The Effect of Annealing Temperature on the Bond Strength and Structure of Interface in Ag/Cu Strips

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Abstract
Copper–silver bimetallic strips were produced by cold roll welding process and were treated by diffusion annealing in the temperature range 250–800 °C. The interface bonding strength was determined by bending and peeling tests, Resistance, conductivity and micro hardness profiles were determined and microstructure in the interface region was observed by optical microscope.
Electrical resistance and bonding strength in the interface depend on the diffusion annealing temperature. Diffusion annealing above 600 °C produces fine-grained eutectic phases in the interface region and silver matrix.
The eutectic phase formation and the movement of interface is a chemical–diffusion process. It is observed that the strength is greatly reduced by increasing the thickness of eutectic compounds. These compounds have detrimental influences on physical and mechanical properties of the interface. The results indicate that there is an optimum annealing temperature at which the sheet exhibits a satisfactory formability together with a high bonding strength.

Key words: Copper – Silver - Bimetallic Strip - Cold Roll Welding - Eutectic compound - Interface Bonding Strength

Introduction
Nowadays, production of two or multi layered sheets using cold roll welding has found specific significance in different industries. Such sheets, due to their unique properties, have been widely used in the electrical, electronics, automotive, telecommunications, semiconductor and appliance industries. Typical applications include connector contacts; switch contacts, wire bond interconnects and semiconductor lead frames. Copper-silver bimetallic strips are one of these multilayered composite materials used in the manufacturing of electronic and electrical components. Therefore, adequate mechanical properties, high electrical conductivity and suitable deformability are necessary. Solid state welding processes such as friction and cold roll welding have been considered as the qualified welding processes for these metals.

Roll welding mechanisms have been studied by Vaidyanath and co-workers [1], Forter and Amatuda [2], Williams [3] and Tylcote [4]. Cold roll welding is one of the solid states welding methods in which, pressure and plastic deformation take place at a temperature lower than recrystallization temperature. In this type of welding, two strips are joined together at room temperature by rolling [5-7], and evidence of non solidified and cast structure in the interface has indicated that no liquid phase is formed and therefore a direct bond emerges in the solid state [8,9].

This paper reports on the results of a study about the effects of different diffusion annealing temperatures on copper-silver bimetallic strips. This included evaluation of the peeling and bending test results, scanning electron microscopy (SEM) micrograph, electrical resistance and micro hardness profiles from interface.

Experimental Procedures
Silver strips (pure fine silver containing, at least 99.9% Ag, as annealed) and copper strips (UNS No. C11000, electrolytic tough-

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pitch copper, as annealed) were roll welded at room temperature.

Cladding Process

Cleaning

Before the cladding process begins, strip surfaces are thoroughly cleaned to remove all surface contaminants such as oil, water and metal oxides.

Pickling in solutions containing 4 to 15 vol% sulfuric Acid or 40 to 90 vol% hydrochloric acid is performed for the removal of oxides formed on the surface of copper and silver strips.

Bonding

Following the cladding process, the metals are fed through heavy rollers where their atoms approach to within ten or twenty atom diameters of each other. This results in an interaction of electromagnetic forces and the formation of a physical bond [10].

In this step, roll surfaces are cleaned by aceton, until the surface roughness of the rolls is increased. The thickness is reduced by 65% by sufficient pressure to force the metal surface into intimate contact and to establish a bond between the metals.

Heat Treating

The composite is then subjected to heat treatment. This promotes diffusion between the metals, resulting in a permanent metallurgical bond. Diffusion annealing was carried out for 20 hours at six temperatures in the range 250-800 °C.

Experiments

For evaluating the bond strength of samples a 15KN tensile testing machine was used and the mean peeling force of welded layers was measured. Schematic diagram of peeling test is shown in Figure1. The peeling force was measured using the following relation:

$$Peeling \quad force = \frac{mean \quad tearing \quad force}{length \quad of \quad bond} \quad \frac{N}{cm} \qquad (1)$$

The strip specimens were reversibly bent between zero and 90 degrees at room temperature until the bonding interface separated locally or one of the strips cracked [11].

Schematic diagram of the test method used to evaluate the interface bonding level of the Cu-Ag bimetallic specimens is shown in Figure 2. (Two tests were done and mean numbers were recorded.)

The electrical resistance of Ag/Cu samples was measured using a high precision micro-ohmmeter. The micro-ohmmeter was passing a certain current (I) parallel to layers of sample and measured the potential difference between two points of the sample with defined distance (L) of the bimetal by dividing the difference of potential to the passing current, i.e.;

$$R = \frac{\Delta V}{I} \qquad (2)$$

The other dimensions of the sample (width and thickness) were measured by a micrometer and then the resistivity (ρ) was calculated from the electrical resistance (R), length (L) and thickness cross section area (S) of the sample using the following relation:

$$\rho = \frac{R.S}{L} \qquad (3)$$

The metallographic samples were cut longitudinally, and then ground, polished, and etched in a solution of 50 ml 6% hydrogen peroxide and 50 ml ammonia for 20 s [11].

Results

Evaluation of bond strength by peeling test

The bond strength is decreased with increasing the annealing temperature. The variation of peeling force versus annealing temperature is shown in Figure3. There is a critical annealing temperature at which the bond strength is reduced sharply and a ductile to brittle behavior is observed. In this investigation the critical annealing temperature was about 550 °C.

Evaluation of bond strength by bending test

Eutectic compounds are brittle and when these compounds are in interface affected on bond strength. The repeatability is tested by two specimens. The numbers of reversible bends are listed in Table (3).

There is an optimum annealing temperature at which the sheet exhibits a satisfactory formability together with a high bonding strength. This Annealing temperature is between 500 and 600 °C.

Table1: silver and copper specifications.

Alloy	Chemical Composition, Wt%	Common Name	Heat Treatment	Hardness, Hv 3Kgf	Tensile Strength, MPa
Cu-UNS C11000	99.95% Cu	Electrolytic Tough-Pitch Copper	Annealed	45	250
Pure Fine Silver	99.9% Ag	Pure Fine Silver	Annealed	40	150

Table 2: pickling conditions for copper and silver base materials.

Sulfuric Acid Bath

Constituent or Condition	Amount
Sulfuric Acid	15-20 vol%
35% Hydrogen Peroxide	3-5 vol%
Water	Bal
Temperature of Solution	Room Temperature to 60 °C
Immersion Time	15 s to 5 min

Hydrochloric Acid Bath

Constituent or Condition	Amount
Hydrochloric Acid	40-90 vol%
Water	Bal
Temperature of Solution	Room Temperature
Immersion Time	1-3 min

Table 3: The number of reversible bends results for roll clad Cu-Ag bimetallic strips.

Annealed Temperature, °C	As-Roll Cladding	250	400	500	600	700	800
Specimen 1	2a	2a	11a	17b	18b	8a	2a
Specimen 2	1a	1a	11a	17b	19b	7a	2a

a: specimen failure resulted from bonding interface separation.
b: specimen failure resulted from strip component cracking.

Table 4: Micro hardness (HV) profiles for bimetallic strip.

Annealed Temperature, °C	As-roll Cladding	250	400	500	600	700	800
Silver Matrix	72	50	40	38	35	30	30
60µm to interface	77.05	61.3	52.58	52.58	50.8	50	50.1
Interface	*	53.51	51.24	42.44	49.11	57.47	60.1
60µm to interface	103.14	99.54	81.27	79.74	77	73.15	73.2
Copper Matrix	125	95	60	50	48	47	47

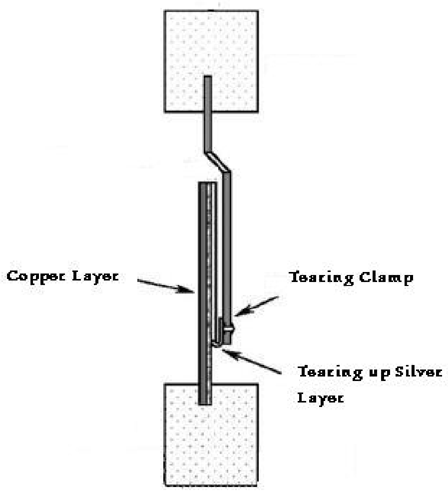

Figure1: Schematic diagram of the peeling test.

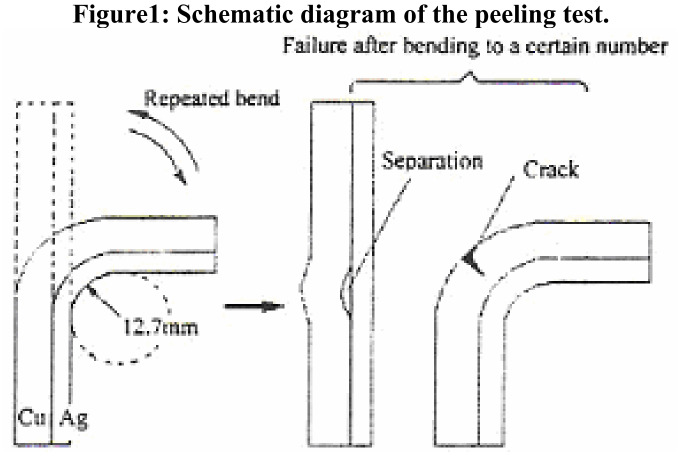

Figure2: Schematic diagram of the bending test.

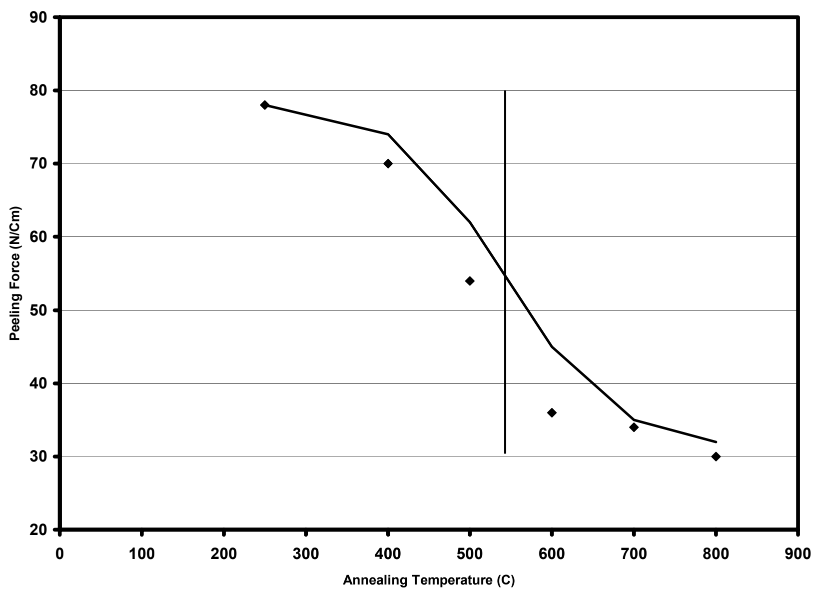

Figure3: Variation of peeling force versus annealing temperature.

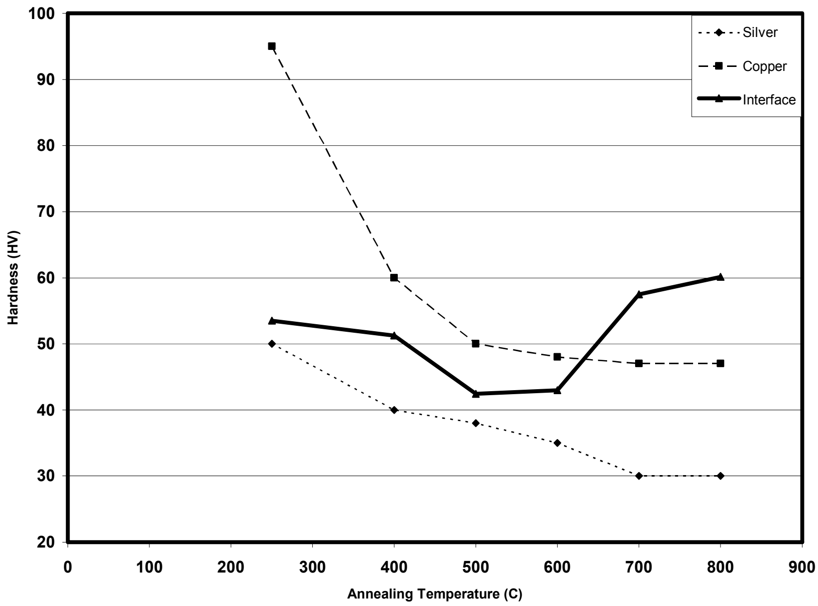

Figure4: Hardness versus annealing temperature.

Evaluation of bond strength by micro hardness profiles

Micro hardness results are shown in Table 4. Micro hardness in the interface of as rolled specimen was not available, because this specimen was not flat. These results show a decrease in hardness from 250 to 500 °C and then an increase from 600 to 800 °C. The minimum hardness is in 500 to 600 °C. Hardness values (HV) versus annealing temperature (°C) is shown in Figure (4).

Resistance and Conductivity of the bimetallic strips

Resistance and conductivity at various annealing temperatures are listed in Table (5). Conductivity decreases sharply with increasing in annealing temperature. The conductivity of eutectic compounds is much lower than copper and silver and with formation of these compounds the total conductivity reduces highly.

Microstructure in the interface (silver on up and copper on bottom) for as-rolled and annealing temperatures 500 and 800 °C are shown in Figure (5).

Discussions

Whenever two clean metallic surfaces are pressed together, free electrons can move across the interface and form metallic bonds. Highly conductive metals have many such free electrons. These bonds will increase in strength with temperature, due to the arrangement of atoms at the interface.

Considerable interdiffusion across the Ag/Cu interface occurs, with copper being the faster diffusing elements because the copper atom has a higher diffusion rate than the silver atom [12].

Copper-silver have a eutectic point at 779 °C. (at Cu-28.1%Ag composition) at a higher temperature the copper constituent in the silver matrix has a higher solubility than the silver constituent in the copper matrix. Copper atoms should make up the mainstream of the diffusion matter passing the original interface [12]. The Cu-rich secondary particles can precipitate in Ag-rich solid solution.

Some cavities or vacancies in the copper side may be accumulated during annealing treatment. The hardnesses of silver and copper are decreased for 250 to 500 °C and then are constant for 500 to 700 °C. The hardness in the silver component is generally lower than that in the copper component.

Hardness of the interface decreased for 250 to 500 °C and then increased for 500 to 700 °C annealing temperature. With further increasing of annealing temperature above

500 °C, recrystallization occurred for silver and copper strips and the hardness of interface increased due to the formation of eutectic compounds. From 500 to 600 °C the lowest hardness of the interface, Figure (4), and the largest numbers of bends, Table (3), occurred.

Naturally, the Cu-rich secondary particles can precipitate from Ag-rich solid solution because the copper solubility in the silver matrix decreases with the reduction in temperature after diffusion treatment. Microstructure of the secondary phase particles precipitated in the fine grain area (silver side) next to interface fewer than 700 °C annealing is shown in Figure 5c. The copper side as-rolled clad shows the morphology of a mixture that includes elongated grains and some finer recrystallized equiaxial grains since the recrystallization temperature of silver is lower than copper.

In both strip components (copper and silver) that annealed at 500 °C, are formed the equiaxial grains, therefore the toughness of both strip components is the best in this annealing temperature.

During the repeated deformation action, this pile-up produces a stress concentration next to the grain boundaries or to interfaces coincident with the coarse grain boundaries. This should promote the formation of fracture in the strip component or separation in the interface, leading to a reduction in the interface bonding level.

Table 5: Variation of conductivity with annealing temperature.

Annealed Temperature, °C	**As-roll Cladding**	**250**	**400**	**500**	**600**	**700**	**800**
Elecrrical resistance of bimetallic strips $(\mu\Omega)$	22.42	25.36	26.14	28.27	29.34	34.21	37.12
Bimetallic strips electrical conductivity $\frac{1}{\rho}\left(mm/\Omega mm^2\right)$	60169.49	53194.01	51606.73	47718.43	45978.19	39432.91	36341.59

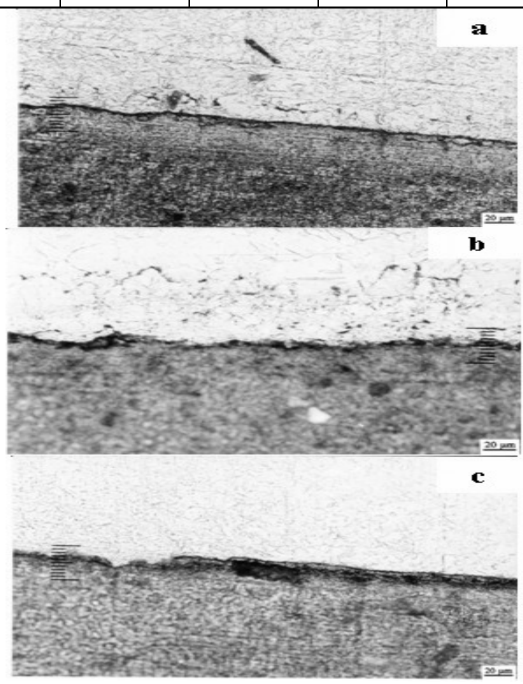

Figure 5: Microstructure of bimetallic strips a) as-rolled b) 500 °C C) 800 °C.

Conclusions

The following conclusions maybe drawn from the test results:

1- Diffusion annealing between 250 to 700 °C produced higher bonding levels, particularly with annealing at 500 to 600 °C.

2- Hardness for copper and silver strips is decreased when annealing temperature is increased. Hardness for silver strip is lower than hardness for copper strip.

3- When the specimen is annealed at 500 °C, repeated bending could not cause these interfaces to separate even when the strips fractured.

4- The lowest hardness and the best bending strength happened at annealing temperature of 500 °C.

5- The lowest bonding strength in the interface is seen at 700 °C.

6- Annealing at 800 °C causes the partial fusion in the bonding interface.

7- Diffusion annealing treatments that can induce recovery, recrystallization, or partial fusion in the bonding interface can lead to enhancement of the interface bonding level.

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