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# Seventy ways to make ceramics

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#### Abstract

This is an attempt to classify ceramic manufacturing processes in such a way that the connections to related operations in other industries and to the ancient crafts of antiquity become apparent. The aim is to make it easier for students of ceramic processing to move seamlessly across a terrain that is conceptually integrated and therefore to find solutions to manufacturing problems through creativity informed by a pan-materials taxonomy of processes. This approach veers towards the 'systematic' method of creativity as exemplified by TRIZ but it is important to recognise that in some organisations the 'chaos' approach is also gaining recognition and what at first appears to be an oxymoron; 'management *for* chaos' is gaining acceptance. The relevance of an integrated approach to processing of materials is discussed in relation to the efficacy of the National System of Innovation (NSI).

Keywords: A. Processing; Manufacturing

#### 1. Introduction

On an occasion that honours a person who has demonstrated the capacity to provide leadership, guidance and encouragement to the whole ceramics community, it seems both appropriate and admissible to take an historical and broad perspective of what is often called ceramics 'processing'. A 'process' is "a systematic series of actions or operations directed to some end". The 'end' in a ceramics context, is usually an object which has shape and form or a part of an object such as a coating. So we are really talking about making shapes. Ceramics cannot be melted, forged or machined quickly so ceramics processing is a bit more of a nuisance than it is for other materials! Much of this discussion is concerned with the taxonomy of ceramics processing and hence with how we teach it to the next generation of scientists and engineers but closely allied to classification is the question of creativity and inventiveness and how they are fostered. Then arises the question of how well does the NSI foster innovation by transmitting needs to scientists and engineers and how well does it guide the outputs of scientists and engineers into commercial practice when it comes to ceramic processing. These three issues; classification, inventiveness and practice are closely linked in any area of scientific activity but

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0955-2219/\$ – see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.jeurceramsoc.2007.12.015 in ceramics processing the connections could be made much clearer.

As will be demonstrated and as is appropriate for this auspicious occasion, there are at least seventy ways to make ceramics. If we are paying attention to ceramic science and technology as it is delivered to students, we should perhaps be slightly dissatisfied with the structure of ceramic 'processing' as a subject and we should take little comfort from the fact that the same accusation can be levelled at the other materials sciences. Should science and engineering students have to learn manufacturing processes in much the same way that student linguists learn a new language? Should they be expected to memorise a long list of obscure words and acronyms for processes that are apparently disconnected both from each other and from others used in diverse industries? It is probably fair to say that the descriptions of processes are often deliberately veiled in ambiguity to help defend proprietorship but this does not account for the problems of taxonomy. There is a suggestion that even textbooks in manufacturing present somewhat confusing taxonomies of processes. Some textbooks on manufacturing processes have identifiable allegiance to restricted classes of materials. It is arguable that such allegiance has no place in a modern Materials Science, the unity of which allows for a common currency in materials processing. Are we reluctant to do joined-up science and engineering when it comes to delivery on processing? Science is about making connections. Inventiveness is about making connections.

## 2. Taxonomy in ceramic processing

Students of materials often learn manufacturing pathways in the form of lists of disconnected processes. There is no recognition that the processes might have some relationship to each other and to processes in other industries by a network of intersecting pathways. There is no idea that they may be connected rather like a family tree to antiquity or indeed that they might share 'genetic defects'. Students learn these processes in the same way a child learns to spell and it must seem that they were plucked out of thin air unencumbered by antecedent and unconnected by principles. To the student, processing is all about memory work; names to be learned for an exam, names soon to be forgotten.

The real situation is not like that. Actually, ceramic processing has learnt from and borrowed procedures from other industries. I use the term borrowed deliberately because ceramicists have often given those processes back with a far higher level of understanding than attended them upon receipt. They have paid their interest on these loans in the form of enhanced knowledge.

When it comes to textbooks on manufacturing processes, the choice of chapter headings reveals just how problematic is the taxonomy even though these are mostly books that disclose no allegiance to a specific materials class in the title. One of the pitfalls of education is that if the same subject is taught under different course unit headings, the students tend to see it as two separate subjects. The main aim of undergraduate students at lectures is to get their notes into the right folders. So a course on materials processing delivered by a metallurgist can be seen as quite a different subject to a course on materials processing delivered by a ceramicist. Undergraduates tend to perceive knowledge as intrinsically fragmented because that is the way the assessment system is structured; students are tactically alert!

One of the most direct and standard classification of materials processing is found in Ghosh and Mallik.<sup>1</sup> After a chapter on 'Properties of Materials' we get the straight unambiguous four-way division into 'Casting Processes, Forming Processes, Machining Processes and Joining Processes'. There follows an added chapter on 'Unconventional Machining Processes' which could have formed part of 'Machining' if the focus had not been so heavily metallurgical. DeGarmo et al.<sup>2</sup> follow the same approach except that casting and forming are thrown together in the same chapter. They differ at a fundamental level because casting involves a state change and deformation processing does not. One text gives the four classifications in relation to metals and then adds, to a chapter list of different processes, the heading "Plastics" as though this is a new process.<sup>3</sup> Kalpakjian<sup>4</sup> does much the same thing, separating both 'Processing of Polymers and Reinforced Plastics' and 'Processing of Powder Metals and Ceramics' as though these involve fundamentally different processes to those used for metals. Lindberg<sup>5</sup> puts "Plastics and Adhesives" and "Powder Metallurgy" into separate headings. This means that adhesive joining is seen as distinct from other joining processes which have already been described in a separate chapter and that powder processing must sit on its own. Alexander et al.<sup>6</sup> are keen to keep to the four standard divisions but have a problem in how to include powder processing,

which some texts on manufacturing forget to mention. They do it rather cleverly by redefining the states of matter to give a chapter headed "Forming from the liquid and particle state". The justification is obvious; powder suitable for compaction flows like a liquid (having a low angle of repose) into a die (cf. mould), has a free volume comparable to that of a liquid and loses free volume appropriately when it "solidifies" by compaction. Perhaps it is a meta-liquid? The student needs to remember that the analogy does not stretch very far; liquid flows more slowly in a pipe as the pipe gets longer, powder flows more quickly.<sup>7</sup>

In the classification that follows, the four basic divisions are kept and treated as universal for all materials, as indeed they are at a conceptual level. Compaction processes are placed in with casting using the meta-material, free volume argument but forewarning students not to go treating powders as fluids in general. The freeforming processes are separate but it is pointed out that they can individually be loaded into the four classes (albeit with some conceptual acrobatics).

#### 3. Inventiveness: serendipity or systematic thought?

Shaping ceramics continues to provide challenges to the scientific community especially as computer controlled methods open up the capability for macro and microstructure design and for computer control of 3D functional gradients. There is a popular idea that inventions are plucked out of thin air, unconnected to previous ideas, uninformed by organised thought and equally accessible to all. The open access of the patent protection procedure, at least in principle, is a motivating force in our economic system and there is plenty of evidence to support the serendipity of invention. To argue from such examples towards a general rule of the dependence of invention on serendipity would, of course, be to use the fallacy of converse accident. Indeed, just as there are some who claim that Shakespeare's plays can be reduced to seven themes, so too there is an idea that inventions have their own taxonomy. Booker<sup>8</sup> puts forward the idea that most stories ever written can be reduced to seven plots (Overcoming the Monster, Rags to Riches, The Quest, Voyage and Return, Rebirth, Comedy, Tragedy). The arguments are complicated and the book is substantial as Booker searches for order in apparent chaos. What is relevant for us working in ceramics processing is that others have done the same for the patent literature.

The soviet engineer Genrich Altshuller believed that a 'method for inventing' must exist and during his work in the 1940s for the Russian Navy, began to develop a method that has become known as TRIZ (the acronym for Teoriya Resheniya Izobretatelskikh Zadatch) or 'Theory of Inventive Problem Solving'.<sup>9,10</sup> His finding was that invention is the removal of technical contradictions with the help of principles that can be identified; he logged 40 such principles. TRIZ is one of several systems for invention and is probably the most well-known. Vincent et al.<sup>11</sup> show how TRIZ can be used to adopt in technology, methods used in nature, so-called biomimetics but they point out that the database contains limited biological knowledge. Vincent et al.<sup>12</sup> go on to show how the TRIZ system can be extended.

The important idea for our work in ceramics processing is that Altshuller recognised that the principles he found when analysing patents from one industry were applicable to problems in another. He presents an idea of the universality of technical problem solving which shows a striking similarity to the ethos expressed in Richard Feynman's well-known 'tapestry' metaphor: "Nature uses only the longest threads to weave her patterns, so that each small piece of her fabric reveals the organization of the entire tapestry".<sup>13</sup> The issue for those of us in education is whether these tenets can be used to guide the career development and peer structures of our systems of scientific and engineering education and professional advancement, part of the aim of which is to contribute indirectly to the NSI. It can sometimes seem that our systems favour intellectual isolationism. Since we embrace the principle of excellence through specialisation and we have a well-trenched system of disciplines supported both by the universities and professional institutions, structures not noted for their fluidity, it is quite possible for practitioners in one subject area to become progressively separated from those in another adopting the caricature of a tribal identity. The need to ameliorate these schisms is now recognised and the interdisciplinary efforts of the professional institutions and the initiatives of research funding councils go some way to broadening our outlooks. It is fair to say that the ceramics processing community has, over the last two decades, embraced the organic and physical chemistry of surfactants, dispersants and polymers in its quest to control particle behaviour; some ceramicists have become colloid and polymer scientists and the community has benefited.

TRIZ and similar 'systematic' approaches to creativity appeal to the science and engineering community partly because of their organised nature but there is another putative route to inventiveness and originality that is gaining popularity; the 'chaos' approach. The transfer of ideas or principles between subjects and between industries is considered to be due to serendipity and to depend on a host of unpredictable prompts and interactions. This does not mean that we are helpless to accelerate the process. Advocates of 'chaos in organisations', 14-16 promote the guiding principle of "management for chaos" in contrast to the obsolete "management of chaos". Changing work patterns, a flux of new interactions between people, the appearance of meeting rooms and tea rooms, the emergence of UK research council's 'sandpits' are signs that the organisation recognises that new ideas nucleate on the edge of chaos. Encouraging and exploiting chaos is seen by some as a positive challenge to the established organisational structures. Surprisingly, the universities have been quite slow to adapt, often being hamstrung by rigid budgetary structures and, in the UK, by national competitive research assessment "exercises".

Fascination with the source of creativity has spawned a large and diverse literature among which one of the more cautious analyses has identified three important characteristics.<sup>17</sup> The first is "openness to experience" or "extensionality" in which a person accepts stimuli without distortion caused by emotional defensiveness. This category includes the well-known 'toleration of ambiguity' concept, namely the ability to accept contradiction without the discomfort that stimulates a need to find a quick answer, even if it be a wrong answer. This is an idea that also pervades John Holt's 'How children fail'.<sup>18</sup> The second is "internal locus of evaluation"; the creative person is deemed to be relatively unaffected by praise or criticism. It is sometimes said that their 'centre of judgement' lies within the 'boundaries of self'. In some assessments this appears as 'disregard for authority' which can be misleading; the authority exerted by peers can be forceful yet imperceptible. An example might be the way in which research funding 'priorities' sometimes lurch from one theme to another under the 'authority' of collective thought and by analogy with fashion. The third is "ability to play with elements or concepts"; On this, Rogers<sup>17</sup> waxes lyrically and is worth quoting in full. "... the ability to play spontaneously with ideas, colours, shapes, relationships, to juggle elements into impossible juxtapositions, to shape wild hypotheses, to make the given problematic, the express the ridiculous, to translate from one form to another, to transform into improbable equivalents.".<sup>17</sup> The literature on creativity is so vast and often so bizarre that conventional science and engineering departments are reluctant to introduce it at undergraduate level but it is rapidly accessing the research schools.

# 4. Intellectual integration and the NSIs

Part of the reason for the state of materials processing is historical and is to do with the essential difference between the aims and objectives of university scientists and manufacturers when they engage to do ceramics processing research. The scientist is primarily interested in *causation* and is asking questions of the external world; "Why does it happen?", "Why is it cracked?" Why is it full of holes?". The manufacturer is primarily interested in goals and purposes and is making statements like; "We need to make this happen and we need to stop this happening", "We want this to happen faster". There is a tragic sense in which the scientist is listening to an external world but can hardly hear it while the manufacturer is instructing an external world which is recalcitrant in inattentiveness. It is no wonder that when these two meet there are often difficulties in devising a joint research strategy that will fulfil the business and professional goals of each. On the one hand, these are matters of personal interaction to be resolved by individuals but viewed collectively, they define the effectiveness of the National System of Innovation (NSI).

The efficiency of National Systems of Innovation (NSI) is a controversial issue because in western cultures, NSIs can only be debated against a background context of state control vs. the free-market, some arguing that government agencies should not interfere with the way businesses develop their technologies. This dualism makes it difficult to achieve the co-operation needed for effective functioning of an NSI. In some of the advanced free-market economies that are less ideologically driven, NSIs are highly integrated and productive. The NSI in the UK comprises an association of Manufacturers, Investors, the Department of Innovation, Universities and Skills, the Universities, the Research Councils, Charitable Trusts such as the Leverhulme, the Professional Institutions and the Research Associations each of which has its own remits and

# Table 1

Casting/solidification processes for ceramics<sup>a</sup>

Process	State Change	Comments	Ref.
Slip Casting &	Capillary removal of liquid	Liquid state formed by suspension.	22
1	into porous mould.	Complex shapes possible.	
drain casting	Capillary removal of liquid	Liquid state formed by suspension;	23
Filter pressing	Removal of liquid into porous	Ideal for drying powders. Limited use	24
ritter pressing	Kenioval of inquid into porous	Ideal for drying powders. Ellinted use	24
	fabric assisted by applied	for shaping.	
Pressure filtration/slip	Removal of liquid into porous	Automated moulding process derived	25,26
pressing	mould assisted by applied pressure.	from slip casting.	
Centrifugal Casting	Removal of liquid into porous	Derived from slip casting.	27,28
(1) - Charles and The Science Constraints and the Science Scie	mould assisted by spinning.		
Electrophoresis	Separation of solid from liquid	Suitable for coatings and shells.	29
	by electrokinetic effect.		
Soft mud process	Yield stress of paste then	Traditional method of brick making by	30
	evaporation of water.	casting paste into wooden mould and	
		drying.	
Tape casting	Removal of solvent from	Liquid suspension cast onto moving belt	31
Freeze Casting (water) &	Solidification of water in the	and dried. Moulding process that can be assisted by	32 33
Treeze Casting (water) &	suspension	freeze drving	32,33
freeze Casting (organic)	Solidification of camphor &	Binder is removed by sublimation.	34,35
0.00	related compounds		
Injection moulding	Solidification of polymer or	Very complex shapes possible.	36,37
• and the second second states •	wax.		
Low pressure injection	Crystallisation of wax.	Uses lower pressures and less expensive	38
Heated sprue injection	Solidification of polymer or	Allows complete solidification without	30-
moulding	wax	gate sealing	41
Insulated sprue injection	Solidification of polymer or	Prolongs gate solidification.	42-
moulding	wax.	0.0	43
Open ended injection	Solidification of polymer or	Allows control of preferred orientation.	44
moulding.	wax.		
Modulated pressure	Solidification of polymer or	Assists in moulding large sections.	45-
Transfer moulding	Wax Crosslinking of thermoset	Moulding process suited to	47
Transfer moulding	Crossninking of thermoset	thermosetting resins & hence ideal for	40
		carbides.	
Coagulation gel casting &	Flocculation of dispersed	Allows concentrated aqueous suspension	49
	suspension by pH change.	to change state by changing inter-particle	
a share an institution and another	Balamaniantian of a soluble	forces.	50.51
polymensation ger casting	monomer	he used in shaping	30,31
Colloidal isopressing	Pressure overcomes repulsion	Excess liquid is absorbed into powder	52
1 5	between colloidal particles.	added to RTV mould cavity.	
Vibraforming	Flocculation by pH change.	Reshaping of concentrated colloid by	53
		vibration in a mould.	
Replication foaming	Drying of slurry by	Slurry is cast onto the walls of a	54-
Lithographie	Any state change	Mould is made by electroplating a	57
Galvanoformung	This state change.	patterned polymer substrate (resolution	
Abformung (LIGA)		is ~1 μm).	
Single crystal growth	Crystallisation.	Controlled solidification from a melt.	58,59
Die pressing	Formation of particle contacts.	Collapse of free volume under uniaxial	60
Call is a static managine	Environtian of montials contacts	pressure in a die (mould).	(1.(2
Cold isostatic pressing	Formation of particle contacts.	Collapse of free volume under triaxial	61,62
Roll compaction	Formation of particle contacts	Compaction to produce continuous	63.64
ron compaction	r officient of particle contacto.	sheet.	00,01
Hot pressing	Neck growth and sintering	Limited shape capability but produces	65,66
	under pressure.	high density with low grain growth	
Hot isostatic pressing		under uniaxial pressure.	67
	Neck growth and sintering		
	under pressure	Shaped elsewhere; confers high density;	
Class assemic:	Annuach to alter transitio	cladded or cladless methods.	68
Glass ceramics	Approach to glass transition	All moulding methods for glass apply.	08
CVD/ PVD	Solidification on a substrate	Designated a solidification process	69 70
	from vapour phase	because of fluid-solid transition.	0,70
Self propagating reaction	In situ chemical reaction to	Limited shape forming.	71
synthesis	produce ceramic		

<sup>a</sup> These tables are not exhaustive of the processes in each class.

targets. Various knowledge transfer (KT) initiatives attempt to bring these diverse organisations together.

It is well known that NSIs in western developed nations have limited efficacy in stimulating manufacturing growth and the Peters study<sup>19</sup> highlights this by using as a case study, the route to market of TFT-LCD displays, a journey that took nearly 40 years. It is an interesting case study because the development of both thin film transistors and fast liquid crystals were necessary but neither was sufficient. The aetiology of failure for several western companies that participated in the early work is the so-called 'Hayes and Abernathy syndrome'<sup>20</sup>; short term cost reduction in existing product lines rather than long term development of technological competitiveness, an emphasis on early return on investment and a distancing of senior management from the technological base giving rise to 'management by numbers'. It is likely that in assessing the history of high technology, those names, Hayes and Abernathy, will pop up again and again in an attempt to account for missed opportunities. Japanese and Korean NSIs were more integrated and it is from those nations that displays emerged into the market place. There is a sense in which the Peters study holds up a mirror to show the extent of fragmentation of some NSIs.

Defermation mode

Table 2

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Deformation 1	processes
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# 5. Classification of the 70 ways

Tables 1–5 are not intended to be exhaustive of the multiplicity of processes that have and are being used to shape ceramics but they do aim to portray a classification that can be used to identify similarities. Furthermore, the classification can be arranged to lead to new methods of forming.

#### 5.1. Casting/solidification processing

What most textbook authors on processing omit is that all the processes listed under *casting* in Table 1 follow the same principle but that the method of state change can vary. It does not much matter that the state change mechanism differs because in each case we have usually one surface (the mould) which can even be a flat sheet, which will define the final shape; and that is casting. This is why replication foaming appears in this section; topologically, there is one surface upon which the slurry is cast as in tape casting. In the classification, the state change is a second order identifier but it should be remembered that in each state change method, free volume at some level of structural hierarchy generally (but not always) decreases. Free

DC

Frocess	Deformation mode	Comments	Ref.
Pinch forming/slab forming/throwing	Shear and elongational flow of paste.	Tradition clay forming methods.	72
Jiggering, Jolleying	Shear and elongational flow of paste.	In jiggering, a pattern defines the inner surface; in jolleying it defines the outer.	73
Coil forming	Shear and elongational flow of clay.	Origin of extrusion freeforming.	74
Extrusion	Shear flow of suspension.	Complex cross sections are possible eg for catalyst supports also used for brickmaking in the wirecut process.	75-77
Extrusion of helices	Shear flow of polymer- based suspension.	Able to make springs and windings.	78
Co-extrusion	Miniaturisation of shell-core structure by shear flow.	Able to make complex cross sections using fugitive cores.	79-81
Vacuum forming	Elongational flow of polymer-based suspension.	Able to make contoured shapes from thin sheet.	82
Blow moulding	Elongational flow of polymer-based suspension.	Able to make complex tubular structures.	83
Film blowing	Elongational flow of polymer-based suspension.	Makes thin film.	84
Fibre spinning	Elongational flow of suspension.	Forming fibres.	85,86
Spinning and Bending	Elongational flow of polymer-based suspension.	Analogous to metal spinning.	87
Gel foaming	Elongational flow of polymer solution.	Foam is set by polymerisation of water soluble monomer.	88,89
Expanded ceramic foam	Elongational flow of polymer-based suspension.	Analogous to expanded polystyrene.	90
Suspension foaming	Elongational flow of polurethane suspension.	Foam is set by polymerisation of PU.	91
Superheated extrusion foaming	Elongational flow of superheated starch.	A method drawn from food industry.	92
Ceramic foam from protein solution	Elongational flow of aqueous solution.	Foam is set by denaturation of protein.	93
Super-plastic forming	Plastic deformation mainly by grain boundary sliding.	Suitable for fine grain ceramics above $0.5 T_m$ .	94-96

Commente



Fig. 1. Changes in specific volume on solidification of a ceramic injection moulding mixture. The specific volume change for the organic vehicle is 5.8 vol.%. This is lowered by adding atactic to isotactic polypropylene. (1) No ceramic powder, (3) 40 vol.% powder and (5) 51 vol.% powder.

volume as defined by Haward,<sup>21</sup> decreases by about 5% in the crystallisation of metals and by slightly more in semicrystalline polymers. Fig. 1 shows the specific volume changes on melting a ceramic injection moulding blend, state change is controlled by the reduced crystalline fraction in the polypropylene. Thus injection moulded semicrystalline polymers and most metals undergo a phase change on solidification but amorphous polymers such as atactic polystyrene, oxide glasses and glassy metals change state by an increase in viscosity at or near to a glass transition. In reaction injection moulding, free volume generally decreases by chemical reaction and the change is slightly lower. Fig. 2 shows a modern injection moulding machine; its principle of operation is the same as that of a metal die casting machine. The free volume change often produces shrinkage defects and they appear in large metal sand castings, die castings and injection mouldings. If this was a taxonomy of living things, we would call these genetic defects! Another 'genetic defect' is that wherever state



Fig. 2. A modern injection moulding machine with wear resistant barrel insert for ceramic injection moulding; the principle is similar to that used in metal die casting; injection moulding is a casting process.

change advances from the defining (mould) surface and there is a free volume change, residual stresses develop.

In slip casting, state change is achieved by phase separation by capillarity and particle interstitial free volume decreases by ~35%. In tape casting, state change is by evaporative phase separation and the free volume change is about 25% as solvent is lost. In compaction, state change is due to the collapse of free volume induced by pressure and represents the difference between tap density and compact density, being typically around 20%. In slip casting, tape casting and compaction, the free volume collapse is often non-uniform throughout the body so that deformation occurs on sintering. In slip casting, the casting rate is parabolic with time so the first layers cast quickly with lower packing efficiency. In compaction, the non-uniform packing is due to pressure drop throughout the section and the density gradient is the reverse of slip casting, being higher near the plunger wall.

In the coagulation casting processes, state change is by flocculation, often induced by change to pH. Electrophoresis, like slip casting, involves phase separation but unlike slip casting, the liquid is stationary while the particles move. CVD and PVD are treated as casting processes because they involve a gas-solid state change by analogy with a liquid-solid state change and can produce macroscopic objects of several millimetres in thickness. Sputtering on the other hand is treated as a joining process because it rarely produces a macroscopic object; the thin film generally being dependent on the substrate to which it adheres. Self-propagating reaction synthesis is included even though it has limited shape-forming capability; methods of controlling shape particularly with foamed SPRS have been demonstrated. On the other hand, reaction bonding is not included because it requires one of the extant shaping methods. Sol-gel appears in the guise of individual shaping methods because it is really a state change mechanism not a shaping process per se.

All solidification processes have an associated state change and, conversely, it should be possible to derive several casting processes for every mechanism of solidification state change. Viewed in this way there is no need to treat the principles of solidification processes as being different for different materials. Furthermore, there is little technical justification to do so; if our classification has an empty box in the list of state changes, it may be that a new process is waiting to be found!

# 5.2. Deformation processing

Methods of changing the shape of an object by plastic deformation appear in ceramics processing in several disguises (Table 2). Superplastic forming allows some fine-grained ceramics to be forged at temperatures above 0.5  $T_m$  but where this is not possible, the deformation can be applied to a ceramic suspension where it is the continuous phase that deforms if permitted by the displacement of particles. The boundary between deformation processes and casting processes becomes blurred in the case of shaping of glasses or amorphous polymers where the distinction between solid and liquid is some arbitrary viscosity value. Deformation can also be used to shape pre-ceramic polymers, often by elongational deformation as in fibre spinning;

Table 3	
Machining/material	97-108 removal

Process	Comments	Ref.
Diamond machining	Using diamond or cubic BN particles in metal matrix.	97
Ultrasonic machining	Usually used to enhance abrasion.	98
Plasma-assisted machining	Local heating to enhance conventional cutting.	99
Fluid jet erosion	Best suited to coarse microstructure eg cementitious materials.	100
Electrodischarge machining &	Mainly used for conducting ceramics.	101,102
Electrochemical machining	EDM with electrolyte.	103
Laser Machining	Fine detail and smooth surfaces are now possible.	104,105
Cold pressing and machining	Conventional machining of compacts.	106
Thermoplastic green machining	Conventional machining of powder + binder.	107
Turning	Used by the potter on leathery clay.	108

# Table 4

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		•			

Process	Mechanism	Ref.
Metallization and brazing	Metallization of ceramic/ partitioning of glass and brazing to	
	metal/glass layer.	
Direct brazing/reactive	No metallized layer; oxidation/ reduction reaction at interface.	112-115
brazing		
Diffusion bonding	Local creep deformation permits intimate contact at asperities.	116,117
Glass sealing	Oxide glass used to replace metallic brazing filler.	118
Adhesive bonding	Low temperature (<200°C) applications.	119
Mechanical joining &	Use of compliant layers.	120
Shrink fitting	Mechanical joints based on differential thermal expansion.	
Co-sintering	Development of interfaces during same-rate sintering.	
		123
Solvent joining before firing	Polymer welding of a suspension.	124
Sticking up	Used by the potter to join clay before firing.	125
Butt fusion welding before	Polymer welding of suspension.	126
firing		
Ultrasonic welding before	Ultrasonic welding of suspension.	127
firing		
Sputter deposition	Adhesion of thin film to substrate.	128

the polymer is subsequently converted to a ceramic. Many of the foaming processes for ceramics involve elongational flow of a powder suspension and are thus distinguished from replication foaming which is casting upon a free surface.

# 5.3. Machining/material removal

The common feature in this class of processes (Table 3) is removal of material from a blank to leave any one of an infinite number of shapes. These are subtractive processes and anything that cuts, abrades, ablates or corrodes provides a potential new process.

# 5.4. Joining

Joining (Table 4) is given a separate category even though most joining processes could be inserted into 'casting' or 'deformation'. Thus the use of metallic brazing fillers or oxide 'solder' glasses can be identified with casting between two surfaces and diffusion bonding involves microscopic plastic deformation, often by diffusional creep, to achieve intimate surface contact by conforming to the asperities of the surfaces. At a macroscopic level joining is treated as a manufacturing process because the final product depends upon the successful assembly of separately manufactured parts. The case of solid oxide fuel cells is a good example to which practically all ceramic–ceramic and ceramic–metal joining methods have been applied during development.

# 5.5. Solid freeforming

Solid freeforming (Table 5) can be defined as the creation of a shape by point, line or planar addition of material without confin-

Table 5 Solid freeforming

Process	Pseudo-dimensional	Ref.
	order of deposition	
Direct ink-jet printing &	point	129,130
indirect ink-jet printing		131,132
Electrostatic atomisation printing	point	133
Screen printing		134-136
Direct selective laser sintering &	line	137
indirect selective laser sintering		138
Direct stereolithography &	line	139
indirect stereolithography		140
Fused deposition of ceramics	line	141,142
Solvent-based extrusion freeforming		143
Multiphase jet solidification		144
Robocasting		145
Laser chemical vapour deposition	line	146, 147
Laminated object manufacture	plane	148
3D Xerography	plane	149
Atom manipulation	point	150



Fig. 3. A model of the maze at Hampton Court Palace made with a Xaar inkjet printer using zirconia and fired at  $1400 \,^{\circ}$ C. The distance marker is 1 mm. The likely applications are for high temperature gas phase microreactors.

ing surfaces other than a base.<sup>151</sup> Fig. 3 shows a sintered zirconia part that was made by ink-jet printing using a state change brought about by evaporation of solvent while Fig. 4 shows an extrusion freeformed ceramic lattice. It would of course, be possible to force each SFF process into one of the four categories because some involve state changes (stereolithography) some deformation (extrusion freeforming) and some joining (laminated object manufacture) but an important concept would be lost. A good example of solid freeforming is the growth of biological systems; indeed SFF processes can be identified with biomimetics. Into which of the other four categories should the fabrication of living things be placed? There is no requirement in this definition of SFF that the shape must be downloaded from a digital computer. The definition deals with the nature of the physical processes of construction, not its morphogenetic encodement. This is also true of other definitions of processes; machining, for example, can be manually controlled or by com-



Fig. 4. This superb regularity is now obtainable with extrusion freeforming. This ceramic structure is made of two-phase calcium phosphate with  $80 \,\mu$ m filaments and  $70 \,\mu$ m gaps and is formed as part of a study of hard tissue scaffolds but similar structures are being used as microwave band gap metamaterials.



Fig. 5. An array of blades made from zirconia by ink-jet printing. Such structures can be used in miniature motionless mixtures in microfluidics for highly corrosive liquids.

puter numerical control but it is still machining and the physical mechanism of material removal is unchanged by the process control method. Living organisms are 'downloaded' in part from 'digital' DNA although it is accepted that a multiplicity of external factors make a significant contribution to morphogenesis.<sup>152</sup> Furthermore, there are examples of solid freeforming that are admitted by this definition that have no digital control whatever. Compare, for example, the array of pillars in Fig. 5, which are made by ink-jet printing droplets of zirconia suspension and then sintering with Fig. 6 which shows columns from the Postojna caves in Slovenia made by deposition of droplets of mineral-rich rainwater. Their shape has been determined by minute surface irregularities that are progressively accentuated by surface wetting followed by mineralization. The rate of build can be as low as 0.1 mm per year<sup>153</sup> (it is often argued that SFF methods are slow). This constitutes solid freeforming in nature just as the plastic deformation of the geological strata under high hydrostatic stress represents deformation processing of ceramics in nature, the weathering of rocks represents one of nature's ceramic machining operations and the filling of fissures by silica is analogous to joining of ceramics in nature. The ultimate in solid freeforming is atom-by-atom construction, now made possible by manipulation in the AFM.

Much of this discussion has emerged from the problems that academicians inevitably become aware of when presenting



Fig. 6. Solid freeforming in nature; columns in the Postojna caves (Slovenia); compare these structures with that in Fig. 5.

ceramic processing to students and the attempt here has been to ameliorate them by dealing in concepts of processing before introducing individual precisely defined processes. This method of delivery still retains lacunae because the processes of interest tend to be 'high technology' or 'state of the art' and these are the ones that command the most interest for students. Their historical antecedents are largely ignored. Science and engineering students, often having dispensed with the study of history in earlier years, find such antecedents to be less relevant to their education. Nevertheless the five basic processing routes have antecedents in the history of human development just as they have antecedents over geological time as expressed above. They are, in a sense, ubiquitous throughout time. The picture is not complete without these historical and geological connections. Essentially, the *learning outcomes* for a course unit on materials processing should include; 'the ability to identify one or more of the five processing routes by which any object, living or dead came into being',

A few examples serve to illustrate such connections. The casting of metals can be traced to 3000BC and used mainly sand moulds. Die casting, under pressure into metal cavities was invented in 1849 and the first polymer injection moulding machines (1872) were just modified die casting machines. The first ceramic injection moulding was carried out in 1937 and is 70 years old as this paper is written. It used modified polymer injection moulding machines.<sup>154</sup> It is interesting to notice that metal injection moulding but now probably more widely used, has come through this historical loop. In a similar context, tape casting is essentially the solvent casting of polymers with added

powder. Solvent casting was largely replaced for polymers in 1949 by tubular film blowing. A similar process has been used for casting lead–tin alloys under a doctor blade as a traditional way to make sheet for organ pipes. Early examples of solid freeforming include masonry, which can be traced to the 4th millennium  $BC^{155}$  and the formation of coiled pots which is first recorded in the 5th millennium  $BC^{156}$  which is an antecedent to extrusion freeforming.

# 6. Concluding remarks

Although each ceramic processing method has detailed and specific steps that distinguish it from others which often serve to confer proprietorship and although the names given to ceramic processes are sometimes obscure, a review of seventy processes reveals that each one falls into one of five classes. Furthermore, these classes include historical antecedents that connect the inventiveness of modern day scientists with the ingenuity of their predecessors. Some of the geological processes also fall into these five classes. This taxonomy has two advantages. It allows students of science and engineering to apprehend materials processes in generic terms rather than by memorising lists of apparently disconnected processes. It also assists in the invention and development of new processes by allowing a pan-materials and pan-industry view of materials processing.

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