PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

A Perspective on New Ceramics and Ceramic Composites [and Discussion]

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A perspective on new ceramics and ceramic composites

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[Plates 1 and 2]

The present status, characteristic features and important aspects of new ceramics and ceramic composites in high-technology industries are reviewed. Current problems requiring urgent solution are described, and some possibilities for solving them by introducing new ideas and results of some trials are discussed. Based on these, the prospects for the new ceramics and ceramic composite industries in the 1990s are reviewed.

1. Introduction

As well as so-called traditional ceramics such as porcelain, glass, refractories and cement, several new ceramics are being produced that are attracting much attention. These include high-quality ceramics that are processed and finished by controlling microstructures, chemical ingredients and dimensions by using refined raw materials to optimize their special properties. These ceramics are called 'fine ceramics' in Japan because they are often made from extremely pure and ultra-fine particles. The major uses and classification of the new or fine ceramics are listed in table 1.

In Japan, nowadays, not only ceramics companies but also those companies belonging to other technological branches such as the textile, chemical, iron and steel, non-ferrous, machinery, electrical, heavy, engineering and automobile industries are participating in the research and development of ceramics, and some of them have already found applications or made products. Many people believe that ceramics and composites will become extremely important 'high-tech' industries in the near future. The relative market shares (in Japan) of all these new ceramics are shown in table 2.

Of the functional ceramics, the most developed and mature are the electronic ceramics, which represent approximately 82% of the whole new-ceramics market in Japan. Structural engineering ceramics are relatively new compared with electronic ceramics and may be said to be technologically immature, with only a small market. Bioceramic and optical ceramics are the newest and have, as yet, a relatively small market. These last three categories, however, should have potentially larger markets in the near future if major technological problems can be solved, and therefore can be expected to produce highly important new materials that will support various kinds of 'high-tech' industries.

Ceramic composites may also be divided into several groups but research and development in each has only just started. In Japan, ceramic fibre-reinforced metals (FRM) have been introduced into passenger car parts. Ceramic-matrix composites (CMC), which use ceramics as the matrix, are expected to become one of the most promising materials to improve the brittleness or high-temperature mechanical strength of engineering ceramics, and research and development work in this area has recently become very active.

TABLE 1. CLASSIFICATION OF THE NEW CERAMICS

materials	uses
functional	electric/ electronic
	optical
	thermal
	biocompatible
structural	irradiation
	mechanical
	thermal

TABLE 2. SALES VOLUME OF NEW CERAMIC MATERIALS AND CERAMIC PARTS IN JAPAN BETWEEN 1983 AND 1985

(Units are thousand million yen, percentage values given in parentheses.) (Japan fine ceramics association.)

	electro	mechanical	chemical	thermal	optical	remainder	total
1983	573.7	39.0	29.8	26.6	17.3	8.6	695.0
	(82.5)	(5.6)	(4.3)	(3.9)	(2.6)	(1.2)	(100)
1984	722.9	50.8	37.2	36.5	20.7	10.9	879.0
	(82.2)	(5.8)	(4.2)	(4.2)	(2.4)	(1.2)	(100)
1985	858.6	58.0	43.7	46.8	22.9	11.5	1041.5
	(82.4)	(5.6)	(4.2)	(4.5)	(2.2)	(1.1)	(100)

In the following sections, the current status, future possibilities, and emerging problems for each material will be discussed. Some of the progress in Japan that is helpful in solving these problems will be presented and based on these the prospects for the 1990s will be given.

2. THE PRESENT STATUS OF FINE CERAMIC TECHNOLOGY

The manufacture of ceramics is probably one of the oldest technologies of mankind: ceramic utensils have been found in ruins from thousands of years ago. During the 1950s the new ceramics sprouted in the rapid growth of the electrical, electronics, iron and steel, and mechanical industries. The new ceramics were then recognized as important materials that support many other industries and 'the second ceramic age' was born.

Some characteristic features of the new ceramics may be summarized as follows:

(1) they include various kinds of materials;

(2) they have various kinds of specific functions and properties;

(3) these properties are sensitive to microtexture, phases and purity as determined by the processing method;

(4) for machine parts, special design criteria are necessary to use the new products.

From the research and development point of view, the new ceramics do not have a firm scientific, theoretical background. Although much progress has been made in the physics and chemistry of solid surfaces, rheology of powder systems, sintering theory, fracture mechanics, etc. it has not yet progressed sufficiently for widespread application in ceramic technology. Much experience is needed in research and usually it takes a long time before good results are obtained.

Furthermore, relatively expensive equipment is required for research, examination, and

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processing. As already mentioned, the scale of the market increases in the order: biological, engineering (or structural), and electronic (including optical) ceramics (see table 2).

In the following sections, the present status of some representative ceramic materials is described.

(*a*) *Electronic ceramics* (*dielectrics*, *piezoelectrics*, *semiconductors*, *etc.*)

There are many kinds of electronic ceramics because many types of functions are required in a wide range of applications. According to their microscopic texture, they are classified as (I) single crystals or very dense polycrystals (high purity with few pores), (II) controlled grain-boundary ceramics or (III) controlled pore ceramics. Class I includes single oxides such as Al_2O_3, perovskite-type oxides ABO_3, and spinel-type oxides AB_2O_4. The grain boundaries in class II are either segregation-type or phase-separation-type. In polycrystalline ceramics, the additives tend to concentrate in the grain boundaries, resulting in changes in the basic properties of the semiconductor grain boundaries that can be used for practical purposes. The fine open pores in class III collect various kinds of gases such as H_2O through adsorption, absorption and condensation. The resulting changes in electrical properties of the surfaces can be used as humidity or gas sensors.

It should be noted that, although the characteristics of (I) were pursued in the early stages of the development of the electro-ceramics and are still pursued now, the usefulness of the grain boundaries, the boundary phases, and the pore surfaces as in (II) and (III) was recognized much later and is more widely applicable to the ceramic technology. The chemical compositions, crystal structures, grain boundary main functions and properties, and applications of many new electronic ceramics (Nitta 1985*a*, *b*) are summarized in tables 3, 4 and 5. As an example of class I, a new processing technology has been developed (Ono 1986) that can continuously produce very thin films of sintered Al_2O_3 by sol–gel tape casting.

(*b*) *Engineering ceramics*

The purpose of developing engineering ceramic materials is to make improved machine parts or machines, which must bear vibrations, shocks and high tensile stresses for long periods, by using the heat-, corrosion- and erosion-resistive properties and low densities of these ceramics. In Japan, under the initiative of the Ministry of International Trade and Industry (MITI) a ten-year national programme was started in December 1981. In that programme, industry, national laboratories and universities are collaborating to establish the basic technology for the processing, evaluation and use of high-strength, high-corrosion- and friction-resistant materials

TABLE 3. MULTICOMPONENT SOLID-SOLUTION CERAMICS FOR ELECTRONICS APPLICATIONS

crystal structure	chemical composition	function and application
perovskite type (ABO_3)	$BaTiO_3$, $SrTiO_3$, $CaTiO_3$	capacitor
	$Ba[Zn_{1/3}(Nb,Ta)_{2/3}]O_3$, $(Sr,Ca)[(Li_{1/4}Nb_{3/4}), Ti]/O_3$	microwave dielectrics
	$Pb(Ti,Zr)O_3$, $Pb[Mg_{1/3}Nb_{2/3}), Ti,Zr]O_3$	piezoelectrics
	$PbTiO_3$	pyroelectrics
	$(Pb,La)\ (Ti,Zr)O_3$	electrooptics
	$(La,Sr)CoO_3$	heater
	$Ba(Pb,Bi)O_3$	superconductor
spinel type (AB_2O_4)	$(Mn,Zn)Fe_2O_4$	soft ferrite, magnetic head
	$CoFe_2O_4$	memory ferrite
	$(Mn,Cu)(Mn,Co,Ni)_2O_4$	thermistor
	$Mg[Al,Cr,Fe]_2O_4$, $CoAl_2O_4$, $NiAl_2O_4$	high-temperature thermistor

TABLE 4. ACTIVE USE OF GRAIN BOUNDARIES IN ELECTRONIC CERAMICS

electronic ceramic	crystal grain	grain-boundary region	grain-boundary property
PTC thermistor	n-type $BaTiO_3$ semiconductor	grain-boundary segregation of acceptor ions such as Mn, Cu, Fe	positive temperature coefficient of resistance (PTCR action)
boundary layer capacitor	n-type semiconductor such as $BaTiO_3$, $SrTiO_3$, and TiO_2	continuous film type grain-boundary layer (0.1 ~ 1 μm) formed by grain-boundary diffusion of acceptor ions such as Bi, Cu, Mn	dielectric layer (high-capacitance action)
ZnO varistor	n-type ZnO semiconductor	continuous film type intergranular phase (1 μm) formed by liquid–phase sintering with Bi_2O_3	voltage dependency of resistance (varistor action)
SiC varistor	n-type SiC semiconductor	continuous film type intergranular phase formed by liquid–phase sintering with Al_2O_3 and SiO_2	varistor action
ferrite	(Mn,Zn)Fe_2O_4 ferromagnetics (low insulation-resistance)	continuous film type intergranular phase formed by liquid–phase sintering with CaO and SiO_2	high-resistance layer (reduction of eddy current loss)
CdS–Cu_2S solar battery	n-type CdS semiconductor	continuous film type grain-boundary layer consisting of p-type Cu_2S semiconductor phase formed by grain-boundary diffusion of Cu^+ ion	photovoltaic action
ZnS–Cu_2S electroluminescent ceramics	n-type ZnS semiconductor	grain-boundary precipitation of p-type Cu_2S semiconductor phase	electroluminescence action

TABLE 5. EXAMPLES OF CERAMIC SENSORS

sensor	sensor ceramic material	sensor function
temperature	(Mn,Cu) (Mn,Co,Ni)$_2$O$_4$, CoAl$_2$O$_4$, NiAl$_2$O$_4$, Mg(Al,Cr,Fe)$_2$O$_4$, SiC	NTC thermistor
	BaTiO$_3$	PTC thermistor
	VO$_2$, (Mn,Zn)Fe$_2$O$_4$	temperature switch
humidity	MgCr$_2$O$_4$–TiO$_2$, V$_2$O$_5$–TiO$_2$, ZnCr$_2$O$_4$–LiZnVO$_4$, Al$_2$O$_3$, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$	H$_2$O(ionic conduction)
	ZrO$_2$–MgO	H$_2$O(electronic conduction)
gas	SnO$_2$, ZnO, γ-Fe$_2$O$_3$ α-Fe$_2$O$_3$, TiO$_2$,CoO-MgO	CH$_4$, i-C$_4$H$_{10}$ etc. O$_2$ electronic conduction
	ZrO$_2$–CaO, MgO, Y$_2$O$_3$	O$_2$(ionic conduction)
ion	AgX(X:C1,Br,I,CN,SCN) PbS-Ag$_2$S, CdS-Ag$_2$S CuS-Ag$_2$S, LaF$_3$	ion-selective electrode
position-velocity	Pb(Zr,Ti)O$_3$	piezoelectricity
optics	PbTiO$_3$,LiTaO$_3$ LiNbO$_3$,Pb(Zr,Ti)O$_3$	pyroelectricity (infrared detection)
	CaF$_2$,Li$_2$B$_4$O$_7$	thermoluminescence

containing SiC or Si$_3$N$_4$ as a main constituent. The details have been reported (Suzuki 1986) and, in general, the project has already achieved the objectives expected in its first stage and various kinds of unit-process technologies are being rapidly developed. This in turn stimulates further research and development in this field in Japan.

In addition, many industrial enterprises are carrying out their own research projects. They have established the Japan Fine Ceramic Association (President, S. Saito) to collect and exchange information. Their research and development activities are focused not only on SiC and Si$_3$N$_4$ but also on ZrO$_2$-based systems, $3Al_2O_3 \cdot 2SiO_2$ (mullite), $2MgO \cdot 2SiO_2 \cdot 5Al_2O_3$(cordierite), AlN, TiN, ZrB$_2$, BN, low-temperature and low-pressure synthesized diamond, special glasses, etc. Of course, various kinds of ceramic whiskers and fibres have also been developed, and research into composites that use them is becoming more and more active.

Table 6 summarizes the properties of some sintered materials that became commercial a few years ago. For engineering ceramics, in addition to the technology of processing, it is important to establish methods of measurement, evaluation and characterization and to develop methods of designing new products in collaboration with the users. Although some efforts have been made, they are relatively recent and have been reported much less than processing technology and will not be dealt with in detail here. As the Japan Fine Ceramic Center (FCC) has been founded, more emphasis will be placed on evaluation technologies and the establishment of data bases. Some private companies appear already to have obtained results that have led to commercial products, for example, turbo-charger rotors and pre-chambers. Rocker arms and valves of automobile engines and gas blowers, skid buttons and radiant heaters in high temperature industries will all be in use in the near future.

TABLE 6. TYPICAL PROPERTIES OF ENGINEERING CERAMICS

(Data in square brackets from Toyota, sintered by hot-pressing: other data from NGK. NS, normal sintering; RS, reaction sintering.)

main composition	Al_2O_3	ZrO_2	Si_3N_4		SiC	Fe,Ni
method produced	NS	NS (PSZ)	NS	RS	NS	— (713c)
bending strength/MPa	440	1020	880	296	500	850
room temperature	[500]	[1200]	[1000]	—	[1100]	(tensile)
1000 °C	340	—	510	300	475	—
1200 °C	300	450 (800 °C)	350	370	480	—
		[350] (800 °C)	[600]		[1100]	
fracture toughness	4.5	8.5	7.0	3.6	2.4	80~100
K_{Ic}/(MPa m)	[4]	[9]	[6]		[4]	
thermal-shock resistance (into H_2O, ΔT/K)	200	350	900	600	370	—

3. MAJOR PROBLEMS

To ensure that the market for the new ceramics and ceramic composites will expand smoothly into the 1990s, many related technological problems must be at least partly solved. Only technological aspects will be described here, although the use of these materials is also affected by social factors such as natural disasters and the international environment. The problems with electronic ceramics and bioceramics are quite different because their histories are very different. Engineering ceramics are situated between these two, somewhat closer to bioceramics and having rather many unsolved problems and a larger possibility for future growth. Problems in the electronic ceramics and in the engineering ceramics sectors only will be discussed here.

(a) *Electronic ceramics*

Referring to class I above, new compounds having unique functions are sought and also the techniques required to grow very thin and small single crystals. As for categories II and III, although much progress has been made in those products that use grain boundaries or pores positively, the efforts have been limited largely to application oriented fields. Information on ceramic surfaces, grain boundaries and interfaces, which should form a scientific background for the technology, has not been sufficiently obtained. After having established appropriate examination methods and developed these scientific areas, the range of application of electronic ceramics may be expected to expand further. This will help the development of materials having multiple functions, which may, in turn, lead to savings of natural resources.

(b) *Engineering ceramics*

To permit the steady development and wider application of this type of fine ceramics, the technology of processing should first be better established. Among the many unsolved problems, some of the most important are given below.

(1) *Increase the Weibull modulus, m, to more than 20, for example, and thereby increase the reliability.*

Because the strength of ceramics is lowered according to the size, number, and positions of surface and bulk defects (pores, inclusions, cleavage surfaces, grain boundaries, cracks, residual stresses, etc.), it will be necessary to establish processing techniques that prevent large defects or flaws. It is also necessary, of course, to assure the non-existence and avoid the production of defects while the materials are in use.

(2) *To increase the critical stress-intensity factor* K_{Ic}.

O. Kamigaito at the Toyota Central Research and Development Laboratory, has suggested (Kamigaito 1986) that K_{Ic} larger than 6 MPa $m^{\frac{1}{2}}$ is desirable. If the factor is large, the critical defect size will be large, which is quite favourable to processing, examination and lifetimes that are strongly dependent upon erosion and surface damage generated by the impact of particles. However, whether K_{Ic} or the work of fracture, γ_f, is more important has to be the subject of future studies. Many kinds of toughening mechanisms have been studied and proposed since the discovery of ZrO_2 toughened ceramics (PSZ, ZTP, etc.) and composites are attracting more attention at present.

(3) *The cost of products.*

At present, the cost is very high and this will remain a central problem when the development of ceramic parts is completed, which will be soon. To reduce the cost, we must improve the technology of processing and create further demand to enable mass production. Because multitype, small-lot production is expected for most fine ceramics, we will have to resort to new means such as developing internal self-consuming demands or collaborative agreements with user organizations.

(4) *Miscellaneous.*

The establishment of joining techniques between metal and ceramic, or ceramic and ceramic, is necessary when combining different materials to be used under various environments. This problem is urgent and must be solved for practical applications. Cutting, slicing, polishing, etc. are also problematic, as they produce small surface flaws. Also, surface coating may become necessary to help protect the surface from corrosion and particle-erosion and thus prevent fracture arising from the effects of surface microcracks.

4. SOME IMPORTANT EXPERIMENTAL RESULTS

This section is confined to a consideration of engineering ceramics and their problems as described above.

(*a*) *Suppression of internal defects and improvement of strengths for sialon and* SiC

β-sialon is a solid solution of Si_3N_4 and Al_2O_3 that was discovered by K. H. Jack, Newcastle upon Tyne University, U.K. and independently by O. Oyama and O. Kamigaito, Toyota, Japan. It has a general formula of $Si_{6-z}Al_zO_zN_{8-z}$ ($0 \leqslant z \leqslant 4.2$). The sintered materials having high-thermal-shock resistance and corrosion resistance are best where $z = 0.5$–1. However, the strength was not enough: the fracture toughness is only about 3.7 MPa $m^{\frac{1}{2}}$. Recently Kishi *et al.* (1986) of the National Industrial Research Institute of Kyushu (GIRI, Kyushu) examined carefully fractured surfaces and polished surfaces of samples where $z = 0.25$–1 to see what made the materials so weak and observed many internal defects of the size of 50–100 μm. They found some defects where Al_2O_3 had significantly segregated and others where sintering was incomplete because of Al_2O_3 deficiency. In other words, it is difficult to mix a certain amount of Al_2O_3 into α-Si_3N_4 powder homogeneously. Kishi *et al.*, succeeded in avoiding the defect formation by adding Al_2O_3 as a solution of alkoxides such as $Al(i\text{-}PrO)_3$. By this method, they obtained samples with an average bending strength of about 1300 MPa after hot-pressing (300 kg cm^{-2} at 1850 °C), cutting, polishing, and annealing in air for 1 h at 1200 °C. These samples did not show any such large internal defects. The strength was increased by about 70% by suppressing the large flaws and an additional 53% by annealing.

Because it was proved that the theory of strength based on fracture mechanics can be applied to orthodox ceramics, this study gives an important hint for future research and development of these kinds of materials.

For the SiC system, on the other hand, the relation between the size of defects and the strength has been studied (Sakai *et al.* 1986) for sintered samples containing boron and carbon as sintering aids. It has been confirmed that the strength can be improved by about 35% by decreasing the number of the defects and that a homogeneous mixing of additives is essential for increasing the strength and probably also the Weibull modulus. Figure 1, Plate 1, demonstrates some large flaws in sintered SiC. The two methods mentioned above for β-Sialon and SiC ceramics are examples of methods for coating the surface of fine raw powders with sintering aids and other additives. An alternative method is to dissolve or disperse the sintering aids into the powder particles, but there has been no significant progress in this latter method.

(*b*) *Increase of* K_{Ic} (*fracture toughness*) *and composites*

Several toughening mechanisms have been proposed for recent ZrO_2-toughened ceramics. The most effective is the use of the $t \rightarrow m$ martensitic transformation of ZrO_2. It has also been recognized that deflection and branching of the propagating crack also considerably increases K_{Ic}. This technique may be used in particulate- and fibre-reinforced composites that use metals or ceramics as a matrix. The latter are described below.

(i) *Particle-reinforced composites*

For the sintered β-sialon ceramic described above, one of the remaining problems was its low fracture toughness, K_{Ic} being approximately 3.7 MPa $m^{\frac{1}{2}}$. A particulate reinforced composite was tried by adding a large amount of SiC dispersed as a fine powder. The flexural strength, fracture toughness, K_{Ic}, and hardness, H_v, of the β-sialon-SiC system are shown in table 7 as a function of the amount of added SiC. One can see that K_{Ic} could be increased to 5.5 MPa $m^{\frac{1}{2}}$ by the addition of about 50% of SiC. This study is still in progress, and further improvements may be expected. In addition to the research on the β-sialon–SiC system, Kurosaki Yogyo Co. Ltd. has commercialized SiC–Si_3N_4. Many kinds of particle-reinforced composites have already been put to practical use as cutting tools, but there have been few published papers. As for ZrO_2–Al_2O_3, many papers have been published and high strengths and K_{Ic} values have been obtained, but it is believed that the ZrO_2-containing ceramics will show poor strength retention at moderately high temperature. Systems without ZrO_2 are not expected to have as high K_{Ic} as those with it, but it should not be impossible to develop materials with K_{Ic} as high as 6 MPa $m^{\frac{1}{2}}$. As is described below, particle-reinforced systems are increasingly actively studied as they present fewer difficulties in processing than fibre-reinforced composites.

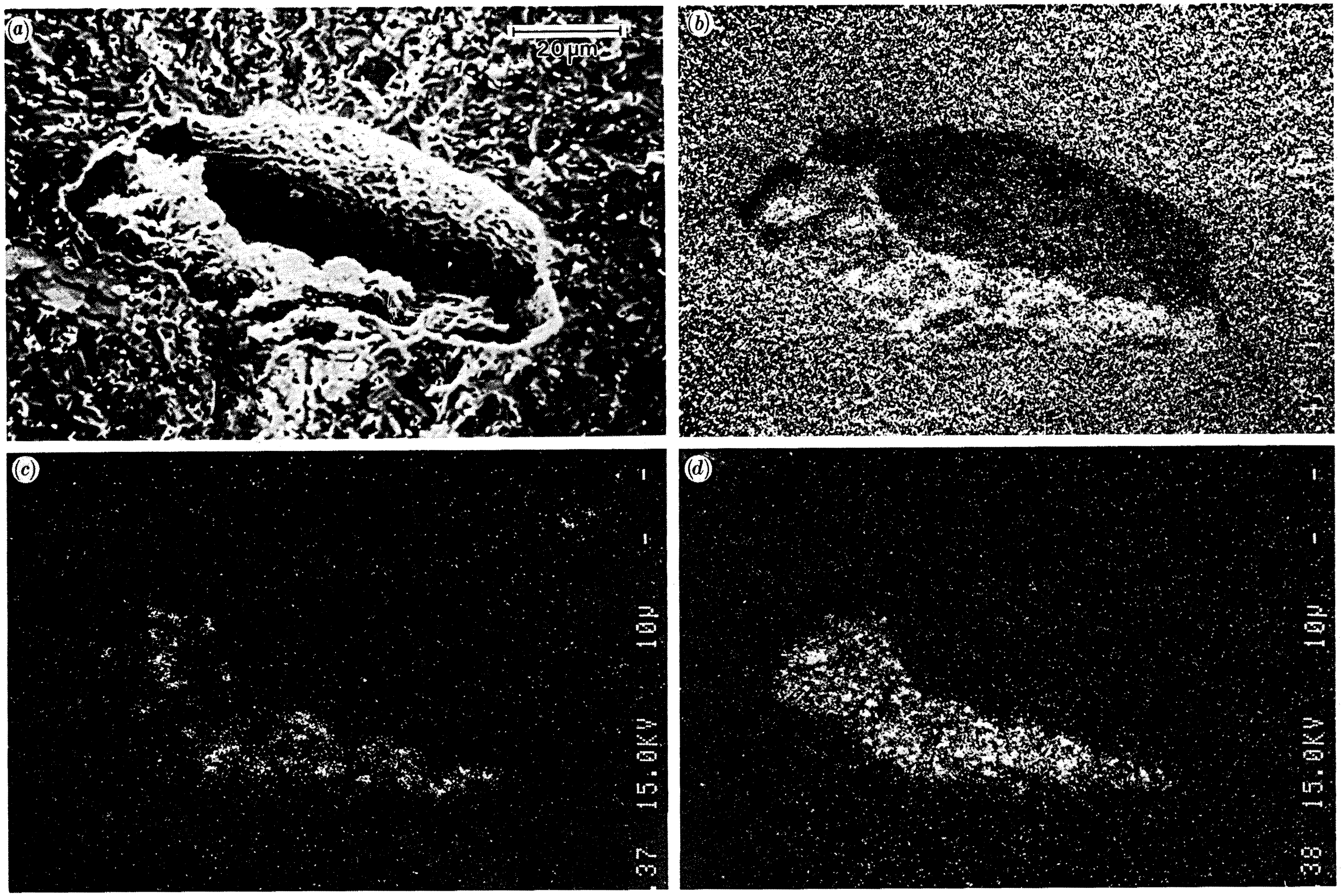

FIGURE 1. Large flaws in SiC ceramics. (*a*) SEM, (*b*) XMA-C (X-ray microscopic analysis), (*c*) XMA-B, (*d*) XMA-Ti.

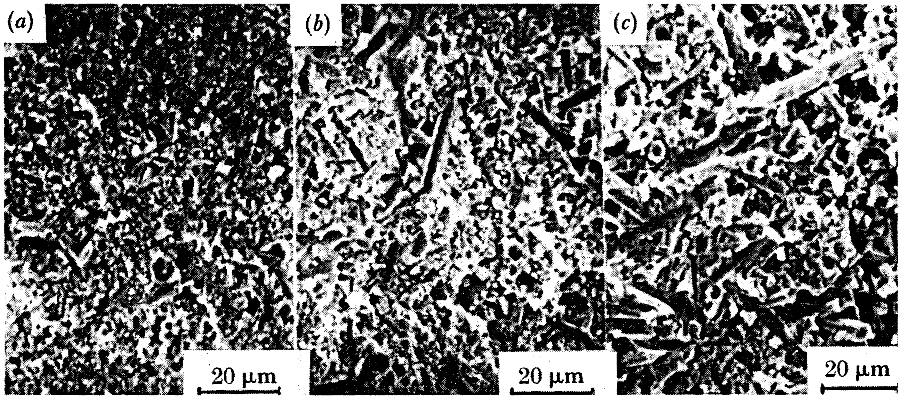

FIGURE 2. Fracture surface of Si_3N_4 gas-pressure sintered with 3% Al_2O_3 and 5% CeO_2 (percentages are by mass). (*a*) At 1800 °C under 2 MPa, (*b*) at 1900 °C under 3 MPa, (*c*) at 2000 °C under 4 MPa.

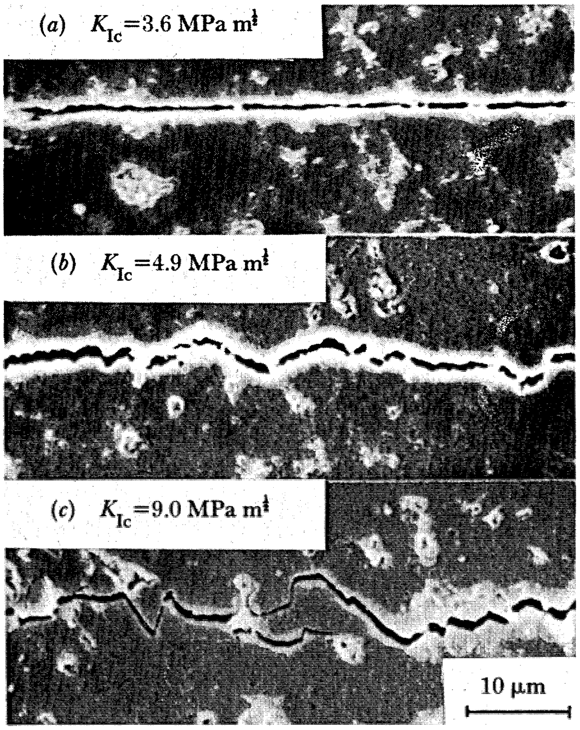

FIGURE 3. SEM photographs of crack evolution. (*a*) HP β-sialon, (*b*) GPS Si_3N_4 with 1% Al_2O_3 and 5% CeO_2 at 1800 °C, (*c*) GPS Si_3N_4 with 1% Al_2O_3 and 5% CeO_2 at 2000 °C (percentages are by mass). (HP, hot pressed; GPS, gas-pressure sintered).

Table 7. Mechanical properties of β-sialon–SiC composites

SiC 0.3 μm (percentage by mass)	strength three-point bend/MPa	fracture toughness, $K_{Ic}/(\mathrm{MPa\ m^{\frac{1}{2}}})$	hardness, $H_v/(\mathrm{kg\ mm^{-2}})$
0	620	3.5	1750
15	745	4.0	1800
30	770	4.4	1960
48	860	5.5	2230

(ii) *Fibre- or whisker-reinforced composites*

This type of composite is attractive because even higher K_{Ic} or γ_f can be obtained. In Japan, the commercial or semicommercial production of SiC fibres (NICALON), Si(Ti)CN fibres (TIRANO), Al_2O_3 fibres, SiC whiskers, Si_3N_4 whiskers, and Al_2O_3–SiO_2 short fibres and their preforms has started. However, applications of fibre-reinforced composites are trailing well behind metal and polymer matrix composites. Many systems are now in the research stage, for example, SiC(w)–Si_3N_4(HP), SiC(w)–Al_2O_3, SiC(w)–Ba–Al–Si–O glass and SiC(w)–mullite. Although they have sufficiently high K_{Ic} and γ_f, some of them are rather weak, probably because of incomplete processing. Future research will be directed to, for example, sol or gel infiltration and chemical-vapour infiltration (CVI).

(iii) *Microstructure controlled ceramics by a new processing procedure*

A very interesting new β-Si_3N_4 having a reasonably high fracture toughness has been produced by a gas-pressure sintering process that involves a controlled heating schedule in a N_2 atmosphere pressure of about 1–4 MPa. By controlling the heating rate and soaking time at the final stage of sintering, the density of the material increases close to the theoretical value and needle-like β-Si_3N_4 crystals grow simultaneously. The microscopic texture of this particular β-Si_3N_4 material is shown in figure 2, plate 2. The texture resembles that of whisker-reinforced ceramic composites and K_{Ic} values of 7–9 MPa $m^{\frac{1}{2}}$ have been obtained. I have named this procedure an 'in-situ reinforcing process' (IRP). Research into unique processes of this kind has been conducted by M. Mitomo (Mitomo & Mizuno 1986) at the National Institute for Researches into Inorganic Materials (NIRIM) and independently by E. Tani *et al.* (1986) at the Government Industrial Research Institute (GIRI)-Kyushu. The results of their experiments are shown in table 8 and figure 3, plate 2. In this photograph an interesting crack propagating feature can be seen where the cracks are deflected and branched at the grain boundary.

Table 8. The relation between sintering conditions and properties (ρ, σ_f, K_{Ic}) of gas-pressure sintered Si_3N_4

	sintering conditions		density	strength/MPa		K_{Ic} (room temperature)
number	temperature/°C	time/h	$\mathrm{g\ cm^{-3}}$	room temperature	1200 °C	MPa $m^{\frac{1}{2}}$
1	1930	1	3.16	818	464	5.5
2	1980	1	3.21	839	509	6.3
3	2000	1	3.19	747	505	5.1
4	1930	2	3.23	910	525	5.7
5*	1780		3.25	982		4.8

* Hot-pressed Si_3N_4.

In the near future, a new material with high strength at elevated temperature and also improved K_{Ic} greater than 6 MPa $m^{\frac{1}{2}}$ might be prepared if the IRP is intensively studied. An especially important problem is to improve the fracture toughness of SiC, sialons and mullite ceramics because these have rather small K_{Ic} values. So far, K. Suzuki *et al.* (1984) have been successful in preparing pressureless sintered SiC ceramics with small amounts of Al_2O_3 additive, containing plate-like secondary crystals and having a K_{Ic} of 6 MPa $m^{\frac{1}{2}}$.

(c) *Research and development for cost reductions*

It is clear that significant efforts will have to be made to reduce the processing costs at all stages of production. Some new concepts or studies which seem promising are presented below.

(i) *Removing organic binders from the green body by extraction with supercritical gases*

Injection moulding and slip casting are important techniques for the forming of engine components such as turbine blades. A new method of removing the binder more efficiently in injection moulding is described here. Figure 4 gives a flowchart of the numerous stages in the injection moulding process with an approximate indication of the time needed for each step (Suzuki & Sasaki 1984). Clearly, the removal of the binder is the rate determining step. Many methods such as thermal (Wada & Oyama 1987) and solvent extraction have been proposed and investigated. Recently, a new method of extraction with supercritical gases was applied to the process and indicated interesting results, although it remains to be developed further. Sumitomo Heavy Industry Co. Ltd. has succeeded in applying this technology to organic binder removal (Nakasima *et al.* 1985) in ceramics. Table 9 summarizes their results at 45 °C and 200 kg cm^{-2} with Al_2O_3 powder compacted samples (25 mm × 15 mm) with stearyl alcohol and stearic acid as binders. Table 9 also includes the results from freon R-12. The results indicate that both fluids can remove more than 80% binder in 2–3 h.

Bench-scale tests have been completed with an auto-controlled system and the apparatus is being used to process small electronic ceramic parts. Progress is promising.

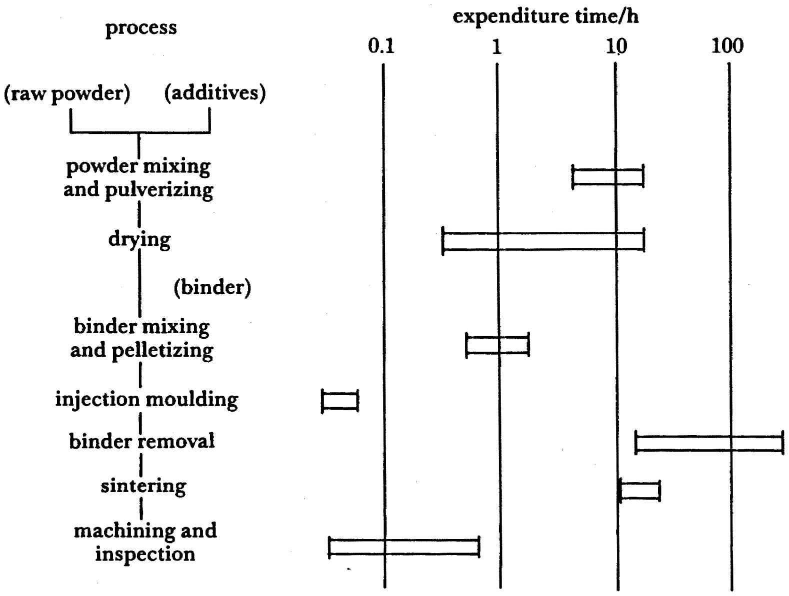

FIGURE 4. An injection-moulding flow chart with estimated time of each step.

TABLE 9. EXPERIMENTAL RESULTS OF REMOVING ORGANIC BINDER FROM GREEN BODY BY SUPERCRITICAL GAS EXTRACTION

binder	fluid	temperature °C	pressure kg cm^{-2}	removal of binder (%)	exposure period/h
stearyl alcohol	CO_2	45	200	70.2	2.2
stearyl alcohol	R-12	120	120	94.7	2.8
stearic acid	CO_2	45	200	85.0	2.5
stearic acid	R-12	120	120	99.0	0.7

(ii) *Joining*

Only a few reports have been made on welding, although several industries are considered to have a high level of technology as it is very important in practice. The Government Industrial Research Institute in Osaka (GIRI-OSAKA), the Tokyo Institute of Technology (TIT), the Nihon Kokan Co. Ltd. and the Production Engineering Dept. of Hitachi Ltd. have studied electric discharge welding (Koyama *et al.* 1986), the brazing of ceramics (Boadi *et al.* 1986), and diffusion bonding methods of ceramics to metal (Yamada *et al.* 1987*a*, *b*), respectively, and are obtaining useful results in each area.

5. SUMMARY

Many predictions of the growth of the fine ceramics market in Japan have been made by MITI, Toshiba Corp., The Mitsubishi Bank, The Long-term Credit Bank of Japan, Ltd, etc., and figure 5 gives a prediction by MITI. Figure 5 also indicates recent actual results (line with crosses). To increase the production of fine ceramics as predicted, it will be necessary to achieve successful developments in many related technologies. However, unless the technological problems of some important processes are solved, progress will be delayed for a considerable time. One cannot say that many people are afraid of the delay. Judging from the current situation as described above, the following technological prospects may be deduced.

(1) Scientific knowledge of surfaces and interfaces such as the grain boundary and pore surface will increase and rapid progress in the productive process technology of electronic (or functional) ceramics will persist into the 1990s, although these ceramics are expected to be substituted to some extent by organic polymers.

(2) The challenges of brittleness and lack of reliable mechanical strength, which are considered to be characteristic of all ceramics, cast a slight shadow on engineering (or structural) ceramics. Recent developments are encouraging, however, with, for example, the commercialization of a ceramic turbocharger by Nissan Corp. Preliminary research and development on various ceramic matrix composites have shown steady progress. Significant advances are expected by the end of the 1990s, especially with particle-reinforced composites and IRP to make pseudowhisker reinforced sintered ceramics that may come to substitute most monolithic ceramics under extreme conditions.

(3) The new ceramics are made from highly purified synthetic and artificial starting materials. Adequate methods of making these starting materials have mostly been established but it is necessary to make the starting material of proper quality to reduce cost and to extend the scale of mass production.

(4) Much of the technology of manufacturing will become mature by the accumulation of

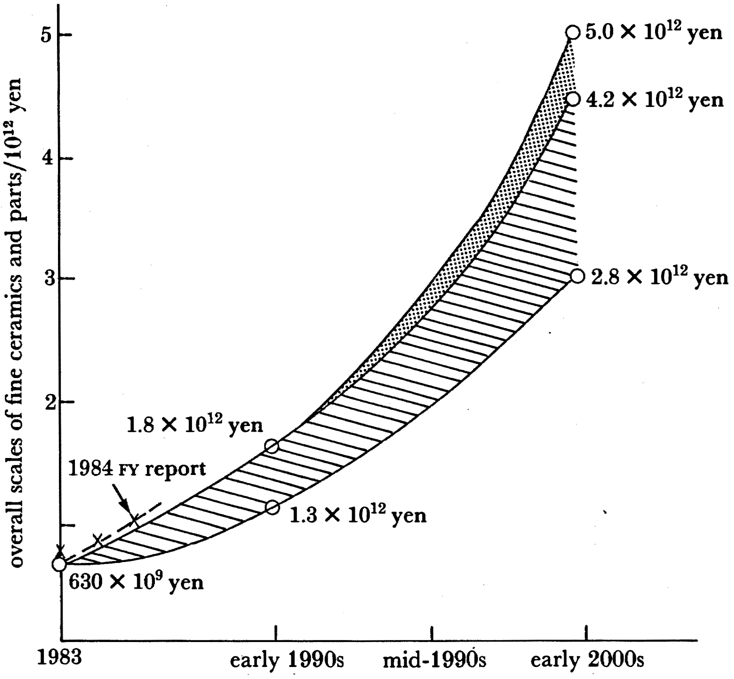

FIGURE 5. Estimates of the scale of the fine ceramics market. Dashed line shows upper limit of estimates taking into account greater growth in parts and technological effects. Shaded area shows scale of the market according to estimates of greater growth in material and parts.

For the fiscal years 1983–1985 the percentages were: electronical, 82.4%; mechanical, 5.7%; thermal, 4.2%; optical, 2.4% (see table 2).

experience. But the technologies of testing and evaluation will not be established in the 1990s because standardization is quite difficult. However, many industries and research institutions are dealing with the problems of design methodology and there need not be special concern.

(5) Because the functions and properties of fine ceramics are intrinsically popular, the needs for these ceramics will increase progressively, even though there will be various types and in relatively small amounts.

(6) Finally, the exchange of information and the avoidance of duplicated research and equipment are necessary. International as well as domestic cooperation should become more active in future. With respect to cooperation, I believe that a competitor is always a good colleague. In other words, it is most important to keep a proper balance between competition and cooperation.

I gratefully acknowledge discussions with Dr M. Mitomo and many friends who kindly gave their valuable data and were helpful in the preparation of this paper.

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Discussion

J. A. Champion (*Division of Materials Applications, National Physics Laboratory, U.K.*). Professor Suzuki mentioned joining techniques for ceramics and included electric discharge welding in a list. Could he please say a little more about this technique?

H. Suzuki. The electric discharge welding is one of the brazing methods in which the electric discharge energy is used as a heat source for the weld region.

Two ceramic bodies to be joined are stacked vertically, and a small amount of adhesive is placed between them under light compressive load. The weld region is preheated homogeneously by two gas flames from both sides with metallic burners that are used as electrodes concurrently. Then, alternative high voltage is applied between the burners so that electric discharge through the flames begins and consequently temperature in the weld region becomes high enough to complete the join.

EXAMPLES OF EXPERIMENTS

ceramic materials tested	sintered silicon nitride
shape	hollow cylinder and plate (thickness *ca.* 6 mm)
adhesives	CaF_2 and caolinite system Si_3N_4 and metal oxide system
applied voltage	60 Hz, 10000 V maximum
current	controllable to 1A maximum
welding speed	several mm min^{-1}
bond strength of the joints (bending strength by three-point bend test)	*ca.* 200–400 MPa at room temperature *ca.* 40–200 MPa at 1000 °C

P. L. Pratt (*Department of Metallurgy and Materials Science, Imperial College, U.K.*). As a target for monolithic ceramics for structural applications Professor Suzuki offered a Weibull modulus of 20 and a K_{Ic} of 6 MPa $m^{\frac{1}{2}}$. Of these the value for K_{Ic} seems too low to be acceptable to design engineers when combined with the high strength levels of which the new ceramics are capable. For the stressed components of automotive engines, the small flaw sizes that this combination entails would seem to be very difficult to detect and to monitor. Has thought been given to this problem in Japan, and how will it be overcome?

H. Suzuki. (1) Silicon nitride ceramics, which are applied to swirl chambers for diesel engines have K_{Ic} of 5.8 and 4.8 MPa $m^{\frac{1}{2}}$ at room temperature and 800 °C, respectively; nitrogen ceramics, which are used as gas-turbine rotor materials for turbochargers at Nissan Motor Co. have K_{Ic} of 6.4 MPa $m^{\frac{1}{2}}$ at room temperature at present.

From these facts, we can understand that it is not impossible to design some machine components with ceramic materials having a K_{Ic} of 6 MPa $m^{\frac{1}{2}}$.

(2) Cautious thought has been given to the problem, related to the small flaw size of the structural ceramic materials in Japan, and several methods applicable to design, to inspections for screening and to reliability evaluation have been established recently for production of ceramic engine components in automobile companies.

An example of the methods of a Japanese company can be found in Kamiya *et al.* (1985).

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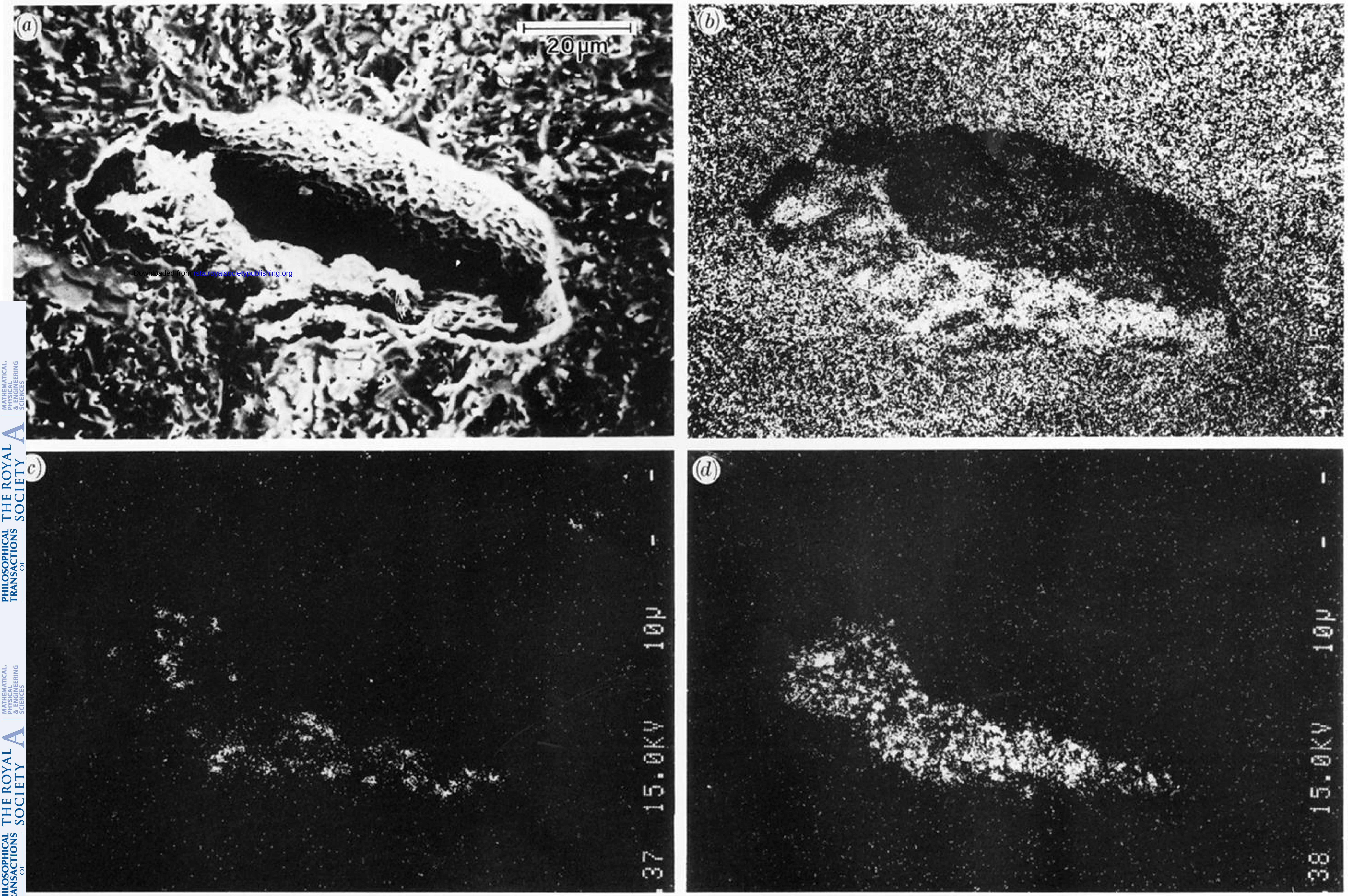
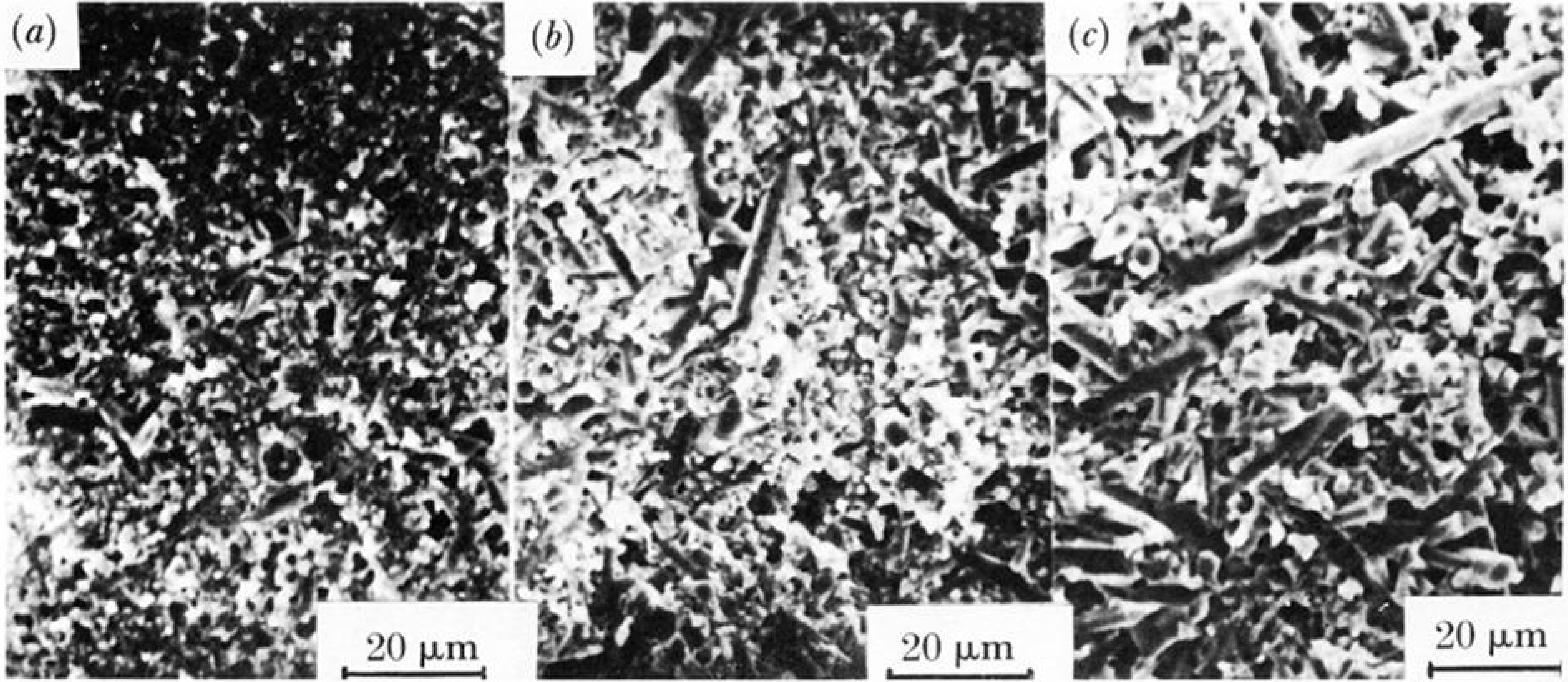
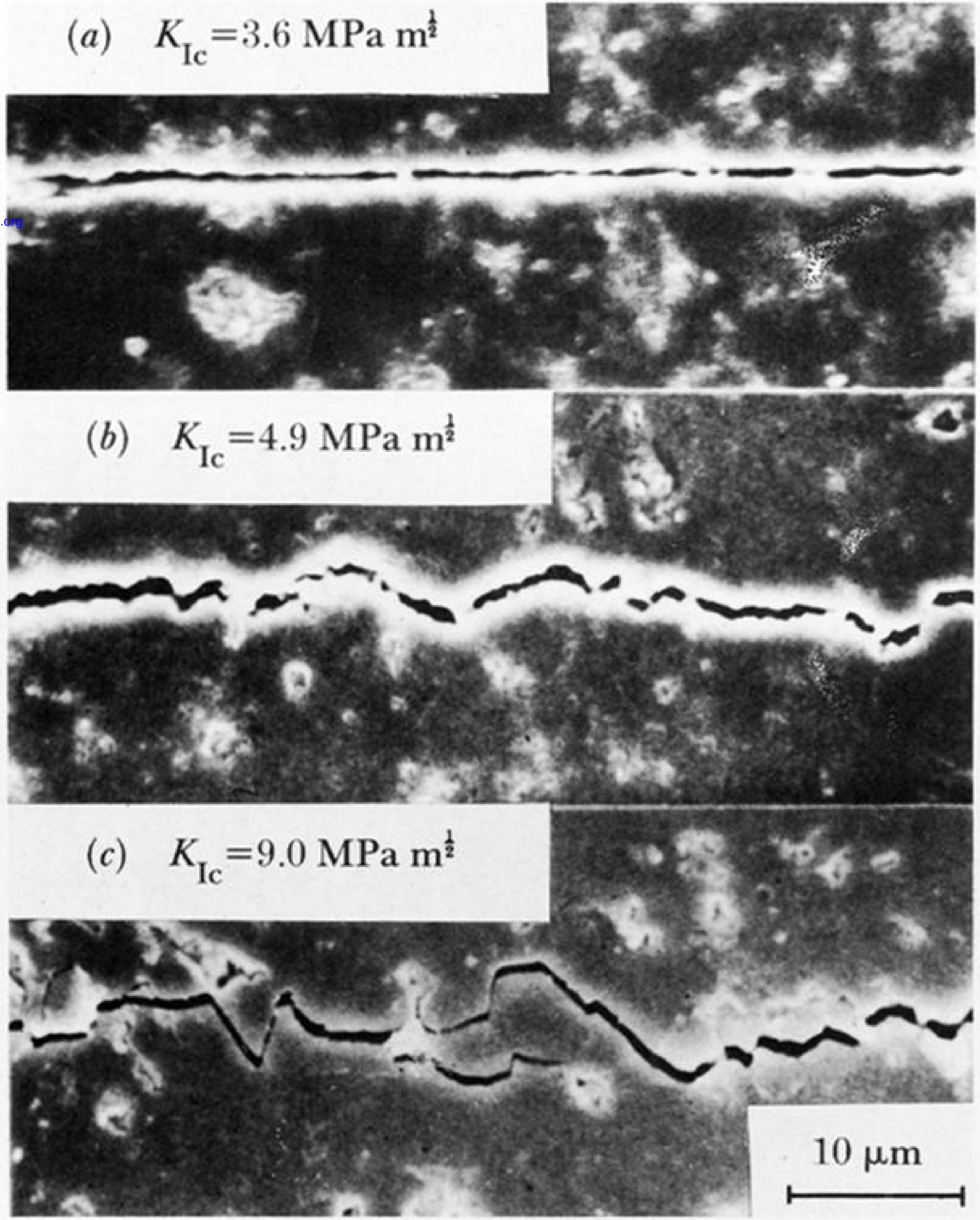


FIGURE 1. Large flaws in SiC ceramics. (*a*) SEM, (*b*) XMA-C (X-ray microscopic analysis), (*c*) XMA-B, (*d*) XMA-Ti.



GURE 2. Fracture surface of Si_3N_4 gas-pressure sintered with 3 % Al_2O_3 and 5 % CeO_2 (percentages are by mass). (*a*) At 1800 °C under 2 MPa, (*b*) at 1900 °C under 3 MPa, (*c*) at 2000 °C under 4 MPa.



IGURE 3. SEM photographs of crack evolution. (*a*) HP β-sialon, (*b*) GPS Si_3N_4 with 1% Al_2O_3 and 5% CeO_2 at 1800 °C, (*c*) GPS Si_3N_4 with 1% Al_2O_3 and 5% CeO_2 at 2000 °C (percentages are by mass). (HP, hot pressed; GPS, gas-pressure sintered).