MULTILAYERED NANO-FOILS FOR LOW-TEMPERATURE METAL-CERAMIC JOINING

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ABSTRACT

Over almost two decades metal-ceramic fusing has been the essential step in obtaining materials which benefit from both ceramic and metal materials, i.e. where the combined properties of the metal and ceramic layers are desirable. Soldering and active metal brazing are the most effective when considering fusing methods.

This paper presents a low-temperature process for soldering and brazing ceramics to metals, which is based on the use of reactive multilayer foils as a local heat source. The reactive foils range in thickness from 40 µm to less than 100 µm and contain many nanoscale layers and/or domains that alternate between materials with high mixing heat.

Key words: Nanofoils, Multilayer, Metal- Ceramic Joining, Low Temperature, Low Stress

1. INTRODUCTION

This paper relates to multilayer structures and, more particularly, to multilayer structures with selectable, rapidly propagating reaction wave fronts, as well as selectable total energies, adiabatic temperatures, and ignition temperatures and powers. The starting points for this approach were D. M. Makowiecki and R.M. Bionta: US Patent 5,381,944; Barbee and T.P. Weihs: U.S. Pat. 5,538,795; T.W. Barbee, Jr. and T.P. Weihs: U.S. Pat. 5,547,715.

The field of this presentation covers a low-temperature process for soldering and brazing ceramics to metals which is based on the use of reactive multilayer foils as a local heat source, in combination with nanostructured coatings on metal and/or ceramic parts. The reactive foils range in thickness from 40 µm to less than 100 µm and contain many nanoscale layers and/or domains that alternate between materials with high mixing heats, such as Al and Ni. By inserting a free-standing foil between two solder (or braze) layers and two components, heat generated by the reaction of the foil melts the solder (or braze) and, consequently, bonds the components. The use of reactive...
foils eliminates the need for a furnace, and dramatically reduces any heating of the components being bonded. Thus, ceramics and metals can be fused over larger areas without those damaging thermal stresses that are typically encountered when cooling during furnace soldering or brazing operations.

The practical application of ceramics often depends on an ability to form strong bonds between ceramic and metallic components. A number of different fusing techniques have been developed over the last few decades. The three most common are: epoxy bonding, diffusion bonding, and active metal brazing and soldering. While each of these methods has benefits in regard to particular applications, each one also has its limitations.

During active brazing or soldering, samples are heated in a furnace to melt braze or solder what is placed between them. An active element in the braze or solder, such as Ti, reacts chemically with the components to enable wetting, and the formation of a strong bond. While active brazing can produce strong bonds, the high reactivity of the active metal requires the use of a vacuum furnace in an inert atmosphere intended to prevent oxidation. In addition, the high melting temperature of active brazes can lead to large thermal stresses on cooling, and fracture or debonding of the ceramic. Reactive solders reduce mismatch in thermal strains on cooling, by lowering the process temperatures but significant thermal stresses can still be present. Ideally, a strong metallic bond at/near room temperature needs to be formed, to avoid large thermal stresses between the components.

2. STATE OF THE ART

There has always been a limited understanding about the nature of interfacial interactions and their relationship to advancing any reaction front resulting from a chemical reaction between layers in the structure. The use of thin foils to investigate the propagation of such a combustion or reaction wave has been demonstrated for a nickel-aluminium system. The initiation of a reaction wave was found to be triggered by the melting of nickel for a large period structure regardless of the composition of the foil, U. Anselmi-Tamburini and A. Z. Munir, J. Appl. Phys. 66 (10), pp 5039-5045, 1989. Additionally, the combustion synthesis of multilayer nickel-aluminium systems has also been reported by T. S. Dyer and Z. A. Munir, Scripta Metallurgica et Materialia, Vol. 30, No. 10 pp 1281-1286, 1994. However, these investigators have not produced multilayer structures with selectable wavefronts.

The process of bonding with reactive multilayer foils is very rapid and easily performed in air (there is no need to join the bonds in a clean room or a specially-designed furnace). However, it requires certain preparation of the components. Most typically, layers of solder or braze are pre-applied to the bonding surfaces of the components. It is also possible to use free-standing sheets of solder placed between the reactive foil and the components, provided the surfaces of the components are easily wetted when using the solder or braze. This implies that most ceramics’ surfaces need to be metalized. Following this preparation, reactive foil is placed between the two components, the components are aligned, and a load is applied. In order to ensure good contact between all the surfaces during fusing, the required value would vary depending on the roughness and flatness of the bonding surfaces. The reaction is then initiated by an electrical or optical pulse, heat is released, the solder or braze refloows, and a bond is formed in approximately one second. For large-area bonds it is common to use multiple, simultaneous initiations of the foil to ensure uniform melting of the solder or braze layers across the bonded area. A number of large-area bonds have been
created using reactive foils as the local heat source. The usual combinations of ceramic materials joined to various metals using reactive multilayer are: (SiC / Ti, Al / SnAgSb 60-75), (SiC / brass / SnAg 25-30), (B4C / Cu, steel / SnAg 25-30) (Al2O3 /Al / SnAg 25-30), (SiN / Ti / SnAg 25-30), (Si / Cu / PbSn 17-20), (Si / Cu / In 4-6).

Localized heating of the reactive foils enables the formation of large-area ceramic-metal bonds by minimizing residual stresses between those components having appreciable differences in CTE. The transfer of heat from the reactive foil into the adjacent components during a bonding operation has normally been numerically modelled and the results experimentally validated using infrared measurements. The numerical modelling is performed using a numerical scheme that is based on finite-difference discretization.

In addition to predicting thermal profiles and thermal stresses, researchers have also characterized the quality of the resulting interfaces for a variety of ceramic-metal systems using two different methods: cross-sectional scanning electron microscopy, and scanning acoustic microscopy (SAM).

The shear strengths of various ceramic-metal configurations joined with reactive multilayer foils and different solders or brazes are available in literature. It is important to know that the measured strengths depend primarily on the strength of the solder and not on the combination of materials being bonded. Finally, the significant localized heating that occurs during the bonding process enables these types of bonds.

3. PROCESS DESCRIPTION

For joining applications, the multilayer nano-foil is placed between the two components needing to be bonded, along with two layers of solder or braze. The foil precisely controls the instantaneous release of heat energy for joining and, thus acts as a controllable local heat source. The proposed technology offers radical improvements in output, outstanding energy efficiency and manufacturing productivity, exceptional bonding quality, and the potential to eliminate hazardous chemical processes.

When considering fusing methods, soldering and active metal brazing are the most effective. These processes involve braze melting and flowing between the two pieces of material. This is commonly referred to as ‘wetting’ and is critical - particularly when brazing ceramics. There are many materials that can be fused to produce joints between materials - those that melt above ~450 °C are classed as brazes, and materials melting below ~450 °C are called solders. If a braze alloy is melted between two ceramics, a poor joint is likely to result, because of poor wetting. There are two basic methods for encouraging wetting: to apply something to the surface of the ceramics so that the braze will wet, or to put something in the braze that will induce wetting. Surface treatments include metallization, metal coating and metal hydride treatments, while braze modification involves a process known as active metal brazing. In either case, the actual brazing operation takes place either in a controlled atmosphere, such as nitrogen or argon, or a vacuum better than 10⁻⁴ Nm⁻².

For almost two decades, metal-ceramic fusing has been the essential step in obtaining materials that benefit from both ceramic and metal materials, i.e. where the
combined properties of metal and ceramic layers are desirable. Ceramics, and in particular engineering ceramics, offer a huge array of mechanical, thermal, and electrical properties. These range from low thermal conduction in ceramics such as alumina, to high thermal conduction, e.g. diamond, and from low-density electrical insulators to superconducting ceramics. Piezo-ceramics offer the almost unique ability to convert electrical energy into mechanical movement, and vice versa. Materials such as beta-alumina and zirconia, which exhibit ionic conduction, are used as sensors. These materials have found application in a wide-range of industries, but their exploitation has been concentrated mainly in the automotive, power generation, and electronics sectors. A common thread amongst all of the above applications is that, at some point, the ceramic component interfaces with something else - another part of the machine/device made from another material, usually metal. At this point, some kind of attachment or joint is required.

There are an unlimited number of ways that nano-foil may be applied. Currently the biggest markets are energetics (propellant ignition) and large-area joining (armor mounting, structural joining and joining of sputtering targets), and small-area joining applications such as sealing and component mounting. Nano-foil could be used to join a broad range of components consisting of metals, ceramics, semiconductors, and polymers. Bonding can be performed in many environments and could be completed in a second or less. Because the heat is localized, components can generally be bonded without thermal damage. Nano-foils would be manufactured by vapour depositing hundreds of nanoscale layers that alternate between elements, such as aluminium and titanium. By thermally-pulsing one end of the resulting foil with energy, the nanoscale layers begin to mix and release heat to the surrounding foil. This leads to more chemical mixing in the joining areas of the foil and a chemical reaction that self-propagates across the full length of the foil (see Figure 1).

![Figure 1: A ceramic component is soldered or brazed to a metallic component using reactive foil as a local heat source. The foil reacts chemically and provides enough energy to melt the surrounding solder or braze layers, but insufficient energy to heat the components significantly. (A. Duchman et al, Advances in Science and Technology, Vol. 45 (2006) p. 1578)](image)

The multilayer structures are thin-film materials that are periodic and in one-dimension in composition or in composition and structure. Composition/structure variation is generated when synthesize the structure, which is typically accomplished using atom by atom, atom by molecule, or molecule by molecule technologies. Individual component layers in a multilayer may vary in thickness from one atomic
layer (~2 Angstroms) to thousands of atomic layers (>10,000 Angstroms) of a given material. Multilayer structures can be synthesized using elemental, alloy, or compound layers to form both microstructures and combinations of elements/materials that cannot be produced using traditional processing technology. Multilayers are made by alternate deposition of two or more different materials. After the first few layers, the structure of all the layers of one material are the same. The structure of each material is clearly of importance for the properties of the multilayer, not only in itself, but also for the influence it can have on the structure of the other material. Each material acts as a substrate for the deposition of the other. The simplest multilayer structures are those that consist of a composition modulation imposed on a single structure. In almost all cases of this type, intermixing can lead to a uniform single phase of the starting crystal structure or atomic geometry.

Figure 2: Schematic drawing of a self-propagating reaction in a multilayer foil, showing a cross-sectional view of the atomic and thermal diffusion that enable reaction formation. (J. Wang et al, J. Appl. Phys. Vol. 95 (2004) p. 248)

The simplest type of structural change in a multilayer is diffusional mixing at the interfaces. Increased interfacial diffusion and the reduced amplitude of composition modulation may affect many properties. The repeat distance of a multilayer period can also change. Individual layer materials may show changes in structure. Crystalline layers may amorphize and amorphous layers may crystallize. The amorphization and crystallization temperatures may be raised or lowered by interactions with the surrounding layers. Polycrystalline layers and mosaic layers may show grain growth. The grain boundaries running perpendicular to the layers are paths for fast diffusion,
and they can enhance diffusional mixing and help destroy a compositional modulation. A further type of structural change is the reaction between materials of the multilayer to give one or more new phases. If the multilayer is composed of elements with a strongly negative enthalpy of mixing, the heat released when the reaction is started with a thermal probe may be sufficient to allow it to proceed unassisted. This has been observed in transition metal/amorphous silicon multilayers. The phase which forms by reaction in a multilayer, may itself be metastable. The possible origins of multilayers’ distinctive properties are: (i) thin film effects, due to the limited thickness of one or more of the layers; (ii) interface effects, arising from interactions between neighbouring layers; (iii) coupling effects between layers of the same type, acting through the intervening layers and (iv) periodicity effects from the overall periodicity of the multilayer. Multilayer properties can be tailored by controlling the periods and structures of the alternate layers. The characteristics of the multilayer which may affect the properties are, (i) layer thickness and its spread (either periodic or non-periodic designs may be desirable), (ii) interfacial structure, including coherency, (iii) the crystal structure and crystallographic orientation (or amor phicity) of the constituent materials, (iii) the grain size in crystalline layers and (iv) the stresses in the layers. Synthesis of multilayer structures can be accomplished by using techniques in which the product is formed by means of atom by atom processes. Such techniques include: (1) physical vapour deposition, (2) chemical vapour deposition, (3) electrochemical deposition, (4) electrolytic deposition, (5) atomic layer epitaxy and in some cases (6) mechanical processing. Multi-vapour-source configurations are used in the synthesis of metal multilayers with thermal sources. These are directly analogous to molecular beam epitaxy systems except that the sources need not be of the Knudsen cell type. In these systems, the sources and samples are stationary and layering is achieved through interruption of the vapour streams to the substrate by the use of a rotating pinwheel, or reciprocating shutters. Substrates can be held at temperatures from 4 to about 1300 degrees K. Heating mechanisms include electron-beam bombardment, and resistive and optical-heating. Sample sizes are dictated by specific system geometries and heating requirements.

Multisource configurations are also used in sputter deposition systems. In these systems, the sputter sources are widely separated and the substrates moved past the sources, a single layer being deposited on each pass by a source. Sputter sources are solid materials, atoms or atom clusters being ejected from the solid target into the vapour by bombardment of the target’s surface with energetic particles. The ejected atoms impinge on a substrate and condense it to form a film. In most cases, noble gases are used as the sputter gas, their ions being positively-charged. The process is called cathodic sputtering. Ions are formed by establishing a plasma in much the same manner as a glow discharge is formed in a low-pressure gas by an electrical field between two electrodes. Factors to be considered include sputter source deposition, surface coupling, energy distribution of the sputtered atoms and the geometry of the vapour source substrate’s configuration. The sputtering process entails the establishment of a plasma discharge and, imposing a potential of the correct polarity, so that ionized gas atoms are accelerated to the cathode’s surface where, if of sufficient energy, they dislodge other atoms. These secondary atoms travel from the cathode’s surface to the deposition surface, being adsorbed to form a deposit.
The multilayer structures of the present invention have a selectable reaction front velocity that is controlled by power delivered to the reaction front by an exothermic chemical reaction, to form the compound \( \text{A}_x \text{B}_y \) in a two component structure. Other important material properties include, but are not limited to thermal property parameters such as, (i) material density, (ii) material-specific heat, (iii) thermal conductivity, and (iv) any mechanisms for heat loss during reaction-convection/evaporation/melting.

Because the multilayer structures of the present invention have selectable propagating reaction fronts, they would be suitable for a variety of different applications including, but not limited to, (i) ignitors, (ii) joining, (iii) new materials, (iv) smart materials, and (v) medical devices and treatments. A multilayer structure has a selectable, (i) propagating reaction front-velocity \( V \), (ii) reaction initiation temperature attained by application of external energy, and (iii) amount of energy delivered by a reaction of alternating unreacted layers of the multilayer structure. The multilayer structure has a period \( D \), and energy release rate constant \( K \) (see Figure 2). Two or more alternating non-reactive layers are made of different materials and separated by reactive zones. The period \( D \) is equal to the sum of the widths of each particular material’s single alternating reaction layer, and includes the sum of reacted zone widths \( t_\text{r} \), over the period \( D \). The multilayer structure has a selectable propagating reaction front-velocity \( V \), where \( V = K(1/D^n)[1-(t_\text{r}/D)] \), and \( n \) is about 0.8 to 1.2 (see Figure 3).

![Graph of reaction front velocity](image)

Figure 3: A graph of reaction front velocity

(T.W. Barbee, Jr. and T.P. Weihs: U.S. Pat. 5,547,715, August 20, 1996)

The chemical reaction between the elemental components in alternating non-reactive layers determines the energy available. The rate at which the energy is released is directly proportional to the rate at which these atoms react by thermally-activated processes or by structurally-enhanced mixing. Because these reactions are thermally activated, the higher the sample temperature the higher the rate of reaction. Additionally, a significant parameter is when the number of atoms in close contact with
an interface determines the rate of energy release at a given temperature. The higher the number of interfacial atoms, the higher the rate of heat release. Therefore, the rate of heat release or reaction delivered power is proportional to the interfacial area per unit volume, which is inversely proportional to the period D (see Figure 4).

![Figure 4: A graph of exothermic heat of reaction as a function of multilayer period D for an Al/Monel structure (T.W. Barbee and T.P. Weihs: U.S. Pat. 5,538,795, July 23, 1996)](image)

Propagating reaction front velocity V is selectable, in that, depending on a variety of different parameters, conditions, and materials, it can be controlled and a desired V obtained. Thus, V can vary for different applications. V is generally within the range of about 0.2 to 100 m/sec. Formation heats are about 10 to 200 kJ/mole. For higher energy multilayer structures including, but not limited to NiSi, VB$_2$ and TiB$_2$, the formation heats are about 70 to 120 kJ/mole. Mid-range formation heats are about 45 to 70 kJ/mole. Suitable mid-range materials include, but are not limited to, Monel/Al 400, NiAl, PdAl, TiSn and SnV. Lower range multilayers, such as ZrAl and TiAl, have formation heats of about 20 to 45 kJ/mole. Formation heats for various binary alloys and compounds are listed in Cohesion in Metals; Transition Metal Alloys, F. R. de Boer et al., Elsevier Science Publishers B. V., 1988, pages 103 through to 634. Suitable multilayer ignitors include Al/Monel 400, NiAl, ZrAl, NiSi, MoSi, PdAl, and RhAl. By way of example, but not intended to limit the invention, an Al/Monel 400 ignitor could be made having a formation heat of about 230 kJ/mole, and V of about 17 to 20 m/sec. However, its sensitivity may be too high over small periods. Other ignitors are ZrAl$_3$ or ZrAl, each with a formation heat of about 188 kJ/mole, and V of about 2 to 15 m/sec. The advantages of these materials is that they have lower formation heats, are less sensitive to smaller periods, and require less energy to ignite. The TiAl ignitor has a formation heat of 142 kJ/mole and V of up to 10 m/sec. The general qualitative explanation for this dependence of velocity on the structure is as follows. Firstly, the chemical reaction between the elemental components in non-reactive layers A and B determines the energy available and, if the reaction is adiabatic, the maximum temperature attained. Secondly, the rate at which the energy is released is directly-proportional to the rate at which these atoms react by thermally-activated processes or by structurally-enhanced mixing. Since these reactions are thermally-activated, the higher the sample temperature, the higher the reaction rate. The number of atoms in
close contact with non-reactive layers A and B at an interface in a multilayer structure determines the rate of energy release at a given temperature. The higher the number of interfacial atoms, the higher the rate of heat release. Therefore, the rate of heat release, or reaction-delivered power, is directly-proportional to the interfacial area per unit volume, or inversely-proportional to the period D. Higher energy release rates result in higher temperature gradients at the reaction front and higher propagation velocities. Over very small periods, D < 150 Angstroms, chemical reactions that occur at the interfaces between alternating non-reactive layers, such as A and B, during synthesis causes the available energy to be decreased. The temperature gradients at the reaction front and the propagation velocity V are smaller when less heat is released over any time-period. The multilayer structures of the present invention have spread wide applications, including use as ignitors, in joining applications, in fabrication of new materials, as smart materials and medical devices, and therapies. In the application of ignitors, a multilayer structure can be a reaction initiator, wide-area heating device, or timed explosive initiator. Joining applications include composite/metal joining, semiconductors (low temperature), honeycombs, field repairs, and as a low energy replacement for spot or arc welding, or joining using the same material. New materials, a multilayer structure can be used to form single crystal foils of reaction intermetallic compounds, metal matrix composites (intermetallic), and near net-form structures (intermetallic). Smart material applications are in the areas of engineering energy release, controlled distortion, light emission signals and sequence processing. They can also be used as local heat sources in medical therapies and devices. The engineering of rapidly reacting multilayer structures with controlled propagating reaction front velocities V is dependent on the following parameters: (1) the formation heat of the compound formed by the reactions of the component layers; (2) the reactive zone width formed during synthesis; (3) the specific heats of the components; (4) values of reactions’ or meltings’ endothermic heats; (5) thermal conductivity; and (6) interdiffusion kinetics.

Three types of measurements are made to characterize multilayer structure. These include, (i) reaction front velocity V as a function of multilayer structural parameters, (ii) available heat of the reaction stored in the multilayer structure as a function of structural parameters by Differential Scanning Calorimetry (DSC) and (iii) structural evaluation by planar and cross-section by transmission electron microscopy-TEM. Differential scanning calorimetry would be used to measure the heats involved with reactions in multilayers as a function of temperature.

Accordingly, there is a need for a multilayer structure that has a selectable chemical reactive wavefront, a selectable initiation temperature from an external energy source, and a selectable amount of energy delivered by a reaction of the multilayer structures’ alternating layers. It would be an advantage to provide multilayer structures in which one is able to determine: the velocity of the chemical reaction wavefront, the total energy release, the rate of energy release, the adiabatic temperature and the ignition temperature or power for such a wavefront. For a rapid heat source, there is a need to know how fast the wavefront travels, thus determining the rate at which energy is released by the structure. It would be desirable to provide multilayer structures that can be tailored for different applications, depending on those chemical compositions and physical structures that control their chemically reactive wavefronts.
4. CONCLUSIONS

Multilayered nano-foils introduce following benefits over traditional solutions:

- bonding of similar or dissimilar materials (ceramics to metal) in a second, in any environment;
- bonds are resistant to corrosion and degradation;
- low stress bonds are formed;
- localized heating;
- there is minimal thermal exposure to the parts being joined;
- there is higher electrical/thermal conductivity;
- room temperature bonding;
- eliminates the need for a standard furnace, torch or laser;
- works with any solder.

This technology could overcome the problems presented by current solutions—generally using a standard furnace, by being more reliable and safer. For joining applications, the bonds created would experience lower stress, the materials being joined would not experience any damage (only the interface is heated) and dissimilar materials such as metal to ceramics would be easily and affordably bonded. In addition, it would be unnecessary to upgrade manufacturing facilities, because these foils would enable rapid room temperature soldering or brazing with minimal capital equipment.

The importance of nano-foils is in its advancement beyond the capabilities of existing technologies. The expanded commercial delivery of nano-foils for reactive initiation and joining applications would respond to the demands that current technology cannot effectively or economically address.

One of the most important developments of this technology is its ability to accurately predict the temperature profiles on the various components when used in a joining application.

5. REFERENCES

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