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Low Temperature Bonding of Pd/Ni Assembly for Hydrogen Purifier

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Abstract **-** For manufacturing a Pd cell for hydrogen purification, a key technology is the bonding of a Pd fine tube with a stainless steel grasp. In this study, the SLID method has been employed to join Pd sheet and Ni plate to evaluate the bendability between a Pd tube and a Ni coated stainless steel grasp. The results indicated that directly inserting a Sn interlayer with a thickness of 8.5μm between the Pd sheet and Ni plate caused the formation of Ni_3Sn_4 and $PdSn_4$ intermetallic compounds, respectively. However, certain Sn interlayer remained after SLID bonding and low shear strength of 5.3 MPa was obtained. Furthermore, the remaining of low melting point Sn interlayer cannot withstand the operating temperature (above 350 ºC) of SLID assembled Pd cell for hydrogen purification. Reducing the Sn interlayer thickness to 3 μm led to the complete exhausting of Sn interlayer. Unfortunately, a long crack appeared at the Ni_3Sn_4/$PdSn_4$ interface and a low bonding strength was resulted. Adding an Ag thin layer between the Sn coated Pd sheet and Ni plate caused an Ag_3Sn intermetallic compound to form between the Ni_3Sn_4 and $PdSn_4$ layers, and cracking of the Pd/Ni joint was prevented. This improvement led to satisfactory bonding strengths ranging from 10.6 to 17.3 MPa. High temperature storage at 400ºC for 100 hr did not degrade the bonding interfaces or bonding strengths.

Keywords**:** Pd cell, solid liquid interdiffusion bonding, Sn/Ag/Sn interlayers, intermetallic compounds, bonding strength, high temperature storage.

1. Introduction

Hydrogen with a high purity of 6N to 9N is required for the manufacturing of IC and LED chips. For example, the purity of hydrogen used in the MOCVD process is above 7N. Even the hydrogen used for fuel cells must have a high purity of 4N to 6N. Therefore, hydrogen purification is an important technique in the IC, LED, and fuel cell industries. Palladium has good selectivity for hydrogen and stable material properties. Therefore, it is often used as the material for hydrogen purification. The principle of hydrogen purification can be described as in Fig.1: The hydrogen gas (H_2) dissociates on the surface of Pd sheet into H atoms, which diffuse through the Pd sheet and recombine on the other side into purified H_2 gas. The other impure gases with larger atom size will be screened during this process. For the hydrogen purification, multiple Pd fine tubes are assembled with a SAE 304 stainless steel grasp as a Pd cell shown in Fig. 2. The Pd cell is then operated at a temperature above 350ºC during the hydrogen purification process. For manufacturing a Pd assembly, a key technology is the bonding of a Pd fine tube with a stainless steel head. Because Pd fine tubes have a diameter of about 2 mm and a thickness of about 60 μm, the Pd cell can be deformed if the traditional brazing or laser welding approaches are used. In contrast, soldered Pd cell cannot endure the high operation temperature above 350ºC for hydrogen purifier due to the lower melting point of conventional solder alloy.

Solid-Liquid Interdiffusion Bonding (SLID) is a bonding method based on the principle of isothermal solidification and interfacial intermetallics reaction. As shown in Fig. 3, this technique makes use of a low-melting metallic thin film interlayer (LT) such as Sn or In inserted between the high-melting bulk work pieces or metallic layers on certain substrates (HT1 and HT2) that are to be joined. The LT interlayer, which is molten at low temperatures, reacts rapidly with the HT1 and HT2 bulk materials or layers. After a short time of interfacial reaction, the LT interlayer is exhausted and has completely transformed into intermetallic compounds (IMCs). The melting point of the newly-formed intermetallic phases is much higher than that of the original LT interlayer, so the resulting joints can withstand considerably higher temperatures when the assembled products are operated [1]. Since solid liquid interdiffusion bonding has the merits of a low bonding temperature process and high temperature application, it has been applied in the past few decades to the manufacturing of microwave packages, high power devices, thick-film resistors, GaAs/Si wafer packages, and even gold jewelry. Recently, diffusion soldering has also been employed for ceramic multichip modules [2,3], MEMS packaging [4], semiconductor packaging [5], hybrid joining [6], and hermetic package sealing [7].

In our previous studies, $Bi_{0.5}Sb_{1.5}Te_3$, (Pb,Sn)Te, and GeTe thermoelectric materials were bonded with Cu electrodes using the SLID process with an inserted Sn interlayer [8-10]. Satisfactory joints with sufficient bonding strengths were obtained in these cases. In addition, SLID method has also been applied in the 3D-IC flip-chip packaging, which indicated that the SLID bonded joints had a higher reliability than that of traditional soldered bumps [11]. The bonding temperature during the SLID process can be further reduced through employment of an indium interlayer [12]. In this study, the SLID method has been further used to join Pd sheet and Ni plate to evaluate the bendability between a Pd tube and a Ni coated stainless steel grasp.

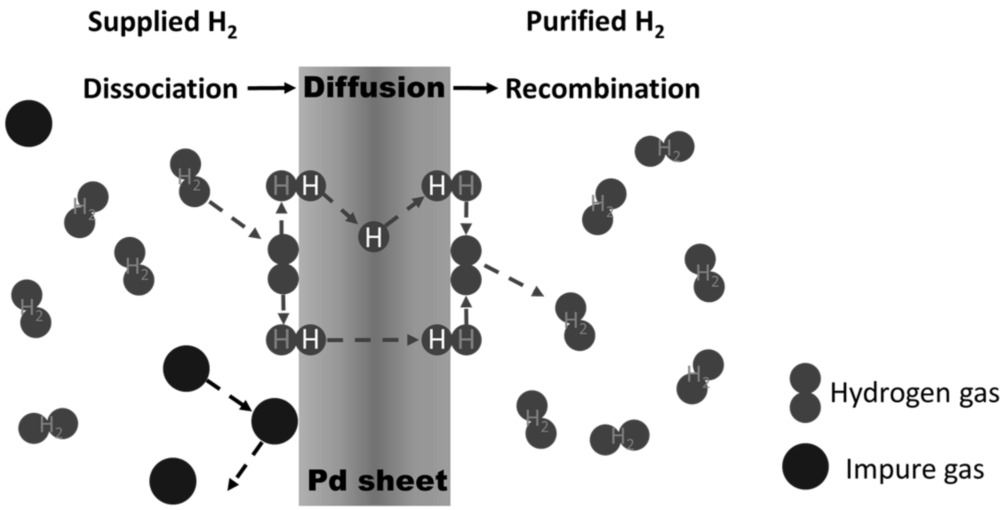

Fig. 1: The principle of hydrogen purification using a Pd sheet.

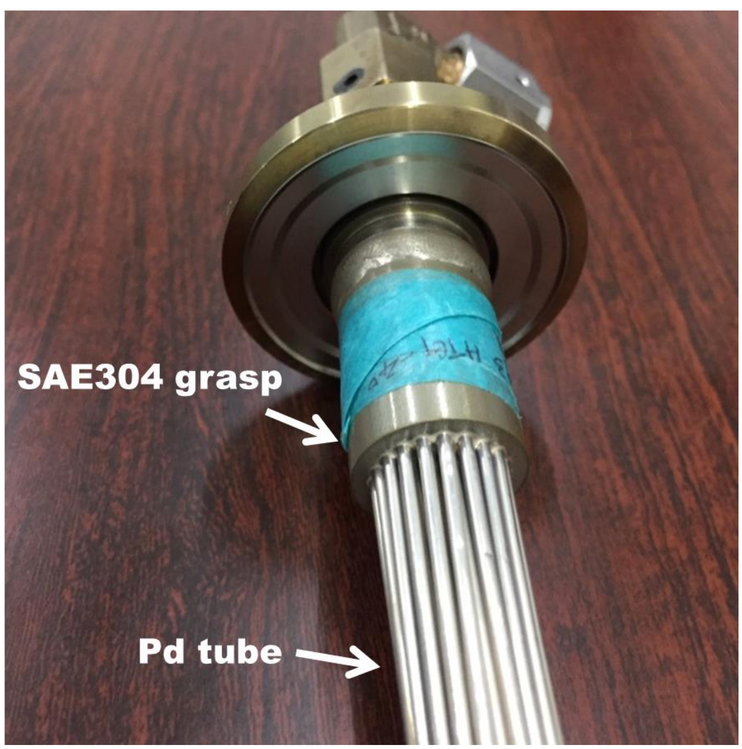

Fig. 2: Palladium cell for hydrogen purification.

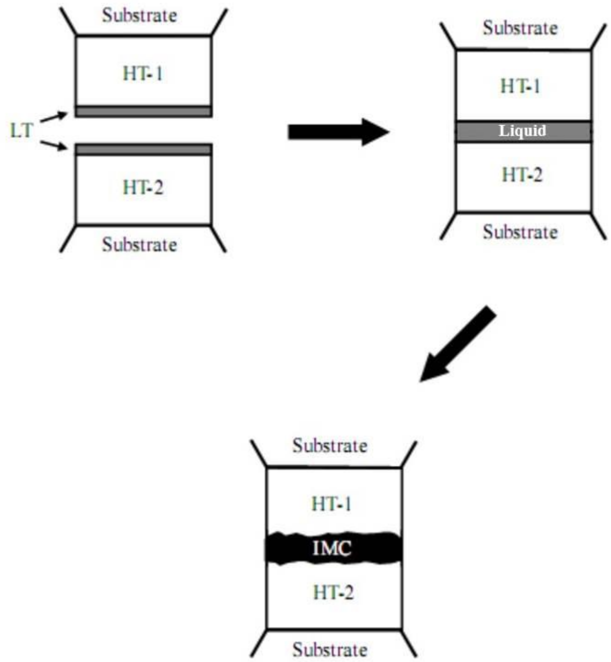

Fig. 3: Schematic representation of the principle of solid liquid interdiffusion bonding.

2. Experimental

A palladium sheet with a thickness of 0.1mm was joined with a Ni plate with a thickness of 1 mm using the solid-liquid interdiffusion (SLID) bonding process shown in Fig. 3. For the preparation of the bonding specimens, the Pd sheet was ground with 4,000 Grit SiC paper, electroplated with a Sn thin film interlayer, and then assembled with a Ni plate. The SLID bonding was conducted in a vacuum furnace of 5.3 x 10^{-4} Pa and subsequently heated at various temperatures between 275ºC and 350ºC for 30 min under a pressure of 3 MPa, as shown in Fig. 4. After the bonding processes, the specimens were cross-sectioned, ground with 4,000 Grit SiC paper, and polished with 1 and 0.3 µm Al_2O_3 powders. The microstructures of the intermetallic compounds that formed at the interfaces were observed with scanning electron microscopy (SEM), and their chemical compositions were analyzed with energy dispersive X-ray spectroscopy (EDX). The shear strengths of various Pd/Ni assemblies were tested with a DAGE 4000 Bond Tester at a speed of 0.3 mm/s.

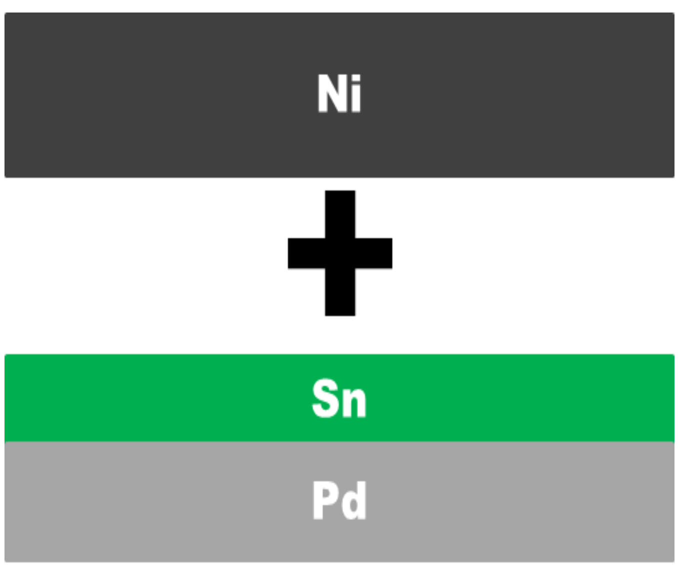

Fig. 4: Schematic representation of the SLID bonding of Pd sheet with Ni plate using a Sn interlayer.

3. Results and Discussion

Figure 5 shows the microstructure of a Pd/Ni joint with an 8.5μm thick Sn interlayer after SLID bonding at 300ºC for 30 min. It can be seen that the Pd sheet and Ni plate reacted with the Sn interlayer to form $PdSn_4$ and Ni_3Sn_4 intermetallic compounds, respectively. In this case, some of the Sn interlayer remained between the Ni_3Sn_4 and $PdSn_4$ intermetallic layers. During the shear test, the specimen fractured through the Sn interlayer, which resulted in a low bonding strength of 5.3 MPa. In addition, the remaining Sn interlayer in the Pd cell assembly would melt during the hydrogen purification process. To solve this problem, the thickness of the Sn interlayer was reduced to 3 μm and SLID bonding was conducted at 300ºC for 30 min. Figure 6 indicates that the Sn interlayer was exhausted under this condition. However, a long crack appeared between the Ni_3Sn_4 and $PdSn_4$ intermetallic layers, and a very low bonding strength was obtained. The appearance of cracks at Ni_3Sn_4/$PdSn_4$ interface is similar to that reported by Bader et al. for the SLID bonding of Ni//Ni and Cu//Cu couples using Sn interlayers [13].

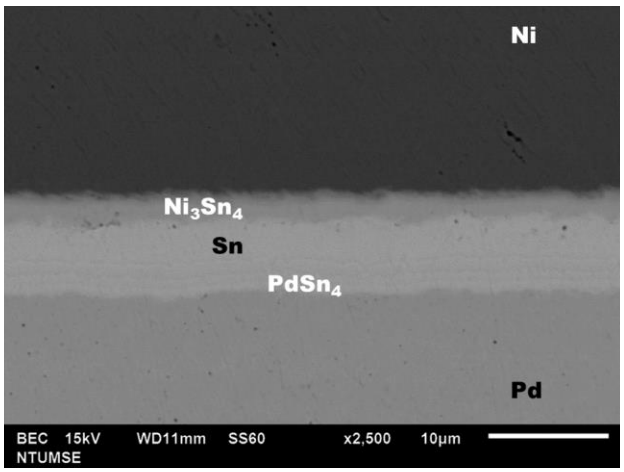

Fig. 5: Microstructure of the SLID bonded Pd/Ni couple using a Sn interlayer of 8.5 μm thickness.

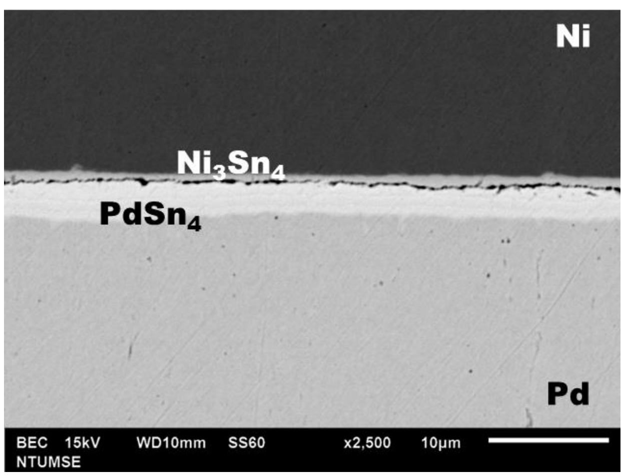

Fig. 6: Microstructure of the SLID bonded Pd/Ni couple using a 3 μm thick Sn interlayer.

In our previous study, it was verified that inserting an Ag_3Sn intermetallic layer between Ni-Sn or Cu-Sn intermetallic compounds eliminated interfacial voids [14]. The SLID bonding process was modified to include a Sn/Ag/Sn multilayer between the Pd sheet and Ni plate, as shown in Fig. 7. Figure 8 shows that this improvement prevented the cracking shown in Fig. 5, and a sound interface was achieved in the Pd/Ni joint. In addition to the formation of Ni_3Sn_4 and $PdSn_4$ intermetallic compounds, a Ag_3Sn intermetallic layer appeared between the Ni_3Sn_4 and $PdSn_4$. Shear tests indicated that satisfactory bonding strengths ranging from 10.6 to 17.3 MPa can be achieved with SLID bonding at temperatures between 270 and 325ºC for 30 min, as shown in Fig. 9. The shear strength of SLID- Pd/Ni joint decreased from the maximal value of 17.3

MPa to 12.2 MPa for the increasing of bonding temperature from 325 ºC to 350ºC, which can be attributed to the high thermal stress during the SLID bonding at 350ºC. For the evaluation of reliability, the Pd/Ni joint pre-bonded at 300ºC for 30 min was aged at 400ºC for 100 hr, which caused the Ni_3Sn_4 intermetallic layer to grow from about 1.2 to 4.7μm, while the Ag_3Sn and $PdSn_4$ intermetallic layers decreased slightly as shown in Fig.10. It was also found that the bonding strengths did not decayed obviously after this high temperature storage.

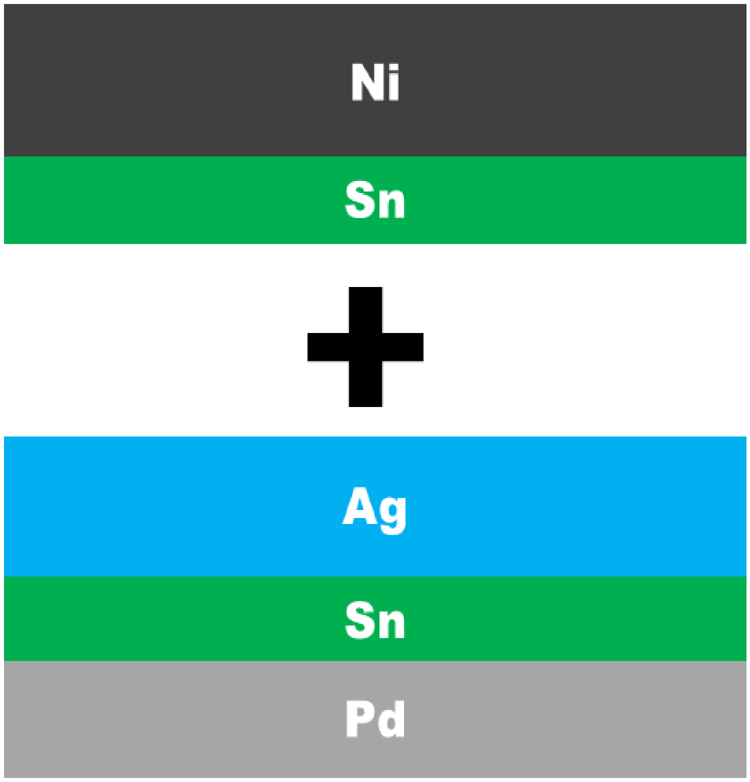

Fig. 7: Schematic presentation of the SLID bonding of Pd sheet with Ni plate using Sn/Ag/Sn interlayers.

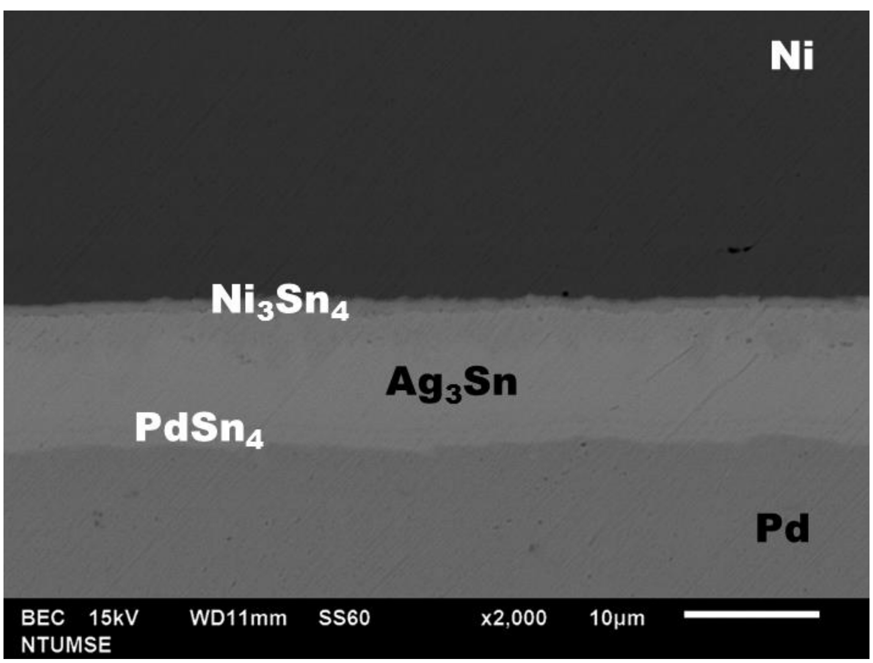

Fig. 8: Microstructure of the SLID bonded Pd/Ni couple using Sn/Ag/Sn interlayers.

Fig. 9: Shear strengths of the SLID bonded Pd/Ni couple using Sn/Ag/Sn interlayers.

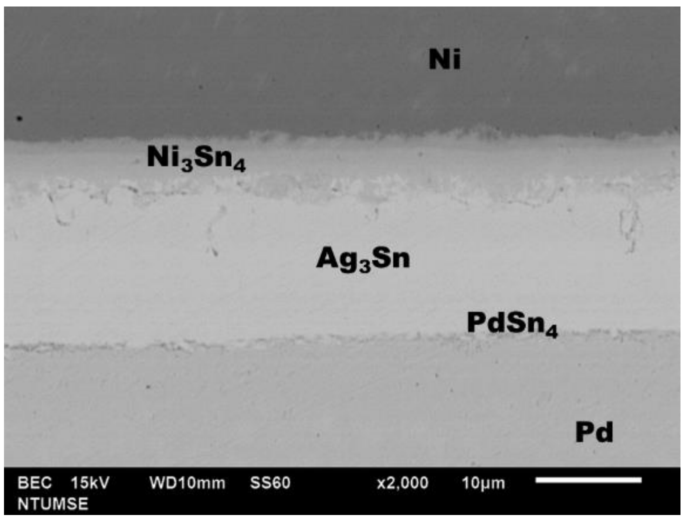

Fig. 10: Microstructure of the SLID bonded Pd/Ni couple using Sn/Ag/Sn interlayers after high temperature storage at 400ºC for 100 hr.

4. Conclusions

Pd sheet and Ni plate can be bonded with the solid liquid interdiffusion bonding method. The results indicated that directly electroplating a 3 µm thick Sn interlayer on the Pd sheet and SLID bonding with the Ni plate resulted in the complete exhaust of Sn film and the formation of Ni_3Sn_4 and $PdSn_4$ intermetallic compounds, respectively. Unfortunately, a long crack appeared at the Ni_3Sn_4/$PdSn_4$ interface, and a low bonding strength of 5.3 MPa was obtained. Inserting an Ag layer between the Sn coated Pd sheet and Ni plate caused an additional Ag_3Sn intermetallic compound to form between the Ni_3Sn_4 and $PdSn_4$ intermetallic layers, and cracking of the Pd/Ni joint was prevented. Satisfactory bonding strengths ranging from 10.6 to 17.3 MPa have been achieved with SLID bonding at temperatures between 275 and 350ºC for 30 min using Sn/Ag/Sn interlayers. High temperature storage at 400ºC for 100 hr did not degrade the bonding interface or bonding strength.

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