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Materials

Ceramics

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THE term ceramics is a general term for a wide variety of materials and only certain sections are mentioned in this review. A list of supplementary references is appended so that a wider coverage of material is obtained.

Since the publication of the previous review[1] many conferences have taken place including two in Europe: the 6th International Scientific Conference Science of Ceramics at Baden-Baden[2] and the 7th International Conference at Juan-les-Pins.

1. Raw Materials

Much work has been carried out on the occurrence, structure and properties of clays and clay materials. Cole *et al.*[3] have presented a paper on the characterization of clays by a more rapid method than the IL/MA procedure. Zircon has been studied very fully in reviews[4,5] which deal with the occurrence, benefication, crystal structure, morphology and many other aspects of the material. Metamict Ceylon zircons have also be studied.[6]

Kaolinite formation from vermiculite has been discussed[7] and modified kaolin clay fillers are described in a British Patent[8] wherein dry kaolin clay is treated with an organic amine under anhydrous conditions in an anhydrous organic diluent.

Steatite materials manufacture are discussed with regards to the physical chemistry of the processes occurring during firing[9] and some research on talcs and steatites in which structural differences other than crystal size has been published.[10]

Balozsovics[11] has presented a paper on the decomposition of raw dolomite lumps.

A review of synthetic raw materials used in fine ceramics, in particular anorthite and cordierite has been presented by Ducarre[12] and patents have also appeared on synthetic wollastonite and synthetic aluminate spinel.[13, 14]

2. Health

This aspect has been studied extensively over the period of this review.

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In this period much interest has been shown in the world on many aspects of pollution and the steady progress that has been made in the ceramics and allied industries over recent years has been maintained.

Meyer[15] in his paper on dust in the ceramic industry suggests that variable toxicity may be connected with impurities in quartz and the environmental problems in the whitewares industry has been discussed by Skelly.[16] Analysis of free silica in respirable dust has been described by Freedman[17] and the gravimetric detection of respirable dust fraction with the aid of a sampling device with an air sifter–preseparator has also been described.[18]

Dust hazards in the ceramics industry and rules devised in West Germany for dust elimination are described by Duwe *et al.*[19] and sampling and analytical conditions for the health hazard assessment of siliceous type dusts using an improved technique of quartz analysis by X-ray diffraction using silver filters has been presented.[20]

Beryllia is extremely toxic and a code of practice for the use of beryllia materials has been drawn up.[21]

3. Glass ceramics, glazes and colours

Much work has been carried out on these facets of the ceramics industry.

The crystallization of cordierite glass with particular reference to glass ceramics of the $MgO–Al_2O_3–SiO_2$ system has been discussed by Gregory *et al.*[22] Huff *et al*[23] have presented computerized predictions of glass compositions from measured properties. In a paper on the function of mixed nucleating agents in glass ceramics of the high-quartz solid type, Muller shows that materials with suitable ionic properties may replace titania and zirconia which are used in many commercial glass ceramics.[24] Ferrandis has investigated the crystallization of glasses in the system $Li_2O–MgO–Al_2O_3–SiO_2$ using an electron microscope, making his studies on the crystallization of the glasses as a function of temperature treatment and of the amount of titania used as a nucleating agent.[25]

In the field of glazes West *et al.*[26] have analysed published data of the properties of glazes and have then analysed these using a computer to derive coefficients which may be used with the chemical composition to estimate various properties.

Electrostatic glaze application has been discussed by Muirhead[27] and another paper[28] describes electrostatic glaze application, using apparatus adopted from that used for electrostatic enamel spraying.

The effect of borates and phosphates in glazes is described by Cool[29] where it is reported that chemically precipitated borates may be used as a base for unfritted lead-free pottery glazes with good colour variation and phosphates increase the opaqueness of alumina-containing borate glazes. Galushko *et al.*[30] have reported on basalt-based glazes for chemical stoneware which are claimed to have good chemical durability. A study in seven parts[31] describes how glazes may be designed to fulfil technical requirements and covers widely different applications, e.g. conducting glazes and thin film circuitry. New compositions for reducing glazes using a Russian tuff as a flux and for which a wide range of colours is obtainable are given in a paper by Kutateladze *et al.*[32]

A paper by Antal-Boza *et al.*[33] describes how silicate aggregates may be coloured by silicate chemistry. Wildblood[34] has studied the effect of fluorides in mineralizers for various stains giving briefly details of the fluorine emissions and Pfaff[35] has described the development of lead and cadmium free colours with higher abrasion resistance than on glaze colours.

4. Pottery bodies

The use and effects of various elements and minerals in pottery bodies has been studied by various workers.

The use of nephelene syenite in ceramic bodies has been discussed by Capucci *et al.* who state that introduction of nephelene syenite in reduced amounts to replace potash and soda fulspars, produces a longer vitrification range and this results in less warpage.[36]

The effect of fluorine in pottery bodies has been investigated by Holmes[37] who finds that gaseous fluorides affect all pottery bodies, retarding vitrification, reducing firing contraction and increasing porosity.

The impregnation of ceramic tiles with sulphur has been investigated[38] and Maslenikova *et al.*[39] in a study on the synthesis of ceramic materials containing lithium found that in ceramics based on lithium monoaluminate additions of BaO and ZnO can decrease thermal expansion and increase the strength.

Green spot faults in sanitary ware have been studied and the fault is ascribed to chalcopyrites in the raw materials or by brass usually from damaged screens[40] and the bloating caused by silicon carbide contamination in bodies and glazes has been described.[41]

Piltz *et al.*[42] have investigated the influence of various minerals on the frost resistance of tiles. Two compositions were investigated and it was found that additions of illite, montmorillonite and kaolinite-refractory have a favourable effect on frost resistance for one body. For the other body similar results were obtained except that kaolinite-refractory clay lowers the frost resistance.

Colour discrimination studies on ceramic wall tiles have been carried out by Malkin *et al.*[43] and Missiroli[44] has reported on studies of colour measurements carried out by various research laboratories under the CEC. A specific method of colour measurement is to be recommended and to establish convenient tolerance limits for the changes in the chromatic features of ceramic articles.

Lead release has been an area for much work in many countries. The British Standards Institution have published the permissible limits of metal release from glazed ceramic ware.[45]

Wildblood[46] has studied the release of toxic metals from glazed fine ceramic altering three factors affecting such release, viz. the duration of attack, the temperature of the solution and the concentration of the acid. Different solutions to the problem that may be used in manufacture of articles are discussed.

An extensive study of lead release by Emilani *et al.*[47] using statistical analysis has led to a new proposal for the admissible limit for lead release for ceramic food containers being proposed.

Lead release problems are discussed by Merwin[48] in which he gives details of the surveillance programme undertaken in America.

5. Phase equilibrium

Various data have been presented on phase equilibrium studies.

Hatfield *et al.*[49] have considered the compatability relationships between solid magnesia containing lime in solution and the silica phases in the system $CaO–MgO–SiO_2$. Equilibrium studies[50] in the system MgO–'FeO'–TiO_2 under strongly reducing conditions have been carried out at liquidus and solidus temperatures and at 1000°C. In addition to rutile and magnesio-wustite (MgO-FeO) these continuous solid solution series appear in the system in these three temperature ranges. Considerable deviations from stoichiometry with respect to the (Mg + Fe)/Ti ratios are possible in all these solid solutions.

Using a quenching technique Kimura *et al.* have studied phase relations in the system CaO-iron oxide-TiO_2 between temperatures of 1100°C and 1350°C for reducing conditions and between 1200 and 1700°C in air.[51]

Shultz[52] [illegible] studied the role of titania in some important refractory systems by [illegible]ing selected equilibria in the system CaO–MgO–iron oxide–TiO_2 in oxygen at 0.21 atmosphere (air) and 10^{-9} atmosphere under extreme reducing conditions.

The structure and thermomechanical properties of partially stabilized zirconia in the $CaO–ZrO_2$ system have been investigated by Garvie *et al.*[53] It was found that although optical microscopy showed the material consisted of grains of pure ZrO_2 distributed in a matrix of fully stabilized material, electron microscopy showed that the matrix grains have a complex substructure of 1000 μm domains of cubic and monoclinic ZrO_2.

Conrad[54] has presented a method of correlating phase transformation with the time and heat treatment in a zirconia nucleated $MgOAl_2O_3 3SiO_2$ glass ceramic.

The important system $CaO–Al_2O_3–CaF_2$ has been studied and the phase diagram shows five ternary eutectics, two ternary peritectics and two invariant points of four phase monectic transformations.[55]

6. Chemical analysis

Many papers have been published dealing with chemical analysis a great deal of them dealing with sophisticated methods.

The use of X-ray fluorescence for analysing oxide system has been discussed by Ambrose *et al*[56] in which the analysis of non-metallic materials occurring in the steel industry is considered. In this method using a gold target tube inter-element effects are reduced to a low level.

Cobb *et al.*[57] have developed a method for the detection of sodium and potassium oxides in iron ores, slags and refractory materials by atomic-absorption spectrophotometry.

Differential thermal analysis has been discussed in many papers. Studies by Sata *et al.*[58] on the crystallgraphic transition in BeO by DTA have shown that the transition temperature of BeO may be used as a second fixed point of temperature above the Al_2O_3 point. Cohen Arazi *et al*[59] have investigated the transformation of β-Al_2O_3 into α-Al_2O_3 by DTA and X-ray diffraction studies between 600 and 1500°C.

Classical methods of analysis are still being improved and many papers have appeared on this theme.

The determination of zirconium in glasses, glass ceramics and refractories with bromomandelic acid has been investigated by Su *et al.*[69] and a method for the rapid titrimetric determination of boron in silicates has been given by Piryutko *et al.*,[61] this method being based on the potentiometric titration to pH 6.9 (in the presence of EDTA) of the H_3BO_3–mannitol complex with 0.02 N–NaOH.

Bennett *et al.*[62] have prepared a method for the chemical analysis of chrome ores and chrome-bearing ores and the cooperative results obtained by a Working Group together with the experimental work leading to the final result are given.

Kalocsai *et al.*[63] have described a rapid titrimetric analysis for silica which it is claimed has advantages over conventional gravimetric or spectrophotometric procedures.

The accuracy of industrial ceramic analysis has been surveyed.[64] Forty firms cooperated in the analysis of twelve samples: ball clay, bauxite, chrome ore, dolomite, firebrick, flint, magnesite, potash and soda felspars, sillimanite, steatite and zircon.

Other more general analytical methods have also been described, e.g. electron probe micro analyser and the electron microscope. Burger[65] has discussed the possibility of using electron microscope panoramic photographs in quantitative structural analysis.

7. Electroceramics

A great amount of work in connection with dielectric and ferroelectric materials has been carried out in the period under review.

In a study of semiconducting barium titanate Heywong[66] investigated the chemical and physical properties of blocking layers which occur at both surface and interfaces, the resistance of these blocking layers being governed by the ferroelectric properties. The use of doped titanates as the basis of two new types of material is described.

Dumoulin[67] has described the solid-state reactions during the sintering of ceramics with a barium titanate base. In a paper on the development of barium titanate with consistent dielectric properties Kulkarni *et al.*[68] show that although this is usually attributed to changes in the $BaO:TiO_2$ ratio and the presence of phases other than barium titanate, better consistency of dielectric properties may be achieved by washing barium titanate calcines with hot water, repeated calcination and prolonged grinding.

The production of barium titanate from barium sulphate and titanium dioxide in the presence of sodium carbonate at temperatures from 960 to 1160°C is described by Chilvers *et al.*[69] who also propose several two-stage mechanisms for the reaction.

A study of lanthanium doped barium titanate with Bi_2O_3 as a grain bonding element has shown a two step anomalous increase of resistivity with nonohmic contact elements, but one of the steps disappeared and the other diminished when indium base alloy electrodes were employed. It appears from this work that Bi_2O_3 from a surface barrier.[70]

A short paper by Conger *et al.*[71] has described non-stoichemistry in barium titanate at 900°C and at pressures between 10^{-6} and 1 atmosphere of oxygen.

Jiminez *et al.*[72] have studied the group of ferrities in the Fe_2O_3–CuO–NiO–ZnO system and these show a very rectangular hysteresis cycle. The best results have been obtained for molar CuO contents of about 25 mol% and sintering temperatures below 1000°C.

The nature of ageing in ferroelectric ceramics has been investigated by Jonker.[73]

Dev *et al.*[74] have investigated the effects of replacing quartz with zircon and the effects of minor additions of talc, wollastonite or combinations of both, to bodies containing 10–20% felspar, on the properties of high-tension porcelain insulators. Body strength was found to be increased with the addition of zircon. Talc and wollastonite increase specific resistivity of insulator bodies at high and low temperatures.

In a paper on conducting glazes Binns[75] describes techniques for examining conducting glazes and their application to the study of commercial and experimental glazes of the ferrite type. Measurements made on glazes containing various proportions of conducting phase showed that a conducting network was set up and the conductivity increased by several orders of magnitude in the range 8–11 vol% of conducting phase.

Russak *et al.*[76] have described the development of a semiconducting glaze for high-tension porcelain insulation. They discovered that a silicate glass composition could be rendered semiconducting by the controlled crystallization of magnetite. Using such a glass as the major constituent of a semi-conducting glaze, appropriate firing and heat treatment provided surface resistivities from 2–30mΩ/square at room temperature.

8. Refractories

Arazi *et al.*[77] have described a new process for the production of mullite which consists of the nucleation of a mixture of kaolinitic clay and aluminium hydroxide through simultaneous grinding and thermal treatment at 980°C followed by shaping the powder and firing between 1500 and 1600°C to obtain pure mullite products. Pure mullite products of low porosity and high density were obtained. The sintering of mullite in a rotary kiln from kaolin and alumina has also been described.[78]

In a study of the sintering of felspar Rasmussen *et al.*[79] the data obtained indicated that a viscous mechanism for the shrinkage of felspar, when sintered isothermally by a modified method, was modified by the residual crystalline content of the materials at the sintering temperature.

The wetting of ceramics by liquid metals has been investigated by Rhee[80] who found a linear relationship between the cosine of the contact angle and the temperature of a liquid sessile drop resting on a ceramic substrate. In addition to the work of adhesion and the effects of surface roughness, porosity, chemical reaction and structural transformation in the substrate surface were discussed.

A summary of the corrosion of refractories, based on the theory of transport phenomena, has reviewed the processes during corrosion in the liquid phase and deals with the problems of corrosion processes inside the refractory materials or in the transport layers.[81]

A great deal of work has been carried out on studies of refractories in and after service. Abratis *et al* [82] have studied the chemical behaviour of refractories in contact with molten steels under vacuum conditions, both in the laboratory and in works experiments. Various high alumina and basic refractories were tested in vacuum vessels.

Experiments have been conducted into the wear mechanism of refractories used in DH vacuum vessels, by means of a laboratory furnace in which brick samples could be brought into contact, at temperatures up to 1700°C with both steel and slag. The experimental and theoretical results of this study have enabled the development of DH vessels which have attained lives of 1000–1500 charges.[83]

Pickering *et al.* [84] have studied carbon-magnesia reactions in BOF refractories. The thermodynamic incompatibility of these under steel making conditions at about 1600°C meant that when a BOF refractory was held for 2 hours in the 1500–1600°C range the reduction of magnesia and oxidation of carbon produced extensive microstructural change. Under oxidizing conditions a mechanism of self destruction could become a serious wear problem at higher temperatures or lower pressures. BOF refractories have also been studied by Leònard *et al.*[85] who studied their wear rate and they attributed the higher wear rate of pitch bonded brick, as compared to burned impregnated brick, to the pronounced porous region created near the hot face when internal oxidation-reduction reactions consume the bond.

The determination of the wear of blast furnace linings by cobalt 60 has been carried out and in the light of the trials suitable refractories for various parts of the blast furnace are discussed.[86]

A radioactive tracer technique for measuring lining thickness has been used in a study of the wear-rate of a tarred dolomite–magnesite lining in an oxygen converter. The effects on lining wear of the composition of the iron and of the slag, and of the position of the lance are discussed.[87]

A study of the oxidation temperature and amount of residual carbon in coked tarred dolomite and magnesite has been carried out by Palin *et al.*[88] The residual carbon found during coking oxidized at a higher temperature in coked dolomite than in coked magnesite samples and tests to elucidate this have shown that the formation of carbonate during oxidation followed by its breakdown at a higher temperature accounts for the apparently high temperature of oxidation of dolomite. The higher residual carbon value of dolomite is also the result of incomplete breakdown of carbonate found during the coking procedure.

The chemical stability and durability of carbon bricks used in blast furnaces have been investigated in laboratory experiments. These tests included the solubility of carbon in pig iron, the reaction of carbon bricks with air, carbon monoxide and water vapours and the attack on carbon bricks of alkalies.[89]

Experiments designed to reduce or prevent the penetration of alkaline materials into phosphate-impregnated fireclay bricks aimed at the delay or prevention of decomposition by alkali (alkali-bursting). An impregnation with a 50% solution of monoaluminium phosphate may eliminate the decomposition by alkali completely. *In situ* experiments were identical with laboratory results showing an improved durability of impregnated fireclay bricks.[90]

Biggar[91] has studied the phase equilibrium in the system CaO–MgO–Al_2O_3–Cr_2O_3–SiO_2 relating to chrome-bearing basic refractories. Amongst other results it was found that the presence of Cr_2O_3 scarcely raises the temperature at which the first liquid appears on heating.

9. Special ceramics

Interest has centred once more around alumina, silicon carbide, silicon nitride, beryllia and other similar materials.

Work on alumina in many forms has been carried out. Jones[92] has described a technique for growing α-Al_2O_3 crystals by Na_2O evaporation. $Na_2O.11Al_2O_3$ is dissolved in a liquid of composition $Na_2O.4TiO_2.3Al_2O_3$ and α–Al_2O_3 is precipitated. The size of the α-Al_2O_3 crystals is related to the Na_2O content of the composition.

Cryochemically prepared alumina powder containing up to 0·65% MgO was sintered at 1700°C in hydrogen and a 99.9% theoretically dense alumina with grain sizes from 2 to 10 μm was obtained from alumina containing 0·25% MgO. Other properties substantiating the high density were discussed.[93]

Matkin *et al*[94] have discussed the fabrication of α-alumina by reactive hot pressing. Low-temperature forms of alumina have been transformed to α-alumina at temperature, under pressure and the influence of the phase transformation upon the densification during hot-pressing was studied for a number of commercial aluminium hydrate powder industry gibbsite and boehmite. Differences in densification curves were observed and reasons for these were suggested.

In a study of rate-controlled sintering in a uniquely instrumentated dilatometer, high density and fine grain size was achieved in a commercially available high purity alumina containing 0·1% MgO.[95]

Gopienko[96] has shown that formation of alumina in the presence of