the various surfaces were controllable and reproducible but are believed to be equipment-specific and would need to be defined for each unit initially by trial and error by reference to the profiles developed. Although the profiles created using the EB gun were found to be very suitable for platinum coating, the problems anticipated with handling very large ceramic blocks, of up to and in excess of 1 Tonne weight, into and out of the vacuum chamber required an additional solution. Subsequent tests indicate that a suitable industrial laser can have substantially the same effect, is operational in a normal air atmosphere, and by using a fibre-optic delivery system attached to a multi-axis positioning system, the laser profiling can be achieved on both

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planar and non-planar surfaces. In either case a pattern of cut blind holes or indentations or slots can be achieved on a macroscopic scale, which is effective to give a keyed surface to which flame-sprayed metal adheres surprisingly well. It is not necessary for any of the blind holes, indentation or slots to have a re-entrant shape. It is not believed that the profile pattern is significant in achieving the remarkable results of the present invention, and it is
5 thought that almost any regular, irregular or even random profile is effective.

Desirably, the holes have a depth to diameter ratio of greater than one, preferably from 3 to 6, and slots have a width to diameter ration of greater than one. Holes desirably
10 have a diameter at the surface of the ceramic of 200 to 500 microns. Slots desirably have a length to depth ratio of less than three; slots preferably have a width of 200 to 500 microns at the surface of the ceramic.

Slots need not be simple slots but may incorporate one or more changes in
15 direction, and may intersect.

The spacing of holes or slots in an array may be determined according to the particular ceramic by routine experiment, but this is suitably less than 20 times the hole diameter. A preferred linear spacing is approximately 1 mm.
20

Physical observations of treated ceramic surfaces indicate that some material is moved during the process. Depending on the conditions of the process, material may be completely or partially ejected from regions of greatest beam impingement. This moved material can be lost to the surface under treatment or may reform in an adjacent region.
25 Experience shows that such ejected material can have a structure suitable for good bonding to the flame sprayed coating, but may also be too smooth, with this being controlled by composition and conditions during ejection. Where deposits are smooth it may be desirable to remove them by grit blasting before metal coating is carried out.

30 The invention also provides a method of metal coating a metallic-oxide refractory ceramic part, comprising treating at least one surface area of said part using a high energy beam to remove a portion of surface area, to form a plurality of slots or closed-end holes which form an effective bonding surface, and subsequently depositing a coating of a platinum group metal or alloy thereof, onto the bonding surface to provide mechanical

interaction between metal pegs formed as part of said coating and positioned within said slots or holes and the ceramic walls and bases of said slots or holes. One surprising aspect of the experimental work has been the discovery that the flame or plasma sprayed metal penetrates deeply into the patterns cut by the energy beam and fills them without developing local through coating porosity. During the original development of platinum group metal coating of ceramics it was identified that porosity and holes in the surface of ceramics were extremely difficult to close during coating, and pre- and post coating methods were developed to avoid this being a problem in service. However, this is not this case for these engineered "holes" and they develop "posts" or pegs of sprayed metal material which are believed to then provide the additional bond strength to allow useful, adherent coatings to be achieved.

The metals useful in the present invention are one or more of the platinum group metals, namely platinum, rhodium, palladium, ruthenium, iridium and osmium, and alloys with each other or with base metals. Preferably, the metal is platinum, an alloy of platinum, eg Pt5%Au, Pt10%Ir, Pt10%Rh, Pt5%Ru, or Pt with up to 1%Zr, or grain stabilised Pt or Pd.

For ease of description, however, this description will frequently use only the term "platinum" or "platinum-coated".

The refractory part may be of any of the conventional fusion-cast refractory or pressure formed engineering refractory compositions, incorporating one or more of SiO₂, Al₂O₃, ZrO₂ and MgO₂, optionally including amounts of other refractory oxides such Cr₂O₃. Preferred fusion-cast refractories are those known as AZS refractories (AZS = alumina/zirconia/silica). Such high density engineering refractories are not defined by nomenclature but by suitability for the most arduous glass furnace applications. Other similar refractory parts, such as fusion-cast chromias, may be platinum-coated using the present invention.

In the casting process, zirconia has the highest melting point of the regular components of an AZS refractory, and tends to crystallise preferentially at the surface of the mould. This can result in the surface of the fusion-cast part not being representative of the bulk material, and can be less amenable to treatment. It may be desirable in such cases that

the surface of the part is machined to expose bulk AZS material; in manufacturing certain parts this was done conventionally as part of the manufacturing process.

5 In a modification of the present invention, one or more intermediate metal oxide and/or metal layers may be applied, using conventional methods or methods known *per se*.

10 The platinum group metal may be deposited on the surface of the refractory part in a number of different ways. A preferred method is by combustion flame spraying in a method analogous to that described in EP 0 559 330. Other methods include plasma flame spraying, and high velocity oxy-fuel combustion spraying. Further methods may be developed without departing from the scope of the present invention, and, for certain uses, sputtering or CVD may be appropriate.

15 The metal coating desirably has a thickness of 50 microns up to 2mm (the thickness is probably limited only by the economics). More desirably, the thickness is 50 to 500 microns, suitably about 200 microns.

20 It should be realised that although excellent results may be achieved according to the invention by treating and coating essentially all exposed surfaces of the fusion-cast or iso-statically/hydrostatically pressed engineered ceramic, for many uses it may be sufficient and economical to treat and coat only a proportion of the surface. For example, in glass-melting furnaces, or other furnaces exposed to similarly aggressive conditions, erosion takes place in a relatively small area at the normal line of molten glass. For such furnaces or vessels, the invention permits coating those regions most at risk.

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Early indications are that platinum-coated fusion cast refractory and high density engineered refractory ceramic parts according to the invention are corrosion resistant at temperatures of up to 1600-1650° C. This can increase the processing options and materials available to furnace users.

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Whilst the initial use of the invention is in the protection of ceramic parts used in a furnace, it is also contemplated that the platinum group metal film may be connected to a source of electricity in a manner that permits resistance heating of the film. This can permit

good temperature control of furnace contents and may reduce viscosity of furnace contents such as molten glass, in appropriate parts of the furnace.

In a further modification of the present invention it has been found that high energy beam treatment or “drilling” of sintered metallic oxide refractories can provide surfaces for very high strength bonds with platinum group metal and alloy coatings. Although such refractory materials are usually easy to prepare for coating, and perfectly satisfactory coatings are usually achieved, there are some specific circumstances where this adhesion is insufficient. The particular circumstance arises when hot-sprayed coatings are required on some internal curved surfaces. This type of component is geometrically challenging, as the stresses that develop in the coating during deposition, may resolve to create a tensile load across the ceramic/coating interface. Without extreme measures these stresses can be sufficient to cause delamination of the coating, to a degree which would promote failure in service. Although methodologies have been developed to overcome this geometric effect, these are costly to apply, and uncertainty always exists. It has been found that the drilled sintered refractories can be readily coated with platinum and platinum group metals, and that the infill of the drilled slots and holes creates posts or pegs which promote bond strengths greater than the mechanical strength of many sintered refractories themselves. Utilisation of this new preparation method can therefore provide an improved basis for coating in these geometrically challenging configurations. An example of such a coating is shown in Example 7.

It will be readily understood that the skilled person may apply the present invention by modifying one or more of the specified details whilst still gaining the benefit of the invention.

The invention will now be described by way of Example.

EXAMPLE 1

Electron Beam Sculpted Fusion Cast AZS Ceramic; ER 1711

Patterns 1 to 11 were prepared using the EB gun inside a vacuum chamber on a single block of fusion cast ceramic ER1711. The specific conditions of the processing were recorded and

defined, but since these are specific to the particular EB gun and equipment, these conditions are not defined here. In practice the conditions required to define any selected pattern would need to be defined for the specific EB unit. The different patterns of this example are generically defined in Table I.

5

Patch	Pattern
1	Short lines, basket weave
2	Short lines, basket weave
3	Short lines, basket weave
4	Lines unbroken?
5	Lines unbroken?
6	Short lines, basket weave
7	Faint lines
8	Square grid of holes
9	Square grid of holes
10	Rows of holes
11	Square grid of holes

10 The level of ceramic movement from the zones of highest beam energy was considered extreme for some pattern types, specifically the weave and slot patterns. As a result in this experiment the decision was made to grit blast the as treated surfaces. The images shown in Figure 1 are of the surfaces after the grit blasting.

15 The grit blasted surfaces were coated with platinum by flame spraying, using the same operating conditions as would be normal for coating sintered refractories. The results of this can be seen in Figure 2.

20 The coatability was excellent with the pattern being less important than having disrupted the surface very significantly to create holes or slots. The additional benefit of the strong bond between coating and "pattern" was a carry over to the untreated areas of ceramic between the treated patches, where it appears that the bonding generated by the treatment has reduced interfacial stresses sufficiently to allow these regions also to be satisfactorily bonded.

25

EXAMPLE 2

Electron Beam Sculpted Fusion Cast AZS Ceramic; ER 1711

5

EB Preparation	Coating Thickness Achieved	Metal / Alloy	Coating Adhesion
Pattern 8 of Example 1	800 microns	Platinum	Well bonded
Pattern 9 of Example 1	800 microns	Platinum	Excellent
Pattern 11 of Example 1	800 microns	Platinum	Excellent

EXAMPLE 3

10 Electron Beam Sculpted Fusion Cast AZS Ceramic; Fused Zirconia

EB Preparation	Coating Thickness Achieved	Metal / Alloy	Coating Adhesion
Slots	400 microns	Platinum	Well bonded
Ditto	400 microns	10%Rh-Pt	Excellent

EXAMPLE 4

15

Laser Sculpted Fusion Cast AZS Ceramic; ER 1681

Preparation	Coating Thickness Achieved	Metal / Alloy	Coating Adhesion
Pattern 4 of Example 1	800 microns	Platinum	Well bonded
Pattern 5 of Example 1	800 microns	Platinum	Excellent

EXAMPLE 5

Fibre Optic Delivered Laser Sculpted Fusion Cast AZS Ceramic; ER 1711

Preparation	Coating Thickness Achieved	Metal / Alloy	Coating Adhesion
Slots	300 microns	Platinum	Excellent
Ditto	300 microns	Platinum	Excellent

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EXAMPLE 6 (Comparative)

Fusion Cast AZS Ceramic;

Preparation	Coating Thickness Achieved	Metal / Alloy	Coating Adhesion
None	50 to 100 microns	Platinum	Very poorly and weakly bonded
Grit blasted	ditto	Platinum	Poor bond
Grit Blasted + Ceramic Interlayer	400 microns	Platinum	Edge Lifting
Grit Blasted + Ceramic Interlayer	400 microns	Platinum	OK

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EXAMPLE 7

Slip Cast & Sintered Refractory; ZK20S

Preparation	Coating Thickness Achieved	Metal / Alloy	Coating Adhesion
Laser Treated; Pattern 1 – drilled holes	800 microns	Platinum	Superb

After the coating had been evaluated, it was removed by mechanical stripping, to assess the bond strength. Figure 3a & b that shows the as coated ceramic and the underside of the coating after stripping. It can clearly be seen that the interface between the coating and the ceramic has been maintained, but the ceramic has failed deep within itself. Clearly this level
5 of adhesion is extraordinary and lends itself to application of coatings for problem geometries.

CLAIMS

1. A refractory metallic-oxide ceramic part suitable for use in the processing of molten glass, said part possessing at least one surface area having a surface drilled to develop an array of slots or closed-end holes, and in which at least a portion of such treated surface carries a platinum group metal or platinum group metal alloy coating pegged thereto by the mechanical interaction between metal pegs formed as part of said coating and positioned within said slots or holes and the ceramic walls and bases of said slots or holes.
2. A ceramic part according to claim 1, wherein the refractory ceramic is a fusion-cast or engineering refractory.
3. A ceramic part according to claim 2, wherein the refractory ceramic is an iso-statically or hydro-statically pressed, and sintered refractory.
4. A ceramic part according to claim 1, 2 or 3, in which the ceramic is composed of one or more of silica, alumina, zirconia and magnesia, and is preferably an AZS refractory.
5. A ceramic part according to claim 1, wherein the refractory ceramic is a slip-cast and sintered refractory ceramic.
6. A ceramic part according to claim 5, wherein the treated surface is a concave surface.
7. A ceramic part according to any one of the preceding claims, wherein the metal is platinum or a platinum alloy.
8. A ceramic part according to any one of the preceding claims, wherein the film is of thickness from about 200 to 500 microns.
9. A furnace incorporating a metal-coated ceramic part according to any one of the preceding claims.
10. A furnace according to claim 9, wherein the metal film is connected to a source of electricity and provides resistance heating when in operation.

11. A method of metal coating a metallic-oxide refractory part, comprising treating at least one surface area of said part using a high energy beam to remove a portion of surface area, to form a plurality of slots or closed-end holes which form an effective bonding surface, and subsequently depositing a coating of a platinum group metal or alloy thereof, onto the bonding surface to provide mechanical interaction between metal pegs formed as part of said coating and positioned within said slots or holes and the ceramic walls and bases of said slots or holes.

12. A method according to claim 11, wherein the high energy beam is an electron beam.

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13. A method according to claim 11, wherein the high energy beam is a laser beam.

14. A method according to any one of claims 11 to 13, wherein the metal is deposited by combustion flame spraying.

15

15. A method according to any one of claims 11 to 14, wherein the thickness of metal deposited is from about 200 to 500 microns.

16. A surface treatment machine for use in carrying out the method of claim 11, comprising means for locating a refractory metallic-oxide ceramic part and a laser connected to a fibre-optic laser beam delivery system controlled by a multi-axis positioning system, such that a laser beam transmitted through the fibre-optic delivery system is directed in a pre-determined manner against a surface of the ceramic part to remove a portion of the surface area of the ceramic part, to form a plurality of slots or closed-end holes.

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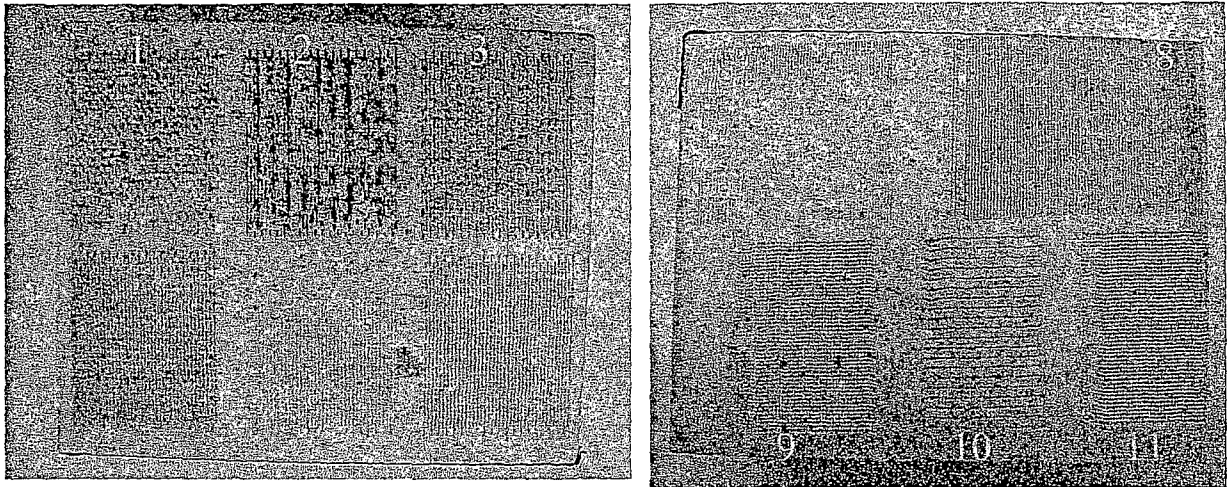


Figure 1; Showing the patterns drilled in Fusion Cast ceramic using an Electron Beam Gun

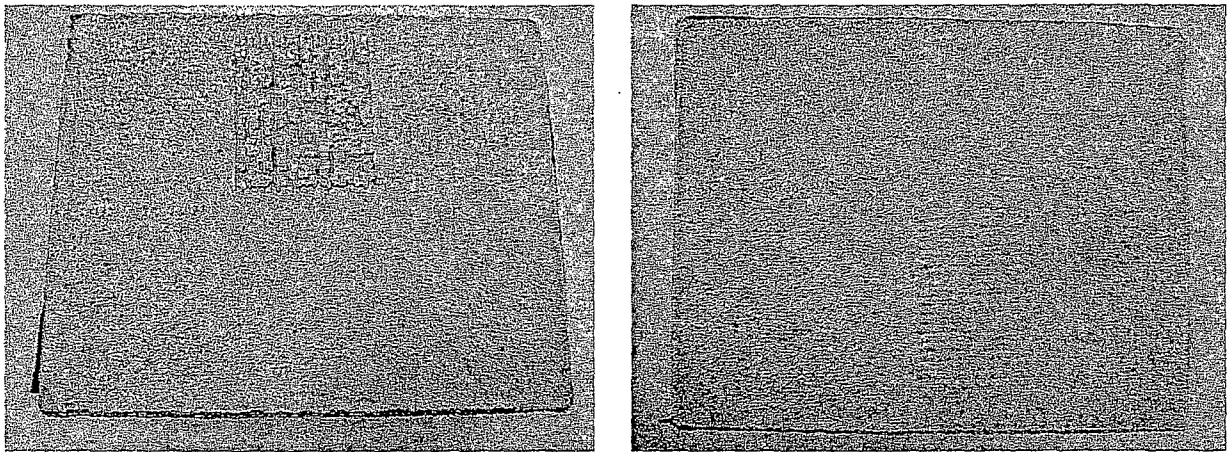


Figure 2; Showing the blocks drilled using the EB gun, after coating with platinum.

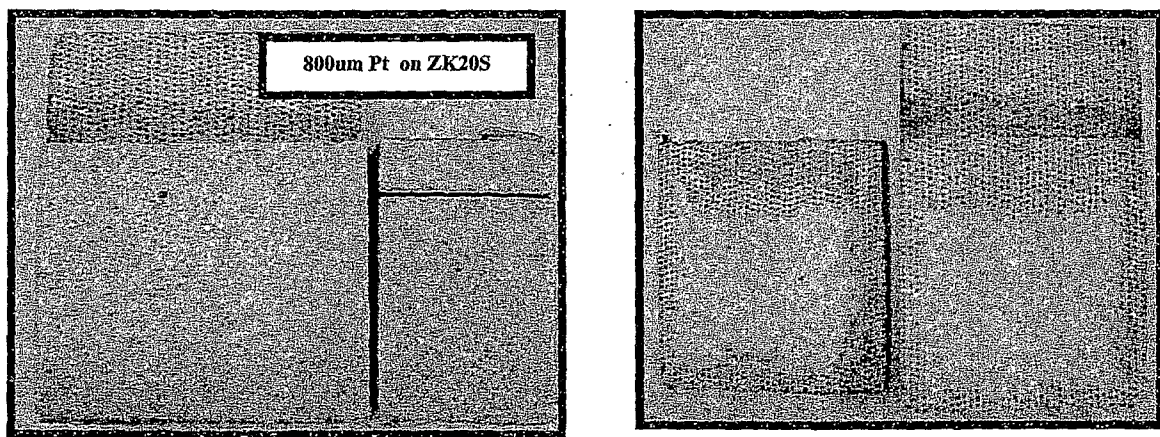


Figure 3a; As Platinum coated Slip Cast ZK20S alumino-silicate refractory.
Figure 3b; The underside of the 800micron thick coating after removal from the ceramic, showing the extensive ceramic failure.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER		
INV. C04B41/88	C03B5/43	C23C4/02 C23C4/08
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C04B C03B C23C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A A A	US 5 465 780 A (MUNTNER MICHAEL S [US] ET AL) 14 November 1995 (1995-11-14) claims column 12, line 41 - line 44 ----- EP 0 559 330 A (JOHNSON MATTHEY PLC [GB]) 8 September 1993 (1993-09-08) cited in the application claims ----- US 5 435 889 A (DIETRICH HERBERT [US]) 25 July 1995 (1995-07-25) cited in the application claims column 1, line 6 - line 10 column 3, line 16 - line 23 -----	16 1-15 1-16 1-16
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 31 October 2007		Date of mailing of the international search report 07/11/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Rosenberger, Jürgen

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