

# FATIGUE LIFE BEHAVIOUR OF SnPbAg/NiTi COMPOSITE

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**SUMMARY** : Uncoated and copper electroless coated fine NiTi superelastic particles have been incorporated into liquid SnPbAg matrix. The wettability of the Cu coating by the molten alloy was determined with a wetting balance. The composite interfaces have been investigated by Auger Electron Spectroscopy. Uncoated NiTi reacted with the matrix to form Ni-Sn intermetallics, whereas the Cu layer of coated particles behaved as a sacrificial layer, leading to a small interfacial zone containing neither Cu-Sn nor Ni-Sn intermetallics. The mechanical characterisation of Cu-coated NiTi/SnPbAg composites shows a reinforcement of the composite material compared to the monolithic matrix, and also an unusual increase of the elongation at rupture. This results can be interpreted with the superelastic properties of the NiTi SMA particles.

**KEYWORDS** : Tin Lead Silver Alloy, Nickel Titanium, Superelasticity, Metal Matrix Composite, Electroless Copper Coating, Interfacial Study.

## INTRODUCTION

Electronic devices are composed, at least, by components reported on printed circuit boards (PCB) with a low melting point solder paste. During temperature variations, the difference of coefficient of thermal expansion (CTE) between the component and the PCB may induce crack nucleation and propagation in the solder joint, leading to its rupture. This CTE induced mechanical and electrical failure is at present the major problem which reduces considerably the life time of these devices [1-5].

The approach investigated to solve this problem consists in replacing the conventional SnPbAg solder paste by a composite one, reinforced by equiatomic NiTi shape memory alloy (SMA) particles, which present superelastic properties. The maximum elastic strain is close to 10% for monocrystal material and 6% for a polycrystal one, whereas it is only 0.1% for a non SMA metal [6-10]. Thanks to the superelastic properties of such SMA particles, stresses can be relaxed, leading to a regeneration of the solder paste material and therefore to the increase of its life time [11-12].

However, because of the non wetting properties of NiTi by liquid SnPbAg matrix, the development of metal coating on micronic particles, as wetting agent, with controlled thickness, morphology and adhesion, has been done. Cu was chosen as a coating, and applied on the powder by an electroless method. The wettability of Cu-coated NiTi by liquid SnPbAg was evaluated with a wetting balance, on NiTi plates for several Cu thickness. In order to determine what are the interfacial reactions occurring at the NiTi/Cu/SnPbAg and NiTi/SnPbAg interfaces, Auger Electron Spectroscopy (AES) linescans have been performed on composite materials elaborated by a liquid way, containing either uncoated or Cu-coated NiTi fine particles as reinforcement. Mechanical characterisation were also achieved in order to evaluate the influence of superelastic particles on the mechanical properties of such composite solder joints.

## **EXPERIMENTAL**

### **Electroless copper coating**

Electroless copper has been chosen as coating element because of its capability to be wet by liquid SnPbAg, its low cost, and its usual application in electronic devices. The process is essentially based on the dipping of the powder in three successive baths, at room temperature [13,14]: a) sensitisation bath : 10g/l SnCl<sub>2</sub>, 40ml/l of 38% Hcl, b) activation bath : 0.25g/l PdCl<sub>2</sub>, 2.5ml/l of 38% Hcl, c) coating bath : 10g/l CuSO<sub>4</sub>, 10g/l NaOH, 50g/l KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.4H<sub>2</sub>O, 15ml/l CHOH, where CHOH initiates the deposition by reducing CuSO<sub>4</sub>. The powders are dispersed in the solutions by the vibrations of an ultrasonic probe with a maximum amplitude and ultrasonic energy of 160 μm and 600 W/cm<sup>2</sup>, respectively. Between each bath immersion, the particles are rinsed in distilled water, vacuum filtrate, and finally carefully dried in an oven at 70°C. The morphology of the coating was controlled by Scanning Electron Microscopy (SEM). The thickness has been optimised with the help of a statistical design of experiments, where the modified parameters are the dipping times in each bath, and the response parameters are the residual Pd and Cu coating thickness.

### **Composites elaboration**

The matrix, a commercial SnPbAg alloy : 62%Sn, 36%Pb, 2%Ag in weight, has a liquidus temperature of 189°C [15]. Its eutectic SnPb microstructure contains fine Ag<sub>3</sub>Sn intermetallics homogeneously dispersed in the Sn areas.

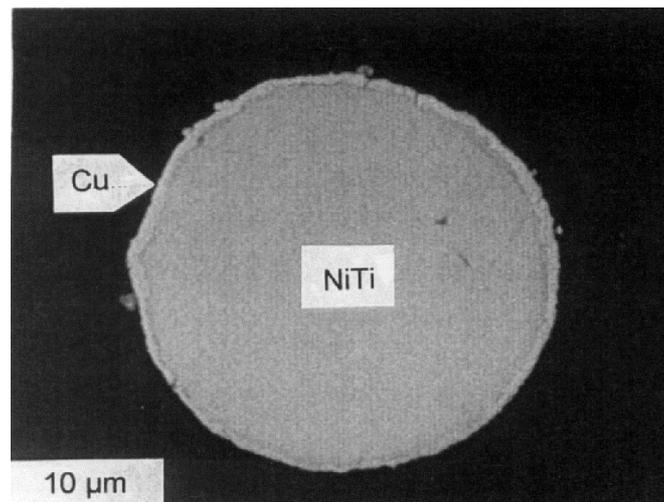
SnPbAg ingots are molten in a crucible heated at 200°C on a hot plate; glycerol has been added on top of the liquid alloy in order to prevent oxidation. Two different methods have been used to homogeneously disperse the uncoated and Cu-coated NiTi particles inside the liquid matrix. For the NiTi/Cu/SnPbAg composite, the coated particles are progressively introduced inside the molten alloy, with the help of a special shaped stirrer. In opposite, uncoated NiTi particles are dispersed in the matrix with the help of an ultrasonic probe dipped into the liquid metal. This method is, in our knowledge, the only way to incorporate uncoated NiTi particles inside SnPbAg. However, very low particle volume fraction composite (1-2%) can be elaborated by this special method. Ended, both composite materials are cast into an open-faced mould and water quenched. Very fast solidification of composite and monolithic materials has been found to be crucial for their microstructure (fine SnPb eutectic, small and homogeneously dispersed Ag<sub>3</sub>Sn intermetallics), and therefore for their mechanical properties.

### **Interfaces analysis**

Composite materials were mirror polished, prior to AES analysis. AES linescan data were acquired on a VG-MICROLAB 310-F Microprobe. The analyses conditions employed were an acceleration voltage and beam current of 10 keV and 1 nA, respectively. The data were taken in the conventional EN(E) mode. The energy windows scanned in this multiplexing technique were, for each element : O : 508-518 eV, Ni : 836-856 eV, Ti : 369-399 eV, Sn : 423-435 eV, Pb : 83-103 eV, Ag : 346-376 eV, Cu : 910-925 eV.

### **Mechanical characterisation**

Tensile tests and low cycle fatigue (LCF) were performed at room temperature and in air, on both monolithic SnPbAg matrix and Cu-coated NiTi/SnPbAg composites, for particle volume fractions ranging from 4% to 8%. The samples are flat dog-bones shaped specimens with 35 mm gauge length and cross sectional areas of 8.42 mm by 3.00 mm in the gauge sections. The apparatus is a computer controlled tensile machine, the test speed is 0.5 mm/mn for tensile tests and 1 mm/mn for LCF. The applied stress limits for LCF are the average yield stress (8 Mpa) and the lowest value of maximum stress (40 Mpa) of the monolithic matrix. The measured parameters for tensile tests are the Young modulus  $E$  ( $E=\sigma/\epsilon$  in the elastic domain) and the elongation at rupture  $\epsilon_R$ , for the LCF tests they are the plastic strain at  $N$  cycles ( $N = 50, 100, 150, 200$ ) and the number of cycles at rupture.



*Fig.1 : Cross section SEM micrograph of Cu-coated NiTi particle*

## **RESULTS**

### **Electroless copper coating**

The statistical method has enabled us to optimise the immersion time in the three baths (2 min each), in order to obtain an homogeneous copper coating, with a thickness lower than 1  $\mu\text{m}$ . As seen on Fig. 1, showing a SEM polished cross section of the Cu-coated NiTi particles, the Cu thickness is uniform and the film shows an apparent fair adhesion with the substrate. Because it is not possible to measure the adhesion of the Cu layer on micronic particles, NiTi wires have been coated with the same electroless baths and experimental conditions. A classical scotch test has been performed on these materials, and the absence of Cu on the scotch, which is representative of a good adhesion of the Cu-film on the NiTi substrate.

## Interfaces analysis

### *Uncoated NiTi reinforced composite*

Fig. 2 shows the trace of the Auger linescan across the NiTi/SnPbAg interface. Inside the matrix, the variation of the atomic concentration of Pb and Sn can be associated with the eutectic structure of the alloy. At the interface, a reaction zone of around 0.5  $\mu\text{m}$  is formed where the NiTi particle has reacted with the solder paste to form a Ni-Sn layer. In the NiTi particle, a constant composition equal to the original concentration (Ni 50 at.%, Ti 50 at.%) is found.

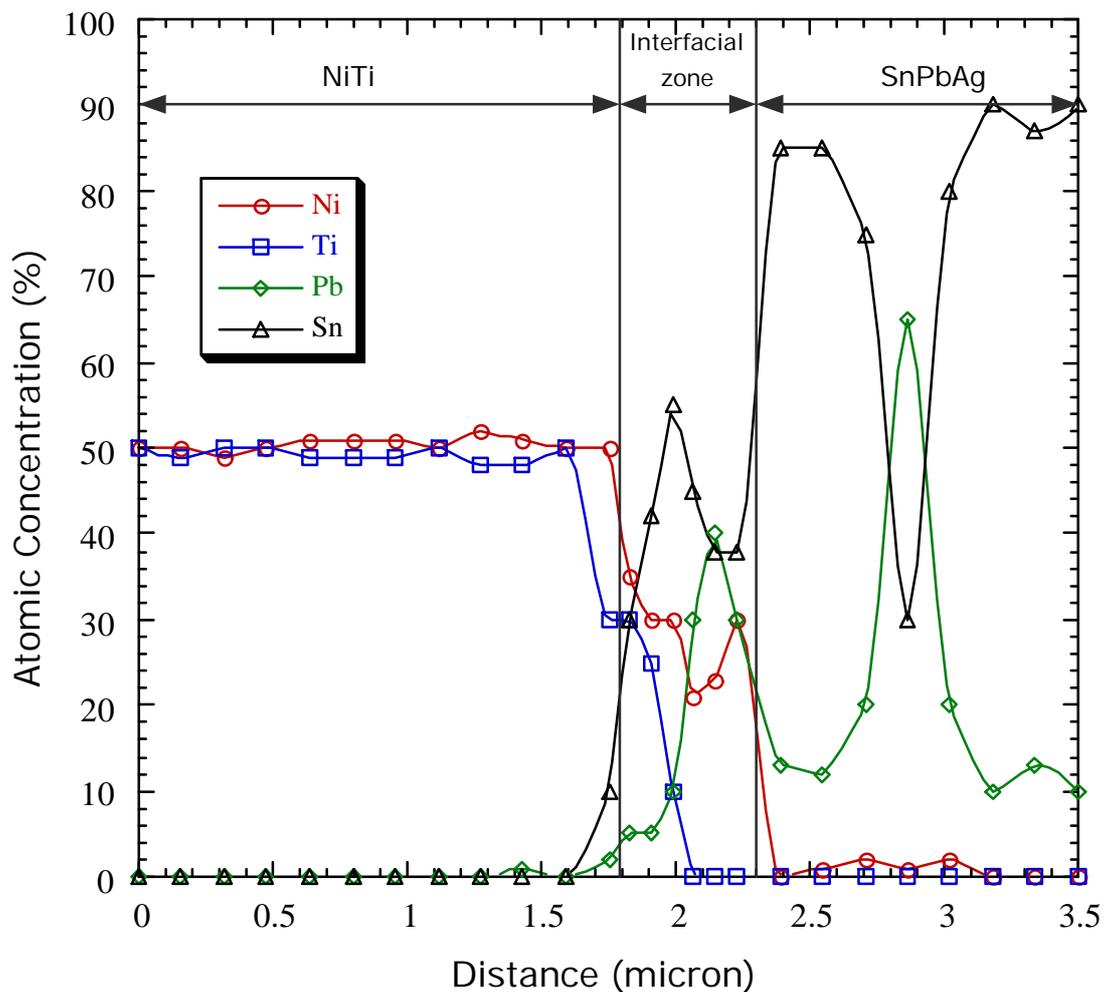


Fig. 2 : AES line scan profile across the SnPbAg/NiTi interface

### *Cu-coated NiTi reinforced composite*

Fig. 3 shows an AES line profile across the SnPbAg/Cu/NiTi interface. At that scale of observation, the eutectic morphology of the matrix is not observed, but a quasi constant Sn85at.%, Pb15at.% alloy. The interface area is very narrow (0.2  $\mu\text{m}$ ) and no chemical interaction between the matrix and the reinforcement is found. The electroless coating (thickness around 1 $\mu\text{m}$ ) has completely disappeared and only traces of Cu has been found

inside the matrix. A constant Ni/Ti ratio equal to 1 can be Auger determined, a constant oxygen concentration close to 15% is also observed inside the NiTi particle.

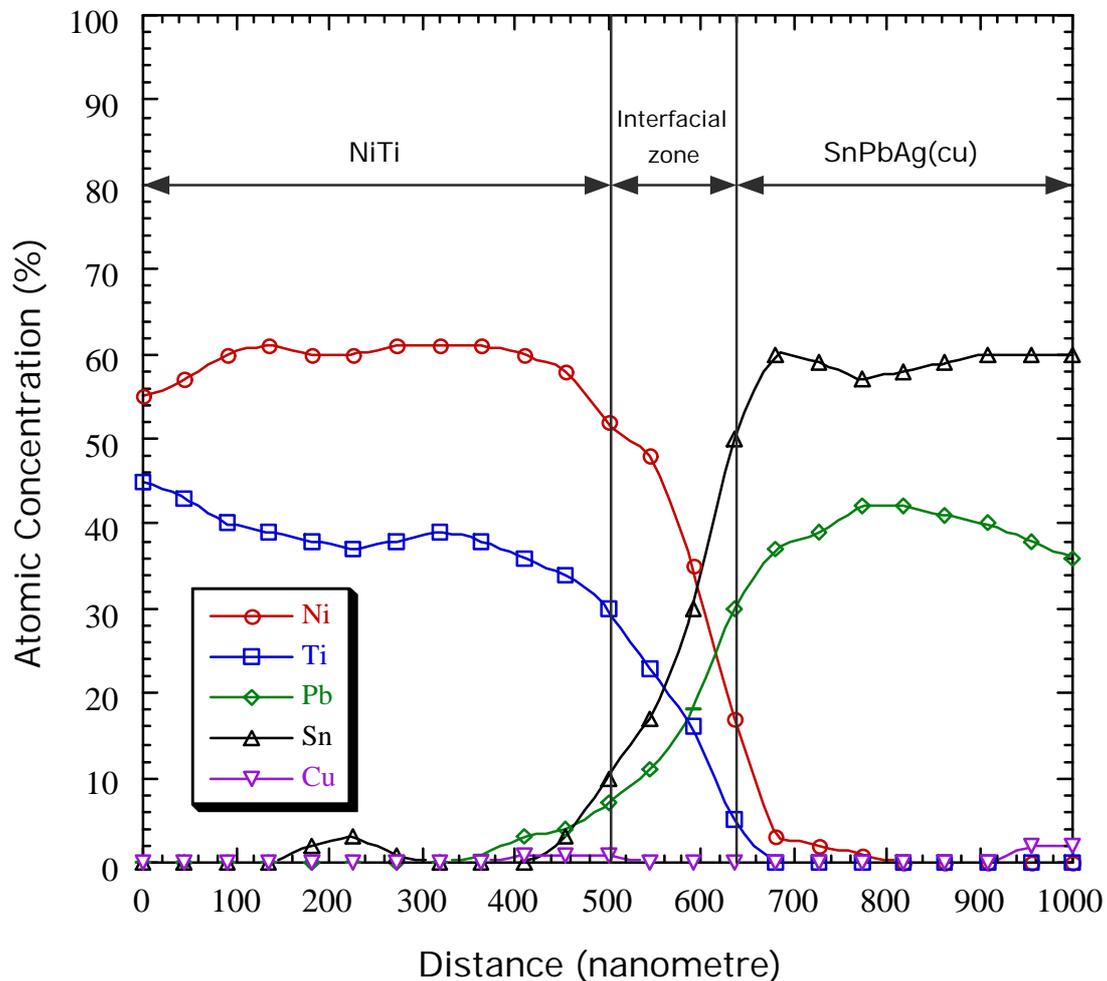


Fig. 3 : AES line scan profile across the SnPbAg/Cu/NiTi interface

## DISCUSSION

### NiTi/SnPbAg composite

The formation of a Ni-Sn interphase for the NiTi/SnPbAg quenched composite has been observed. EPMA analysis shows that  $Ni_3Sn_4$  intermetallic is formed. The nucleation and growth of that intermetallic tend : 1) to deteriorate the NiTi particles leading to a decrease of its mechanical properties, and 2) to weaken the composite by the presence of this fragile interphase.

### NiTi/Cu/SnPbAg composite

The Cu layer helps the NiTi particles to be wet by the liquid SnPbAg matrix and allow the elaboration of 4-8% particle volume fraction composite. Then, copper acts as a sacrificial layer and is found to be completely dissolved into the matrix after elaboration. No interfacial reaction zone is formed. The sharp matrix/particle interface observed is complex and can be

differently interpreted : 1) by the formation of possible Sn-Pb-Ag intermetallics which can lead to a drastic decrease of the reactivity of the matrix with NiTi particles (Cu can react with Sn to form  $\text{Cu}_6\text{Sn}_5$  or  $\text{Cu}_3\text{Sn}$ , in main references [2,3]  $\text{Cu}_6\text{Sn}_5$  is the first to be observed), or 2) by the presence of Cu coating which can act as a diffusion barrier and unable the liquid matrix to react with the reinforcement. Finally, this Cu layer inhibit the formation, in the liquid state, of  $\text{Ni}_3\text{Sn}_4$  intermetallics.

The absence of the eutectic microstructure observed by Auger can either be interpreted 1) as a possible Sn-Pb-Cu intermetallic or solid solution formed after Cu diffusion, or 2) as an artefact of observation due to the low scale of matrix (1.5  $\mu\text{m}$ ) analysed during the linescan. However, diffusion of Cu inside SnPbAg leads to matrix changes.

### Mechanical characterisation

The results described in table 1 are drawn out from statistical measurements on 20 samples of each specified material. The Young modulus calculated from tensile tests on SnPbAg ( $E = 27$  GPa) is equal to the value given as reference by the International Tin Research Institute [15].

The composite Young modulus increases with the particle volume fraction, for  $V_p=10\%$ ,  $E=33\text{Gpa}$ . This is a classical result for a composite due to particle reinforcements, and the value is compatible with the rule of mixture. Nevertheless, the elongation at rupture observed after tensile test is higher for the composite materials than for the monolithic matrix; an 8% increase is found for a 10% volume fraction. This behaviour is never observed for metal matrix composites, where the increase of both the stiffness and the ductility of the material is contradictory. One possible explanation of this surprising phenomenon can be the relaxation of the deformation induced stresses by the SMA particles, thanks to morphology changes. In the plastic domain of SnPbAg, the dislocations which are induced during the deformation of the material can move inside the matrix and are trapped at different microstructural defects, as the NiTi particles. The amount of stress inside the material is proportional to dislocation density. If the dislocations can move from the matrix into the NiTi particles (if we suppose a good matrix/particle adhesion and coherency between the two constituents), then the dislocations or the stress inside the particles can be relaxed by microstructural evolution (austenite to martensite change, and/or martensite plates movements), leading to a total decrease of the stresses inside the composite. This hypothesis, which can explain the increase of the elongation at rupture of the composite material, has to be confirmed by TEM characterisations of the dislocation density inside the matrix, and the microstructure of the NiTi particles.

However, the number of cycles at rupture, at room temperature and during LCF decreases for composite materials (35% decrease); this negative results should be overcome if we used smaller SMA particles (micronic diameter). Moreover, because the SMA properties are stress and temperature dependent, LCF between 20°C and 100°C have to be performed in order to correctly characterise the mechanical properties of these SMA/SnPbAg composite materials.

	Young modulus	Strain at rupture	Cycles at rupture
SnPbAg	27 GPa	36 %	833
Composite ( $V_p=10\%$ )	33 GPa	39 %	539

Table 1 : Mechanical properties for pure SnPbAg matrix and SnPbAg/Cu/NiTi composite

### CONCLUSION

1- Copper electroless coating method has been optimised to obtain a good homogeneity of the coating, a thickness lower than 1  $\mu\text{m}$  and a good adhesion with the NiTi substrate.

2- AES analysis demonstrated that the Cu layer is essential in composite elaboration, as diffusion barrier, to prevent Ni-Sn intermetallic formation at NiTi/SnPbAg interface. This Cu layer behaves as a sacrificial layer, leading to the absence of Cu Sn intermetallic formation, provided that the coating thickness is really suited to the duration of composite elaboration.

3- Tensile tests and low cycle fatigue show that the stiffness and the ductility of the composite materials are simultaneously improved, compared to the monolithic matrix. This phenomenon can be explained thanks to the ability of NiTi particles to relax stresses, by means of its superelastic properties.

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