A New Bonding Process for Ceramics

REACTION WELDING WITH A GOLD FILLER

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Solid state reactions occurring at the interface between ceramic oxides and gold form the basis of a new means of obtaining strong and vacuum-tight joints in a wide range of synthetic ceramics. Industrial applications of the process are now being evaluated.

A wide range of synthetic ceramics, each designed to meet specific requirements, is now available to the electrical and electronic engineer for use in vacuum tube technology, semiconductor devices, high temperature fuel cells, nuclear engineering and other sophisticated equipment. In some cases, however, their applications are limited by the difficulty of joining them to other ceramic bodies to form composite structures. The techniques presently available for this purpose involve a type of brazing operation in which a metal alloy or a glass is heated to above its melting point, the liquid phase then wetting both surfaces. Unfortunately the wetting angles between most alloys and ceramics are substantially larger than 90° and wetting is most difficult to achieve.

A collaborative research programme initiated by the School of Physical Sciences of Flinders University and the Commonwealth Scientific and Industrial Research Organisation has now led to the development of a new method for bonding ceramics, using thin noble metal foils (1, 2, 3). In this process, in contrast to conventional brazing and welding, no melting is involved.

The mechanism of the bonding process has been shown to result from a chemical reaction taking place at the interface between noble metals and ceramic oxides such as magnesia, alumina, stabilised zirconia, beryllia, thoria, and also quartz and silicate glasses. A striking fact, established by scanning electron microscopy and electron probe microanalysis, is the absence of metal diffusion into the ceramic as shown in Fig. 1.

The process itself consists simply of heating both materials to a specific temperature below the melting point of either component in any compatible atmosphere – usually air or vacuum – and under slight pressure to improve contact. Heating, which can be by any appropriate means such as an induction heater or muffle furnace, ranges from a few minutes to several hours.

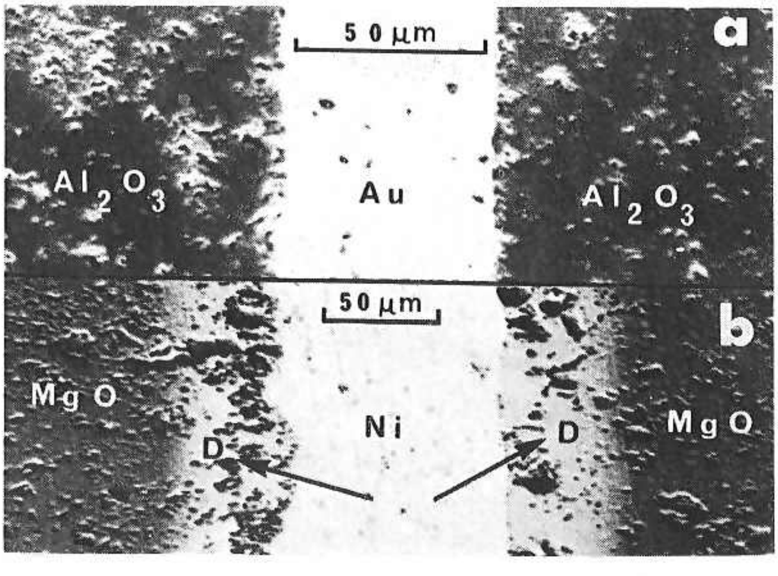


Fig. 1 Energy filtered scanning electron micrographs of reaction-welded composites. The absence of metal diffusion into the ceramic in a noble metal bond is shown in (a), which is a micrograph of an $Al_2O_3/Au/Al_2O_3$ composite. For comparison a nickel-bonded composite with an obvious diffusion region D is shown in (b)

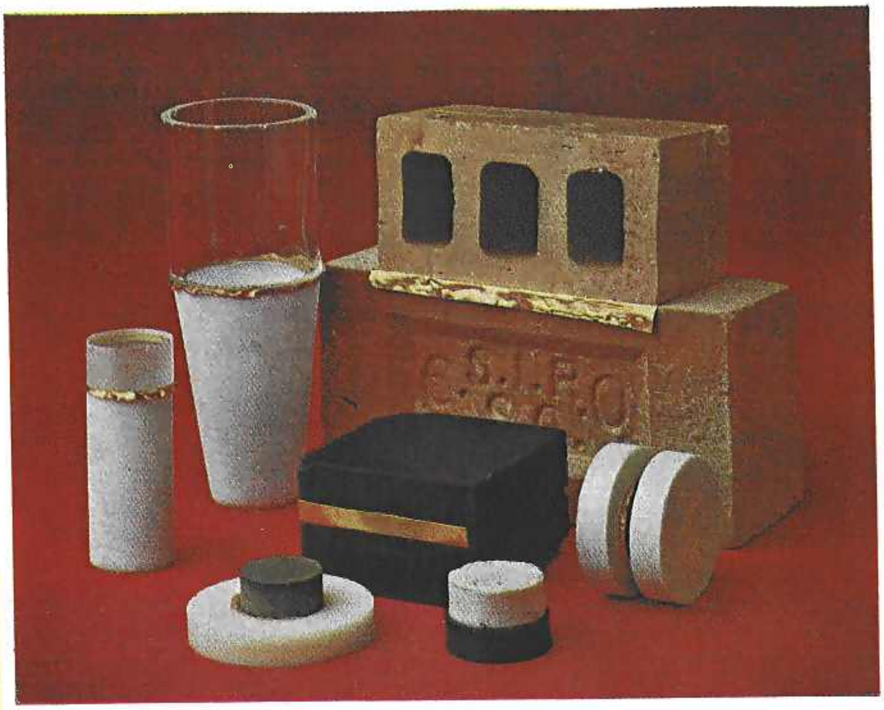
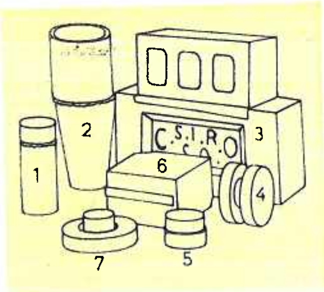


Fig. 2 A group of miscellaneous ceramic components joined by the new reaction welding process, using gold as the jointing medium



KEY: The spectrographic cell (1) comprises an alumina container with sapphire windows; (2) is an alumina crucible reaction-welded to a Pyrex glass tube; the clay bricks (3) merely serve to demonstrate the range of ceramics that can be joined by this process. Item (4) is a beryllia-urania-beryllia sandwich while (5), a beryllia-urania couple, shows the principle of a fission product retentive nuclear fuel element. Item (6) shows a couple made of two different ferrites and (7) a nickel oxide-alumina couple

Vacuum-tight bonds are produced in this way, and their ultimate shear strengths have been found to exceed those of the ceramics being joined.

The illustrations show several examples of reaction-welded ceramics, in each case joined with gold foil about 50 μm in thickness. Gold as a filler is often preferred to other noble metals such as platinum or palladium when the particular application does not demand temperatures above 1000°C. Its high ductility, even in the presence of minor impurities that are inevitably introduced, relieves thermal stresses when materials of greatly differing expansion characteristics are bonded. There is substantial evidence (2) to show that the stresses at the metal/ceramic interface are negligible even on quenching from 1000°C to approximately —100°C in one second. However, thermal expansion coefficients of ceramics can vary by a factor of ten or more.

Gold is chemically compatible with almost all oxides even near its melting point. This makes it attractive as a welding filler for equipment used under corrosive conditions. The spectrographic cell

Fig. 3 A close-up view of the bond in the spectrographic cell made from an alumina container with sapphire windows

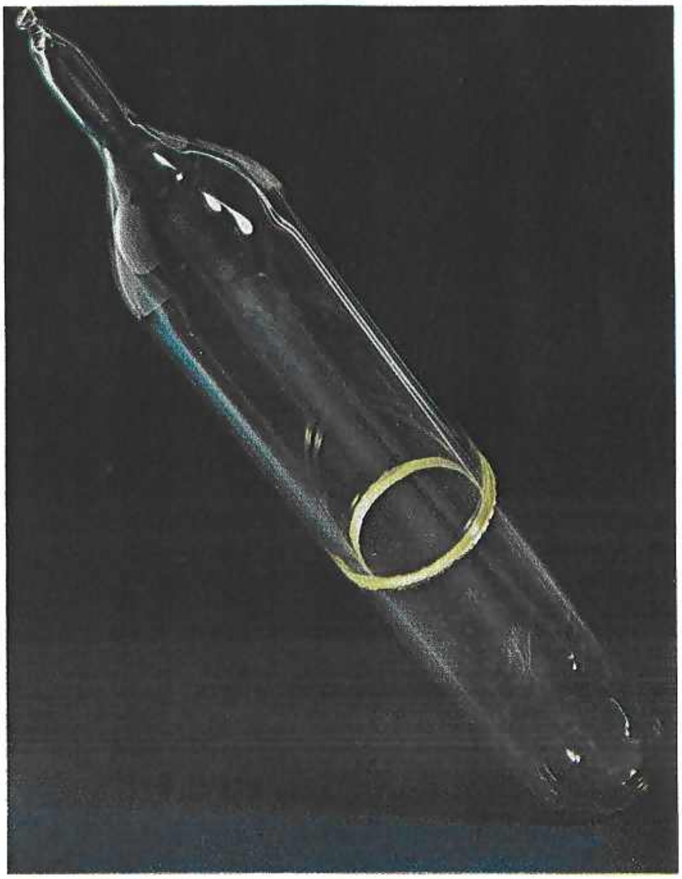


Fig. 4 An example of a vacuum-tight seal made by reaction welding. This Pyrex/gold/Pyrex test assembly has been maintained for eighteen months under a vacuum of 10^{-6} torr

in Fig. 2 (number 1 in the layout diagram) consists of an alumina container with sapphire windows reaction-welded with gold. A close up of the bond is shown in Fig. 3.

Number 2 in Fig. 2 is an alumina crucible reaction welded to a Pyrex glass tube for incorporation in glass equipment as used in high temperature research. The crucible can be simply removed on melting the gold, for instance, by means of a brief burst of power from an induction coil.

It is scarcely suggested that gold should replace mortar in the building industry, but the specimen clay bricks in Fig. 2 (number 3) reaction welded with gold, provide some indication of the range of ceramics that can be bonded by this simple process. Classical ceramics, such as all-clay products for structural and ornamental purposes, so-called super-refractory high purity oxides, as well as many silicates including the glasses fall in this range.

Gold is not an attractive nuclear material. However, the beryllia/urania/beryllia sandwich (number 4 in Fig. 2) and the beryllia/urania couple (number 5 in Fig. 2) reaction welded with gold foil, shows the principle of a fission product retentive nuclear fuel element. This particular fuel-moderator combination has long been under consideration as a heterogeneous fuel element for advanced gas-cooled nuclear reactors. The use of another metal filler in this case would certainly be more appropriate, but the couple shows the scope of the method.

Perhaps the most important area of potential applications is electronic technology. The possibility of making perfect contact between electrical conductors (metals) and insulators (ceramics) is very attractive. This can be done by the reaction-welding process. Non-conducting and high frequency magnetic oxides (ferrites), piezo-electrics, anti-ferroelectrics, and many other special oxides can be reaction-welded. Fig. 2 shows a couple of two different ferrites (number 6).

The compatibility with most oxides is also shown in the welded nickel oxide/alumina couple in Fig. 2 (number 7). These oxides in contact with each other form a range of spinels. Reactions such as these occur widely and prevent the formation of stable bonds between differing oxides by hot pressing, or cold pressing and sintering. The gold foil prevents contact between incompatible oxides and yet bonds both of them very strongly.

Gold is an ideal filler for the making of vacuum tight seals. An example is shown in Fig. 4. This Pyrex/gold/Pyrex test assembly has been maintained for eighteen months under a vacuum of 10^{-6}torr ($10^{-4}N/m^2$).

These are a few examples illustrating the scope of the new reaction welding process and the important place that gold occupies in this new technique. All are 'unfinished' because the use of finished products displaying specific industrial applications is precluded by the present stage of negotiations with the industries concerned. The exact nature of the bond between ceramic oxides and the noble metals is currently under investigation by means of electron microscopy, electron probe microanalysis, radiochemical and several other techniques.

References

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2 H. J. de Bruin, A. F. Moodie and C. E. Warble, *J. Mater. Sci.* (in press)

3 *Australian Patent Appl.* 25585/71

The First Electric Clock

ALEXANDER BAIN'S GOLD CONTACT SYSTEM

A. G. Thomson

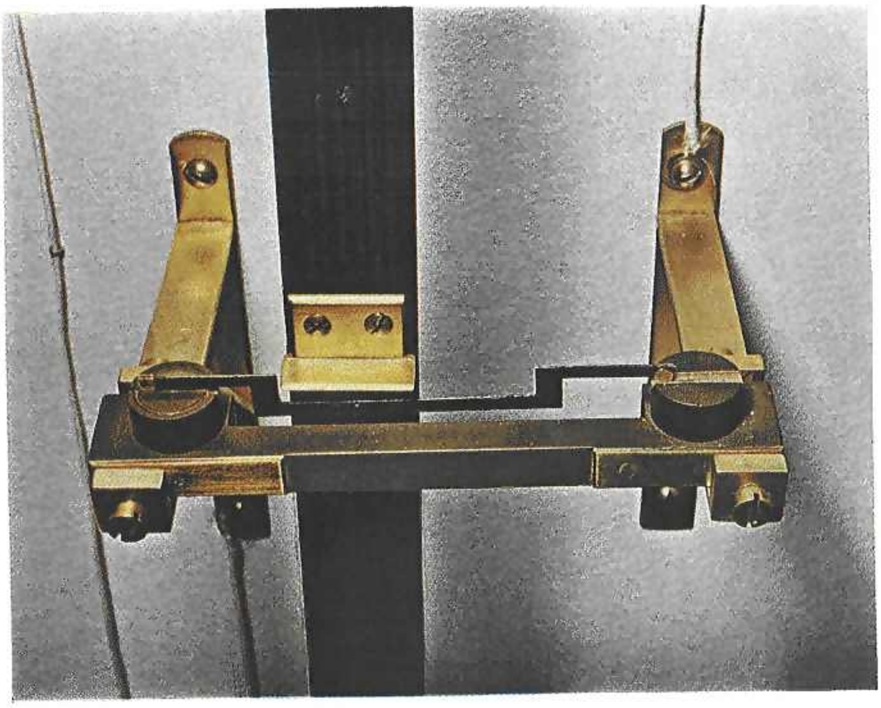
Royal Scottish Museum, Edinburgh

In March 1837 Alexander Bain, a journeyman clockmaker from Wick in the far north of Scotland, came to London at the age of 26 to seek employment. He obtained lodgings and a workshop, first in Wigmore Street and later in Oxford Street, and besides practising his craft he attended lectures at the Polytechnic Institute, having as he later wrote, 'some knowledge of electricity and a strong desire to know more'.

Before long he had conceived the idea of applying the new concepts of electro-magnetism to timekeeping. At that time, of course, the idea that electricity could be carried along wires and could be made to do work had only recently become established and there was very little background knowledge available. However, Bain persisted with his experiments and by the summer of 1840 had designed and built not only a model of an electric clock but also the prototype of a printing electric telegraph.

At this stage Bain began to cast about for someone "to join him in furthering his invention". Now it was in the very month of Bain's arrival in London that Cooke and Wheatstone had agreed to form a partnership, and this uneasy collaboration of two such very

Alexander Bain
1810–1877



The contact system of one of Bain's early electric clocks, now in the Royal Scottish Museum. The slider, impelled by a pin on the pendulum, runs in two grooves, one of which is made of gold and the other partly of gold and partly of ivory, and contact is made only when both ends of the slider are on the metal. This clock is still in good working order

different men had led almost immediately to the filing of their first patent for an electric telegraph. Their achievements had become well known by 1840, and it was not unnatural that Bain should be referred to Professor Wheatstone, who had himself been thinking along the lines of an electric clock. Their first meeting took place at King's College, London, on August 1st, 1840, when Bain produced his drawings of both devices. Wheatstone was interested, and arranged a second meeting at his house in Conduit Street for August 18th for Bain to bring along his models. A vague arrangement was entered into at this meeting, under which Wheatstone paid Bain £5 for his model of the printing telegraph, to be followed by £50 if it became commercially profitable, but advised him to postpone all work on the electric clock.

Unfortunately it was from this meeting that there stemmed a long and embittered controversy as to who was the true inventor of the electric clock. Bain, with his friend John Barwise, the well known chronometer maker, filed his patent—a lengthy and complicated specification—on October 10th and it was granted, as No. 8783, on January 11th, 1841. In the meantime, on November 26th, 1840, Wheatstone exhibited an electric clock at the Royal Society!

The argument and counter-argument raged for some years and involved recourse to the Courts, where it was established that Bain was the first to devise an electric clock. One result was that he was appointed manager for Scotland of the Electric Telegraph Company, which was a Wheatstone foundation, and on the face of all their clocks was to be engraved "A. Bain, Inventor".

Bain was the first to maintain a clock pendulum in motion by means of electromagnetic impulses. The sequential switching to energise the coil was achieved by means of a cranked bracket actuated by the pendulum and rubbing on an ivory or ebonite block in which were inlaid contacts of gold. The actual motion was induced by the attraction of a sequentially energised coil which formed the pendulum bob and which swung over a group of small permanent magnets enclosed in a brass tube.

Bain had chosen perhaps better than he knew in his selection of gold as his contact material. Though perhaps rather soft, its freedom from oxidation and its low electrical resistance combined to give success to an electrical circuit where losses had perforce to be kept to a minimum.

In the Royal Scottish Museum there are two going examples of Bain's clocks, one of which is thought to be his No. "O" or original model, and both are quite reliable; they operate not off the original earth battery but from a $1\frac{1}{2}$ volt Leclanché cell.

It is perhaps interesting to note that some 60 years after Bain's invention the Bentley Engineering Company of Leicester filed patents for what seems in all respects to have been a replica of Bain's clock. But it is to Alexander Bain that we owe the first successful electrically maintained clock and it depended for its success largely on his choice of gold as the contact material.

THIS metal, as has been said, becomes dense because of its thorough tempering and its perfect and uniform elemental mixture, and of such a density that it is given not only an ordinary permanence but almost an incorruptibility and an incapacity to contain any superfluous material, even if it is subtle and in small amount. For this reason it does not rust, even though it be in the earth or in water for a long time, for neither of these has any effect on it, nor does fire, which has the power to reduce to ashes or dissolve every created thing; indeed gold not only defends itself from fire but continually purifies itself therein and becomes more beautiful; nor does it have any effect on the senses of smell or taste, nor is it poisonous if it is eaten either intentionally or by accident—indeed as a medicine it is beneficial in certain illnesses.

From the translation by
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VANNOCCIO BIRINGUCCIO
De La Pirotechnia
Venice, 1540