

3The Effect of Annealing Time on the Physical and Mechanical Properties of Interface in Cu–Ag Bimetallic Strips

A. Haghiriⁱ, M. Ketabchiⁱⁱ and N. Parvinⁱⁱⁱ

ABSTRACT

In low voltage connector designs, precious metal coating are used at the contact interface to ensure electrical continuity. Failure can occur when base metals diffuse to the contact surface, oxidize and form an insulating film that reduces conductivity. Copper–Silver bimetallic strips were produced by cold roll welding process and were treated in 500 °C for 0.5, 2, 5, 10, 20, 40 hours. The eutectic phase formation and movement of eutectic phase interface is a chemical–diffusion process. It is observed that the electrical resistance is greatly increased by increasing the thickness of eutectic compounds. The results indicate that there is an optimum annealing time at which the sheet exhibits a satisfactory formability together with a low electrical resistance.

KEY WORDS

Copper–Silver Bimetallic Strip, Cold Roll Welding, Electrical Resistance.

1. INTRODUCTION

Ag/Cu bimetallic strips are layered composite materials which are used in the manufacturing of electronic and electrical component. These bimetallic strips are used at different temperatures and in different environments. 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 of these metals. Roll welding mechanisms have been studied by Vaidyanath and co-workers [1], Tylecote and co-workers [2, 3] and Milner and Nicholas [4].

In cold roll welding 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 no solidified and cast structure in the interface has shown that no liquid or melted phase is formed and therefore a direct bond emerges in the solid state [8, 9]. Metal to metal cladding joins dissimilar metals through the

application of extremely high pressure without the use of brazing alloys or adhesive.

Cladding is used successfully in a wide variety of industries, including electrical, electronics, automotive, telecommunications, semiconductors and appliance industries. Connector contacts; switch contacts, wire bond interconnects and semiconductor lead frames are some typical applications for cladding.

This paper reports the results of a study on the effect of different diffusion annealing times on Copper-Silver bimetallic strips. This paper also includes evaluation of the electrical resistance of interfaces and micro hardness profiles from interface.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

In this investigation, silver strips (pure fine silver containing, at least 99.9% Ag, as annealed) and copper strips (UNS No. C11000, electrolytic tough-pitch copper,

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as annealed) were roll welded at room temperature. (Table 1)

Table1: Silver and Copper specifications.

Alloy	Chemical Composition , Wt%	Heat Treatment	Hardness , Hv 3Kgf	Tensile Strength , Mpa
Cu-UNS C11000	99.95% Cu	Annealed	45	250
Pure Fine Silver	99.9% Ag	Annealed	40	150

2.2. Cladding Process

2.2.1. Cleaning

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

Two pickling solution were used for the removal of oxides formed on the surface of copper and silver strips. (Table 2)

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

2.2.2. Bonding

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

Rolls surfaces were cleaned by acetone, until the surface roughness of the rolls was increased. The thickness was reduced by 65-75% by sufficient pressure to force the metal surface into intimate contact and to establish a bond between the metals.

2.2.3. Heat Treatment

The metals were subjected to heat treatment. This promoted the diffusion between the metals, resulting in a permanent metallurgical bond. Diffusion annealing was carried out in 500 °C for 0.5, 2, 5, 10, 20, 40 hours. The metallographic samples were cut longitudinally, and then

grounded, polished, and etched in a solution of 50 ml 6% hydrogen peroxide and 50 ml ammonia for 20 s [11].

2.3. Micro hardness profile

After the samples were cut longitudinally, they were ground and polished and Vickers hardness was measured at five different positions.

These 5 positions were:

- 1- Silver Matrix
- 2- Away from interface in Silver matrix; 60
- 3- Interface
- 4- Away from interface in copper matrix; 60 micrometer
- 5- Copper Matrix

2.4. Electrical Resistance

The electrical resistance of Ag/Cu samples was measured using a high precision micro-ohmmeter.

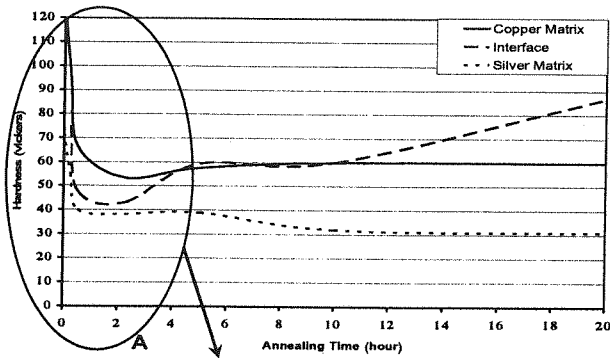
The micro-ohmmeter passed a certain current (I) parallel to the layers of the sample and measured the potential difference between two points of the sample with defined distance (L) of the bimetal by dividing the potential difference to the passing current, i.e.;

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

3. RESULT:

3.1. Evaluation of strength of bond by micro hardness profiles

Hardness (Vickers) versus annealing time (hour) is shown in Figure 1.



Detail 'A'

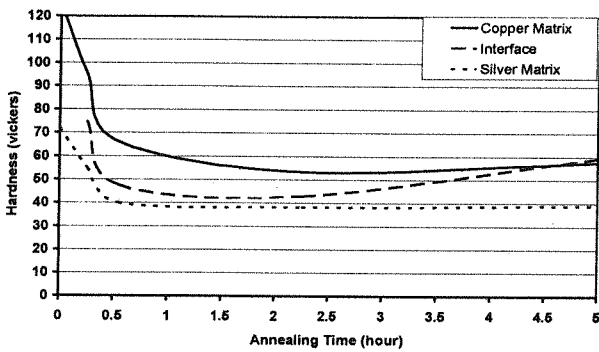


Figure 1. Hardness (Vickers) versus Annealing Time (Hour).

Micro hardness profiles are shown in Figure 2. Micro hardness in the interface of as rolled specimen was not available, because this specimen was not flat.

Table 3: Micro Hardness (Vickers) Profiles for Bimetallic Strips.

Annealed Time, hour	As-roll Clad	0.5	2	5	10	20	40
*	72	38	40	39	32	31	32
**	77.05	52.58	51.24	52.58	50.8	50.28	52.5
***	*	42.44	35.5	54.5	57.1	81.8	96.6
**	103.14	79.74	76.51	74.23	75.87	73.15	73.18
****	125	50	60	55	60	60	58

- * Silver Matrix
- ** Away from Interface, 60 μ m
- *** Interface
- **** Copper Matrix

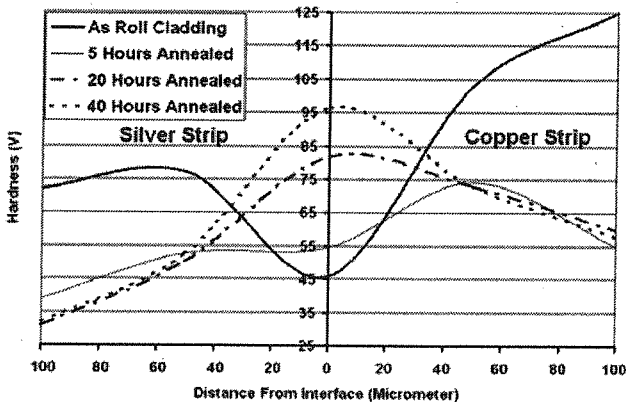


Figure 2. Hardness (Vickers) versus Distance from Interface (Micrometer).

These results show that increasing the annealing time increased the hardness of the interface and decrease the hardness at the silver and copper matrix.

3.2. Resistance and Conductivity of the bimetallic strips

Resistance and conductivity at various annealing time (5, 20, 40 hours) are listed in Table 4. Conductivity decreases highly with increasing the annealing time. The conductivity of eutectic compounds is much lower than the copper and silver and by formation of these compounds the total conductivity is reduced dramatically.

Table 4: Variation of Annealing Time and Conductivity.

Annealed Time, Hour	As-roll Cladding	5	20	40
Resistance of Bimetallic Strips ($\mu\Omega$)	22.42	24.07	28.94	35.13
Bimetallic Strips Conductivity $1/\rho$ (mm/ Ω mm ²)	60169.49	56044.10	46613.04	38399.70

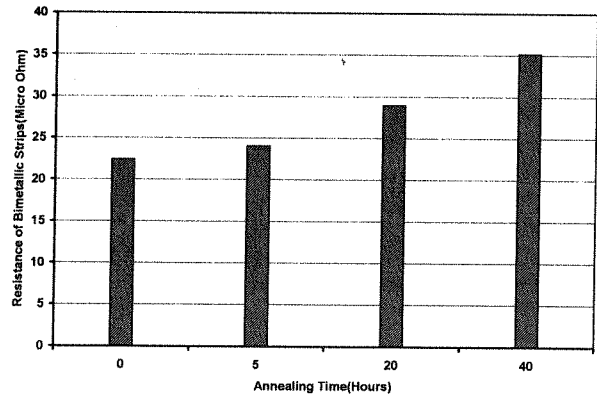


Figure 4. Resistance of Bimetallic Strips ($\mu\Omega$) versus Annealing Time (Hour).

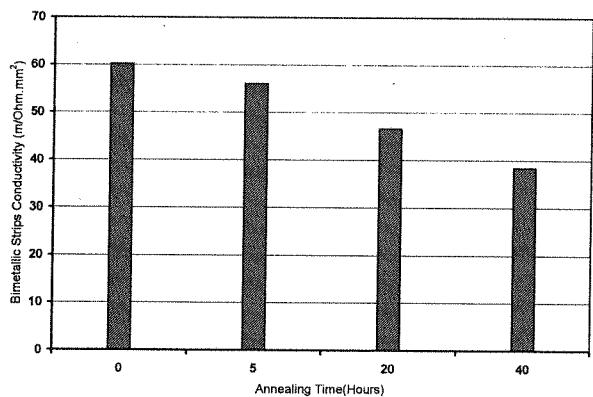


Figure 5. Bimetallic Strips Conductivity versus Annealing Time (Hour).

4. DISCUSSIONS

The mechanisms of diffusion bonding in this study were considered as follows:

1. Plastic deformation: in this stage, ridges of the surface asperities deform plastically in such a way that there is no macroscopic deformation in the parts to be bonded.
2. Surface and volume diffusion: in this stage, because of the difference of the curvature of the voids at the interface of the material couple, forming after plastic deformation, there are matter transfers from the parts having larger curvature to the void necks having a smaller curvature. The matter is also transferred from the bulk into the void surface by vacancy diffusion.
3. Bond interface diffusion and grain boundary diffusion for fine-grained materials: matter transfers from the bond interface to the neck of the voids due to the stress gradient at the interface and from the grain boundaries to the void surface for similar reasons.
4. Coupled creep and diffusion: in this stage, diffusion creep contributes the closure of the voids. 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 [13].

According to Copper-Silver phase diagram, Figure 6, these metals have a eutectic point at 779°C. (At Cu-28.1%Ag composition) At a lower temperature (for example 500°C) 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 [13].

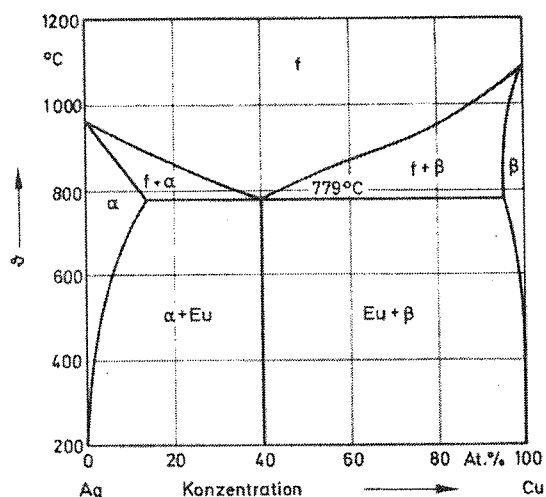


Figure 6. Phase Diagram of Ag-Cu.

Some Kirkendall porosity or vacancy clustering in the copper side may be accumulated during annealing treatment.

The hardnesses of silver and copper are decreased at 500 °C for 0.5 to 10 hours and then are constant for 10 to 40 hours annealing time. The hardness in the silver component is generally lower than that of the copper component.

Hardness in the interface is increased with increasing the annealing time. With increasing the annealing time over 5 hours, recrystallization occurs for silver and copper strips and in the interface because of forming eutectic compounds an increase in hardness is occurred.

Naturally, the Cu-rich secondary particles can precipitate in Ag-rich solid solution because the copper solubility in the silver matrix decreases with the reduction in temperature after diffusion treatment.

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

When annealing temperature is 500 °C and annealing time is 40 hours, because of:

- 1- Kirkendall effect that leads to the appearance of cavities in the interface.
 - 2- Formation of oxide layer in the interface.
- The interface bonding level of the bimetallic strips is small. (is lower than other annealing time.)

5. CONCLUSIONS

On the basis of the test results, the conclusions can be drawn as follows: 2 hours diffusion annealing at 500°C for the Ag/Cu bimetallic strips prepared by roll cladding at room temperature results in the hardness of silver and copper matrix and interface.

Diffusion annealing for a longer time at 500°C produces higher hardness and lower uniformity.

The following conclusions maybe achieved from the basis of the test results:

- 1- Hardness for copper and silver strips is decreased when annealing time is increased.
- Hardness for silver strip is lower than the hardness for copper strip.
- 2- The lowest hardness and the best strength happened at annealing temperature of 500 °C for 2 hours.
- 4- The lowest bonding strength in the interface is observed at 500 °C for as rolled strips.
- 5- Annealing at 500 °C for 40h causes the partial corrosion in the bonding interface.
- 7- Diffusion annealing treatments that can induce recovery, recrystallization, or partial corrosion in the bonding interface can lead to enhancement of the interface bonding level.

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