Diffusion Bonding of Nuclear Materials

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Abstract
Diffusion bonding has emerged as a competitive advanced technique in joining similar and dissimilar materials which are difficult to join using the conventional methods. The technique is elaborated with emphasis on the key variables, the mechanisms involved and optimisation of the process parameters. The use of hot isostatic pressing in diffusion bonding of materials is also outlined. Finally, some of the activities related to diffusion bonding carried out in BARC, with relevant details, have been discussed.

Introduction
The technology of joining materials is vital to the growth of various industries such as nuclear, aerospace, automotive, power generation, shipbuilding, oil, petrochemical and process engineering. Progress in the various joining technologies enhances the productivity and quality of joined components. Improving productivity and quality by incorporating cost-effective solutions in the manufacturing processes, also requires innovative developments in joining technologies and processes.

Solid state diffusion bonding is an important advanced technique for joining both similar and dissimilar materials. Solid state joining processes are those which produce coalescence at temperatures below the melting point of the base materials being joined, without formation of liquid phase during the process of joining [1]. These processes involve either the use of deformation, or diffusion and limited deformation to produce high quality joints between both similar and dissimilar materials. Diffusion bonding is one such solid state bonding process which is accomplished by bringing the surfaces to be welded together under moderate pressure and elevated temperature in a controlled atmosphere, so as to effect the coalescence of the surfaces [2, 3].

Diffusion Bonding
Diffusion bonding of materials is a solid state joining technique carried out at a suitable temperature and pressure and is defined as a joining process wherein all the faces to be bonded are held together by a pressure insufficient to cause minimum detectable plastic flow, at a temperature below the melting point of any of the parts, when solid state diffusion causes coalescence of contacting surfaces. The process of diffusion bonding thus requires subjecting the pieces to be joined to high temperature and compressive stress, for a finite time interval, to cause bonding of the faying surfaces without producing macroscopic plastic deformation. The temperature of bonding is usually lower than the fusion temperature but high enough to cause sufficient diffusion at the bonding interface, and the operation can be carried out either in vacuum or in controlled atmosphere. Depending upon the materials being joined, a thin layer of interlayer is often introduced at the joining interface.
Since the bonding is accomplished by diffusion of the materials species across the interface, it is a very suitable technique for joining of dissimilar materials and materials combinations, which are otherwise difficult to join by conventional fusion welding, due to (a) difference in melting points and thermal conductivity, (b) formation of brittle intermetallic compound at the joint interface, and (c) unsatisfactory behaviour in service, for example, poor corrosion resistance. Low pressure at the joining interface and shallow thermal gradients ensure minimum microstructural changes, associated residual stresses and distortions in the parts being joined.

**Key Variables of Diffusion Bonding**

There are several parameters in the process which needs attention to achieve a sound diffusion bonded joint. The extent of bonding and the manner in which it is achieved is governed both by the properties of materials being joined and the process parameters. The surface conditions, the interlayer materials, the surface, grain boundary and volume-diffusion coefficients, creep properties and yield strength are some examples of the materials properties. The primary process-parameters contributing significantly to the diffusion bonding process are bonding pressure ($P$), bonding temperature ($T$) and dwell time ($t$). Apart from these, initial roughness of the joining surfaces and nature of the interlayer, if used, also play important roles both on the process of diffusion bonding and on the properties of the final joint.

**Optimization of Process Parameters**

The objective of optimization of the process parameters is to obtain the best possible properties of the diffusion bonded joint which is usually quantified in terms of mechanical strength and leak tightness of the joint. The bonding temperature usually ranges between 0.5 – 0.7 $T_m$, $T_m$ being the absolute melting point of the most fusible material in the combination. Elevated temperatures aid interdiffusion of atoms across the interface of the joint and also assist in surface modification by elimination of asperities. The bonding pressure should ensure tight contact between the edges of the pieces, and must be sufficient to aid deformation of surface asperities and to fill all the voids at the interface by material flow. In case of insufficient pressure, some of the voids may be left unfilled, thus impairing the strength of the joint. Importantly, the compressive load also helps in dispersing surface oxide films. This leaves a clean surface and aids diffusion and coalescence at the interface. When dissimilar metals are to be joined, the choice of the bonding pressure is decided by the mechanical strength of the weaker of the two materials. The dwell time ($t$), at a specified bonding temperature and pressure must, in most cases, be kept to a minimum from physical and economical considerations. It should be sufficient for an intimate contact to be formed by elimination of the asperities at the interface through the process of solid state diffusion. However, an excessive diffusion time might lead to formation of Kirkendall voids in the weld zone or even change the chemical composition of the metal or lead to the formation of brittle intermetallic compounds.

![Fig. 1: A typical temperature and pressure cycle during diffusion bonding for bonding copper and stainless steels](image-url)
(when dissimilar metals are being joined). Fig. 1 shows a typical temperature and pressure cycle in the process of diffusion bonding of Cu/stainless steel system.

**Mechanism of Diffusion Bonding**

The entire process of diffusion bonding is essentially accomplished in different stages. The changes that take place at the joining interface in each of these stages can be listed as below [4]:

**Stage A**: Initial asperity or point contact

**Stage B**: Plastic deformation of the asperities; contact areas increase until the local stresses decrease to below the yield stress

**Stage C**: Removal of large, irregularly shaped voids at the interface as well as a simultaneous migration of the interfaces out of planar orientation and away from the voids

**Stage D**: Elimination of the remaining isolated voids by diffusion

**Stage E**: Grain boundary rearrangement and volume diffusion.

**Influence of the Process Parameters on the Stages of Diffusion Bonding**

(a) **Pressure**

Compressive pressure is required during Stage B, to achieve a large area of contact by localised plastic deformation of asperities on nominally flat surfaces. Where appropriate, pressure is also used to bring about the creep mechanisms which contribute to bonding. The applied pressure \( P \) however, must not be so high as to cause macroscopic deformation of the components, as stated earlier, and hence is limited to the yield stress \( \sigma_y \).

\[
P < \sigma_y
\]

(b) **Temperature**

Plastic deformation, creep and the various diffusion mechanisms are all temperature dependent. Temperature determines: (a) the extent of contact area which dictates the size of voids to be eliminated during Stage B, (b) the rate of diffusion which governs void elimination during Stages C, D, and E. Since solid state diffusion is a thermally activated process, the temperature dependence of the diffusion coefficient \( D \) is given by:

\[
D = D_0 \exp\left(-\frac{Q}{RT}\right)
\]

where, \( D_0 \) and \( Q \) are pre-exponential factor and activation energy, respectively.

(c) **Dwell time**

The creep and diffusion mechanisms are time dependent. Hence, sufficient time must be allowed for void closure by material transfer. Bonding time is affected by temperature, the materials and specimen size. Therefore, the time and temperature for each case should be optimized. The width of the interdiffusion zone \( X \) formed at the interface between the two materials during diffusion bonding is given by:

\[
X = k\sqrt{t}
\]

where, \( k \) is the kinetic rate constant at the temperature \( T \) of bonding and \( t \) is duration of bonding.

(d) **Surface roughness**

The grade of surface roughness determines the extent of initial surface contact and the size of voids. This in turn, influences the bonding rate. Surfaces may be prepared by machining, grinding and polishing. In general, a finish better than approximately 0.4 \( \mu \)m is necessary to ensure good initial contact. The removal of surface contaminants and thick oxides prior to bonding is also crucial.

(e) **Interlayer materials**

Interlayer materials are very useful when bonding dissimilar materials. They serve to reduce temperature and/or pressure required for bonding and also prevent the formation of intermetallic compounds. Soft interlayer materials enhance contact and accommodate the residual stress developed at the interface of dissimilar materials due to the thermal expansion mismatch.

Therefore, it is evident that the process and materials variables are interrelated and will affect the relative contributions to bonding from each of the possible bonding mechanisms.
Diffusion Bonding using Hot Isostatic Pressing (HIP)

Hot Isostatic Pressing or HIP, as it is commonly known, is a materials processing technique which involves uniformly heating up the work-load while an inert gas pressure is applied on its surface. The process is used to fabricate components from materials which are difficult or impossible to form by other techniques. It is also commonly used to consolidate fabricated components such as densifying porous materials and healing internal defects. Powder metallurgy, ceramics and casting are three main applications of HIP [5–8]. However, it is also claimed that diffusion bonding was the original application of HIP [9]. When joining jobs with complex geometries and those involving powders, diffusion bonding process is often considered as the best method of joining. In such cases, the multi-directional application of pressure is needed and hence an isostatic press is considered ideal. As the HIP machine can provide high temperature and isostatic pressure simultaneously, even sintering and diffusion bonding of ceramic powder onto a bulk surface can be carried out at the same time, thereby reducing the processing time.

A typical HIP unit operates from 500 °C to 2200 °C with pressures ranging from vacuum to 210 MPa. It generally consists of a pressure vessel, furnace, gas system, power supply, instrumentation and controls and auxiliary systems. Presently, the technique of HIP diffusion bonding is being used largely in joining metals to themselves, ceramics and composites. Successful joints of ceramics such as the carbides (WC, TiC, TaC) and nitrides (Si$_3$N$_4$, TiN, AlN) with metals and alloy like steels, stainless steels, and Ni-based superalloys has been demonstrated using HIP. Development is being made in achieving higher quality bonds in larger numbers of ceramic-metal combinations which can be bonded using HIP.

Interdiffusion and Diffusion Bonding Work at BARC

Diffusion bonding can be employed to effectively join different combinations of materials. Fig. 2 shows the combination of different materials which are amenable to diffusion bonding with or without using interlayers and the work done at BARC. The presence of a low strength intermediate layer is often used to reduce the temperature and/or pressure required for welding. This ductile inter-layer acts as a stress-relieving structure and hence reduces the accumulated residual stresses in regions around the interface. Interlayers are also required in some dissimilar metal systems to prevent the formation of brittle intermetallic phases in the weld. Therefore, understanding of the interdiffusion behaviour of various materials combinations assume significant importance in selection of interlayer. Detailed investigations were carried out to study the diffusion reactions and evaluate the interdiffusion characteristics of various systems such as Zr-Al [10], Zr-Ti [11], Cu-Ti [12], Ni-Al$_2$O$_3$ [13], Mo-Ti [14] and

![Fig. 2: Combinations of different materials those are amenable to diffusion bonding, with and without interlayers. The combinations which were bonded in BARC are identified by pink dots.](image-url)
zircaloy-2-Inconel [15]. In fact, some of the diffusion coefficients were used for optimising the diffusion bonding parameters [16].

On the other hand, diffusion bonding requires a substantially longer joining time. In addition, the equipment costs are high due to the combination of high temperature and pressure in vacuum environments.

**Work Related to Diffusion Bonding of Materials in BARC**

Diffusion bonding technique has been successfully used to join a variety of material combinations and a few of them are discussed below.

**(a) Diffusion bonding of aluminium to stainless steel**

Joining of Al and its alloys to SS 304 is frequently required in cryogenic and nuclear applications. A variety of aluminium alloys are used as storage tanks for cryogenic liquids and transfer links are mostly stainless steel connectors. This requires a transient joint between these two alloys. Such joints find wide applications in the development of neutron-sensitive ion chamber and proportional counter for reactor control and safety instruments. These joints are also used in the development of ion chamber for environmental monitoring of low energy gamma rays and X rays.

The most common methods employed for joining Al alloys to SS are brazing, friction welding, explosion welding, and solid state diffusion bonding. Welding and brazing of these alloys are difficult due to large differences in their melting points, thermal expansion coefficients, and thermal conductivities. Besides, formation of brittle intermetallic compounds at reaction zone may lead to premature failure of the joint. Friction and explosion welding joints generally result in the development of large residual stress and structural discontinuity at interface. Diffusion bonding offers sound strength and high leak-tight joint when silver interlayer was used. Successful Al/SS joints were prepared by diffusion bonding at 300 °C for 2 h, using various interlayers of Zn, Cu, Ag on the Al side, and Ni, Cu, Ag on the SS side [17]. Fig. 3(a) shows joint assembly for use in neutron counters. The microstructure of the interface of cross-section of the SS/Al joint is shown in Fig. 3(b).

**(b) Manufacturing of perforated plate matrix heat exchanger for cryogenic application**

Perforated plate matrix heat exchanger is a compact and highly effective heat exchanger for liquefying of helium in cryogenic application. The heat exchanger essentially consists of a stack of perforated copper plates alternating with stainless steel (SS) spacers. The diffusion bonded joint between Cu/SS has been developed to fabricate a cryogenic matrix heat exchanger. Stacks consisting of plates and spacers (75 each) and two stainless steel end plates were bonded to form monolithic heat exchanger, as shown in Fig. 4(a). A typical micrograph of the SS/Cu interface is shown in Fig. 4(b). Special fixture was fabricated to hold the stack of Cu sheets, SS spacers and the end plates. The process parameters were optimized and the heat exchangers were successfully manufactured, meeting the required properties.

**Fig. 3:** (a) Stainless steel/aluminium joint assembly diffusion bonded with interlayers at 350 °C for 2 h used in neutron counters (b) micrograph showing the transition interface between the two base materials, the pink line shows the regions where EPMA was done.
Many irradiation experiments are carried out in pressurised water loop system in research reactors, to evaluate the design parameters and their effects on the fuel performance. In-pile instrumentation probes are used, for measuring parameters such as temperature and pressure. The joining of Zircaloy-2 (Zr-2) and SS by conventional welding, leads to the formation of brittle intermetallic compounds such as FeZr₂ and FeZr, in the weld pool which impairs the strength of the joint. Further, because of large variation in thermal expansion coefficient and elastic moduli high residual stress develops during cooling of weld leading to failure of the joint. Transient joints between Zr-2 and SS-304 required for in-pile instrumentation in nuclear reactors were made using interlayers of Nb, Cu, Ni and diffusion bonded in solid state at 900 °C for 2 h at 15 MPa stress. The strength of joint is around 300 to 450 MPa and the joint has negligible leak rate. The joints were successfully tested to withstand thermal cycling of 30 cycles from 300 °C to room temperature with reduction in strength only by 10%. Zr-2/SS joint has also been made by the transient eutectic bonding technique.

Joining of SS to Ti is required in nuclear and chemical engineering applications. Apart from having good strength, such joints need to possess stringent leak tightness and corrosion resistance to aggressive corrosive fluids. SS and Ti substrates were bonded directly as well as by using suitable interlayers in vacuum at temperatures in the range 800 – 1000 °C and pressure of 10-20 MPa for a dwell time between 30 min and 2 h. Although a bond strength of about 90% of the strength of the parent materials was achieved using multi layers of foil at the interlayers.

(c) Zircaloy-2/stainless steel joints

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(d) Diffusion bonding of stainless steel to titanium

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interface, such joints were susceptible to degradation in nitric acid environment. Hence direct bonding was optimized for specific applications where good leak tightness and adequate corrosion resistance were achieved. Fig. 5(a) shows a typical microstructure of the cross-section of SS/Ti diffusion bonded interface. The phase maps shown in Fig. 5(b) delineated the formation of a layer of β-Ti in the joint interface due to interdiffusion.

Summary

Diffusion bonding is a versatile technique for bonding metallic materials and has been extensively used for joining both similar and dissimilar materials at BARC. Special mention should be made related to joining of stainless steels to aluminium alloys, copper and titanium for fabricating end products of direct relevance to DAE programmes.

References