

Engineering and Fabrications for Multiple-Submicron-Layer Clad Metals

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Abstract

Clad metal is a layered metallic composite used in different applications. As the layer number increases and the layer thickness decreases, a clad metal may provide special functions, which might be required by electronic packaging. This paper describes engineering and fabrication processes for multiple—submicron-layer clad metals. Examples are given to active brazing alloys, high strength electro/magnetic application material, and thermal expansion control clad metal.

Keywords: clad, bonding, multiple layer, brazing, Nb, Invar

Clad metals, layered metallic composites, play important and special roles in material development and applications. Normally, clad metals have two or three component layers. However, in some cases, special material functions or performance requirements demand a multi-layer clad metal with more than 30 multiple-layers in a certain repeated configuration. As the number of layers in a clad metal increases and the thickness of each layer decreases to sub-micrometer or even to near nano-scale, the clad metal may provide unique properties and functional behavior. It is obvious that designs and engineering of material processes are essential to obtain such multi-layer clad metal and to achieve required material properties and performance.

After reviews of basic clad metal processes, this paper describes engineering considerations and processes of multi-layer clad metals. Composite layer design and process engineering concepts are discussed. Examples will be given on Cu/Ti/CuAg multi-layer clad metal for active brazing filler alloys, Cu/Nb multi-layer clad metal for special electro/magnetic applications, and Cu/Invar for thermal expansion controlled electronic packaging applications.

Roll-Bonding Technology

Roll-bonding is one of the manufacturing processes used to make clad metals. As its name implies, dissimilar metals are bonded together under high pressure through rolling to form a new, layered composite material, clad metal [1-4]. In this process, as illustrated in Fig 1, two or more work pieces (such as sheets, plates or strips) of metals or alloys are stacked together and then passed through a pair of rolls in a rolling mill until proper plastic deformation has been achieved to produce a solid-state welded joint between original individual metal pieces.

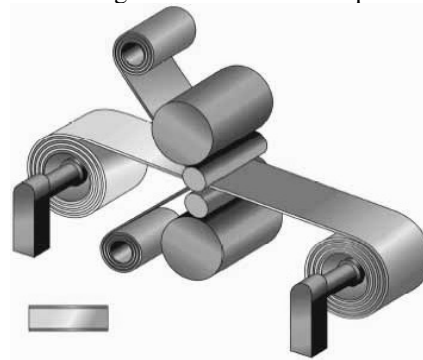


Fig 1 Illustration of Roll-Bonding

Before roll-bonding, proper surface cleaning and preparation must be done to remove organic contaminants, oxides and other barriers to bonding as much as possible. Chemical and mechanical cleanings are two common approaches used, in addition to thermal cleaning in reducing atmosphere or vacuum. During roll-bonding process, a high reduction in thickness of the metals is achieved under the high pressure exerted by the roll-bonding mill. Normally, more than 50% reduction in thickness by one rolling pass is needed if there is no external heating. The high thickness reduction extends the metal surfaces, thus breaking surface oxides and creating fresh surfaces on the metals being bonded. The fresh virgin surfaces along the bond interface are in a self-enclosed environment, where oxidation cannot occur, and therefore do not have bond-impeding oxide barriers. A bond between dissimilar metals is thus obtained mainly through atomic affinity as a result of atomic outer layer electron sharing between the two dissimilar metals. Subsequent annealing after roll-bonding is normally performed to obtain or secure a strong metallurgical bond. Recovery and recrystallization of highly cold-worked microstructures occur during annealing and residual stresses at the bond interface are removed. In addition, residual organic impurities at the bond interface can be gasified and diffused away from the bond interface, and diffusion can occur in the adjacent area of the bond interface between individual metal layers in the clad metals [2-4].

The clad metal strips can be processed to a desirable dimension and a temper through conventional metal strip processes, such as rolling, annealing, cleaning, tension leveling and slitting. To make a clad metal with more than 30 layers with a repeated layer configuration, more than one time of roll-bonding is a viable practice. Between two roll-bondings, annealing has to be performed to soften the cold-worked metal from the previous bonding.

There are many advantages of multiple-layer clad metals over mono-metals or simple two/three layer clad metals. To take advantages of clad metals with a high number of layers in a repeated layer configuration, at least two major engineering considerations have to be made.

- 1) Layer configuration design. It includes an arrangement of each individual dissimilar alloy layer and layer thickness in a multiple-layer clad metal. This depends mainly on the function of the clad metal for applications. The considerations to ease the processes may also affect a clad metal layer configuration design.

- 2) Annealing temperature and time during process. A annealing process is needed between roll-bondings. It is important to select proper annealing parameters. Over-annealing may cause undesirable inter-diffusion between dissimilar alloys while under-annealing can cause difficulties and/or quality issues in the fabrication processes.

The following case studies illustrate the advantages of multiple-layer clad metals as well as engineering design and considerations.

Active Brazing Alloys

Background

Ag-Cu-Ti active brazing alloys usually are produced through powder metallurgy. After sintering by powder metallurgy, a heavy section metal work piece is subsequently rolled to reduce its thickness to a foil thickness through conventional mill practice. However, the Ag-Cu-Ti brazing alloy is not readily processed into foil form, when its Ag% is increased from 78% and Cu% is decreased from 28% of the eutectic composition, or Ti% is increased over 4% [5, 6]. In addition, hard, brittle, dispersed phases inherited from power metallurgy could still survive at foil thickness. This may result in not only undesirable non-uniform chemical composition distribution, but also a risk of damaging the stamping tooling used for making brazing alloy pre-forms.

Processes and Materials

Multiple-layer Ag-Cu-Ti active brazing alloys have been developed by roll-bonding technologies. Three types of raw materials were used to make final Ag-Cu-Ti brazing alloys: commercial pure titanium (Ti>99.2 wt%), commercial pure copper (Cu>99 wt%) and Ag-Cu alloys. Cu/Ti/Cu clad metal was first made using the first two raw materials, Cu and Ti, to facilitate the roll-bonding processes of a multiple-layer clad active brazing alloy. The multiple-layer AgCu/Cu/Ti/Cu/AgCu AgCu/Cu/Ti/Cu/AgCu clad metal strip was then made through several times of roll-bonding. The thickness of the input raw materials was determined by the overall chemical composition of the final clad brazing alloy through simple conversion calculations. Controls of layer thickness ratio in the clad metal were realized through a computer controlled monitor system and adjustments on roll-bonding mill settings. Annealing and cold-rolling were performed between roll-bondings. Annealing temperature was chosen below

the eutectic temperature (779°C) of Ag-Cu alloy but was high enough to secure the metallurgical bond between each layer and soften the cold-worked material. The layer configuration design of Ti layer within AgCu and Cu layers ensured the ease of bonding and cold-rolling as well as annealing, and avoided titanium oxides to form on the clad metal surfaces otherwise. The multiple-layer clad metals can be further cold-rolled and annealed to 0.050 to 0.120 mm thick foils. The layer thickness in the clad metals thus can reach a sub-micrometer.

Figure 2 shows the cross-section metallographic photos of multiple-layer AgCu/Cu/Ti/Cu/AgCu.... AgCu/Cu/Ti/Cu/AgCu clad metal strip. Table 1 lists the nominal chemistry, liquidus and solidus of the multiple-layer clad active brazing alloys developed. Thermal differential analysis (DTA) was performed to examine the melting and solidification behaviors of the clad brazing alloy, as showed in Figure 3 [7]. A wide range between the melting start and complete temperatures could be beneficial where part gap fit-in is required.

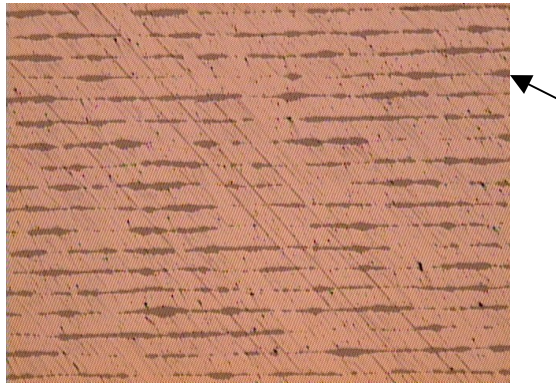


Fig 2 Clad Ag-9.5Cu-2.5Ti Active Brazing Filler Metals. Darker Cu/Ti/Cu layers, as A\arrowed, are between AgCu alloy layers

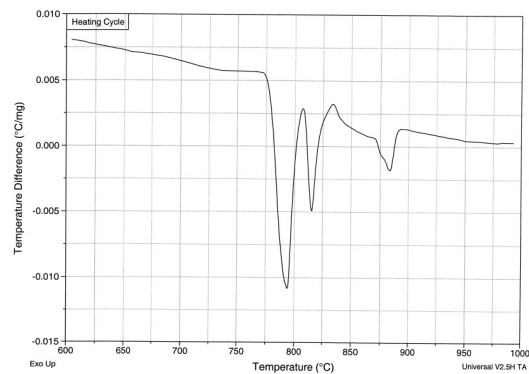
Table 1 Clad Brazing Miller Metals

Alloy	Nominal Composition, wt%			Critical Temperature °C	
	Ag	Cu	Ti	Liquidus	Solidus
TiLam72	70	27	3	884	765
TiLam90	88	9.5	2.5	959	774

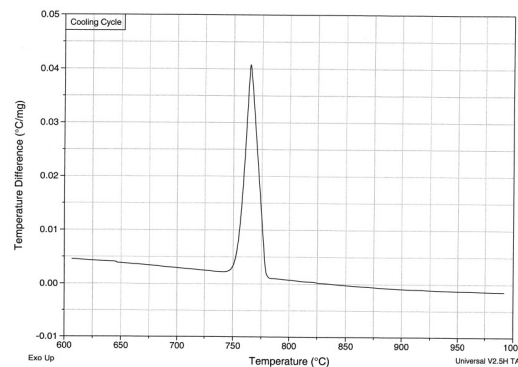
Advantages

There are several advantages of multiple-layer clad Ag-Cu-Ti active brazing alloy over conventional Ag-Cu-Ti active brazing alloys. First, Ti has no direct

exposure to the atmosphere because the Ti layers are sandwiched between Cu layers and then AgCu alloy layers in the clad brazing alloy. Therefore, Ti in the brazing alloy will not be oxidized and consumed during the heating cycle until the surrounding AgCu alloy melts. Upon melting of the brazing alloy, the amount of Ti available to react with ceramic surface remains almost unchanged, and the controls is thus achievable to wet and activate ceramic surface being brazed. This could provide a relief of strict requirements for high vacuum during brazing when the conventional active brazing alloys is used. It is also thought that storage shelf life of clad active brazing alloys should be longer than that of the conventional active brazing alloys.



a) heating cycle



b) cooling cycle

Fig. 3 DTA analysis of Clad Ag-25.2Cu-3.2Ti Brazing Filler Metal

It should be noted that the clad active brazing alloy foil developed in this work can be further roll-bonded as an inlay strip on 4xx stainless steel, alloy 42, Invar or Kovar substrate. Low thermal expansion substrate base metals provide additional joining advantages in thermal expansion management on metal/ceramic joining and for applications with thermal cycles. The active brazing alloy inlay clad metal can be pressed, stamped and formed to specific parts, and shimming of a brazing alloy pre-form into

the joining areas between metal and ceramic parts can be avoided. Therefore, quality of brazed joints and low effective cost of efficient manufacturing can be obtained.

Satisfactory results of brazing with the clad active brazing alloys developed in this work were reported in commercial applications.

Multiple-Layer Nb/Cu Clad Metal

Background

Cu-Nb composites have a unique combination of mechanical, thermal transport and electrical properties, and therefore are suitable candidate materials for highly mechanically stressed electrical devices. One example is an application of such materials to wind high field magnets. However, the strength of conventional Cu-Nb composites is limited, whereas a multiple-layered Cu/Nb thin film deposited by sputtering in vacuum is cost and its size is limited.

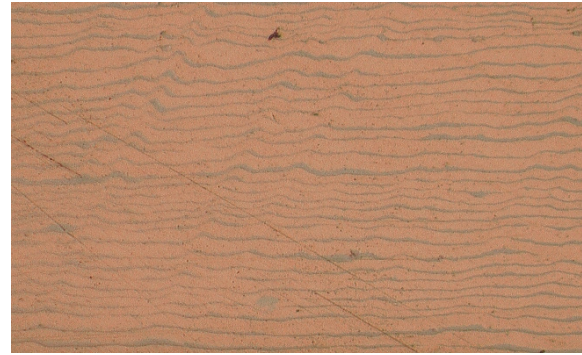
Processes and Material

A multiple-submicron-layer Nb-Cu clad metal has been developed with roll-bonding technologies. The thickness of input raw materials Nb and Cu was decided per final proper Nb/Cu thickness ratio in the clad metal, which was Nb/Cu=1/6 in this study. A simple Nb/Cu clad metal was first made from annealed Nb and Cu by roll-bonding. Then, several strips of annealed Nb/Cu clad metal strips were fed into a roll-bonding mill to make a multiple-layer Nb/Cu ... Nb/Cu clad metal. The bonding processes were repeated until a 1024 layer clad metal was made. Annealing, cold-rolling and other strip processes were done between roll-bondings. The final material was cold-rolled into 0.12 mm thickness.

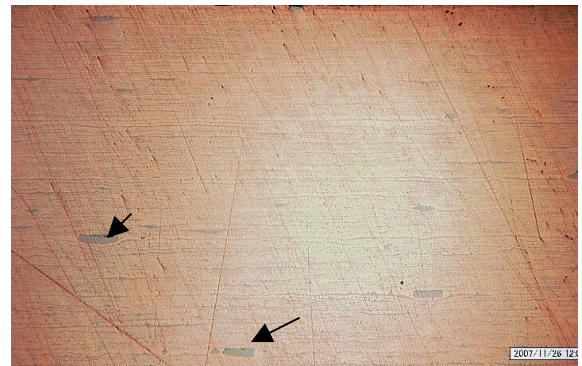
Figure 4 shows the cross-section metallography of the material. The material in Figure 4b had one more bonding than the material in Figure 4a. The thickness of Nb layer (in grey) is between 0.5 to 1.6 μm in the most part of the material in Figure 4a), while the Nb layer thickness in the material of Figure 4b can be as low as 0.1 μm .

Discussions

It should be noted that Nb-layer thickness is not uniform and spheroidization of Nb was developed. Non-uniform thinness of Nb-layer is believed as a result from the fact that annealing of cold-worked Nb for recrystallization requires a much higher



a) after 5th roll-bonding, 1000X



b) after 6th roll-bonding, 700x

Fig. 4 Metallographic Photos of Multiple Layer Nb/Cu Clad metal. Nb is in grey color. Arrows indicate Nb spheroidization

temperature than the temperature for copper. Nb layer in the clad metal from previous roll-bonding or cold-rolling was not fully annealed, while Cu layers was fully annealed and much softer by the same annealing process. Different hardness or work hardening status between Nb and Cu causes plastic deformation instability of the individual layers in the clad metal during subsequent roll-bonding with a high thick reduction. Therefore, non-uniform layer thickness is observed. On the other hand, repeated annealing of the clad metal provided more opportunity for non-uniform or broken Nb layer to spheriodize. Lower annealing temperature would reduce a tendency of spheriodization. It was considered during the process engineering design that annealing temperature between 600 to 800 C should be proper to both soften the cold-worked clad metal and limit the inter-diffusions. 700°C annealing temperature was selected in this study. However, the evidence of some Nb spheriodization indicates the annealing temperature may be required to be lowered, particularly when the layer thickness becomes very thin.

Advantages

The tensile strength of the 1024 sub-micron layer Nb/Cu clad metal foil in cold-rolled temper was reported about 600 to 800 MPa [8]. This is a dramatic increase from the tensile strength between 400 to 480 MPa of cold-rolled simple two-layer Nb/Cu clad metal.

Since layer thickness in the multiple-layer Nb/Cu clad metal is in the order of 10^{-1} μm , microstructure across the layer thickness can be only single grain, and bamboo microstructure of the layer can be formed. This fine grain microstructure limits movability of dislocation slip that is an essential mechanism in metal plastic deformation. Therefore, much higher strength than that of conventional two-layer Nb/Cu clad metal can be achieved.

Multiple-Layer Cu/Invar/Cu Clad Metal

Background

Cu/Invar/Cu clad metal is a thermal expansion controlled material and is widely used in semiconductor and electronic board package applications. Its thermal expansion coefficient can be adjusted by layer thickness ratio of Cu/Invar/Cu, where Invar has a near zero thermal expansion coefficient and Cu processes a very high thermal expansion coefficient.

Whereas a flat piece of Cu/Invar/Cu has a well defined thermal expansion, a bent portion of Cu/Invar/Cu clad metal part could change its curvature during a temperature change. This is because bending during part forming makes Cu layer at the concave surface side (inner side) at the bent curvature thicker than the Cu layer at the convex side (outer side). This also makes the thickness centerline of Invar layer towards to the convex side, away from the thickness centerline of the whole clad metal. This asymmetric layer configuration makes more thermal expansion at the concave side than that at the convex side during heating, and the bent curvature in a hot condition becomes less than that in a cold condition.

To overcome this problem, a multiple-layer Cu/Invar/Cu clad metal was developed. The basic concept is to try to distribute Invar layers more uniform across the thickness and to make a thickness difference of Cu layers between each Invar layer to the minimum during bending. The multiple Invar layers across the thickness restrain the thermal dimension change of each Cu layer across the

thickness. The thermal expansion or contract will be thus distributed more uniform across the thickness at the curvature.

Material and Processes

A simple three-layer Cu/Invar/Cu clad metal was first made with pure Cu and Invar 36. Annealed Cu/Invar/Cu clad metal was then used for making the multiple-layer clad metal. Repeat roll-bondings were performed to make the multiple-submicron-layer Cu/Invar/Cu Cu/Invar/Cu clad meal. Annealing and rolling were performed between roll-bondings. Figure 5 showed the cross-section metallography of the multiple-layer clad metal.

Annealing between roll-bondings is critical. To ensure uniform layer thickness, a high temperature is desirable to make the difference in hardness between Cu and Invar small. However, if annealing tempertue is too high, inter-diffusion may occur between Cu and Invar. Diffusion of Cu into the adjacent Invar 36 layers increases thermal expansion coefficient of Invar 36. However, if annealing temperature were too low, recrystallization of Invar 36 would not be completed. The subsequent roll-bonding with high thickness reduction could cause non-uniform Invar layer thickness along the strip length. In this study, 815°C annealing temperature was applied, and fairly uniform layer thickness is observed.

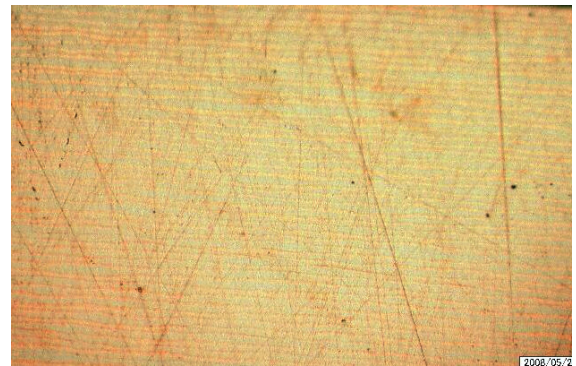


Fig. 5 Metallographic Photo of Multiple Layer Cu/invar/Cu Clad metal. Grey color layer is Invar 36 layer. 700X

Summary

Roll-bonding technologies can be applied to make multiple-submicron-layer clad metals. Repeated roll-bondings with annealing and cold rolling between them are viable to make the materials.

The multiple-submicron-layer clad metals provide special properties and material behavior that mono-metals or simple 2/3 layer clad metals are not able to achieve.

Engineering considerations on clad layer configurations and processes have been made to ensure the final product properties and functions and to facilitate the manufacturing processes. Special attention should be made on annealing parameters and a balance should be made to soften different alloys with different recrystallization behavior and to limit diffusions in such thin layer microstructure.

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