THE THICKNESS MEASUREMENT OF SN-AG HOT DIP COATINGS ON LHC SUPERCONDUCTING STRANDS BY COULOMETRY

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Abstract

Amperostatic coulometry is applied for the thickness measurement of Sn-Ag hot dip coatings, which comprise an extended Sn-Cu interdiffusion layer. Complementary measurements, notably weight loss, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF) and dynamic secondary ion mass spectroscopy (DSIMS) have been performed in order to obtain a better interpretation of the coulometry results.

Based on the experimental results presented in this article the three potential changes that are observed during coulometry measurements are ascribed to (1) the entire dissolution of pure Sn, (2) the formation of a CuCl salt layer and (3) the surface passivation. The measurement of the pure Sn mass is well reproducible despite of strong coating thickness variations that are detected by XRF. Several experimental problems, in particular a coating undercutting, hamper the determination of the Sn mass in the intermetallic Sn-Cu layer.

To be published in the "Journal of the Electrochemical Society"

1 Introduction

For the construction of the Large Hadron Collider (LHC) [1] at CERN about 210 000 km of superconducting (SC) strands [2] are needed for the manufacturing of the LHC magnet coils. The strands, with a diameter of about 1 mm, consist of several thousand NbTi filaments that are embedded in a copper matrix. In the final strand production step the copper matrix is coated by a thin Sn-Ag layer.

The Sn-Ag coating is applied in order to control the contact resistance R_C between the individual strands in the SC cable [3,4]. The thickness of the Sn-Ag coating influences R_C and is therefore routinely measured by the strand manufacturers and at CERN using a coulometric method. During the LHC strand reception phase about 5000 strand samples per year are measured at CERN and a similar number of samples is measured at the different strand manufacturer sites.

Strand coating thickness results and the correlation between coulometry and atomic absorption spectroscopy (AAS) results have been reported previously in reference 5. The present article concentrates on the coulometric measurement technique and in particular on the capability of coulometry to measure the Sn mass in the Sn-Cu interdiffusion layer. X-ray fluorescence (XRF), dynamic secondary ion mass spectroscopy (DSIMS) and energy dispersive X-ray spectroscopy (EDS) were applied for the measurement of the homogeneity and the chemical composition of the coating. Weight loss measurements and X-ray photoelectron spectroscopy (XPS) have been performed in order to get a better understanding of the different processes that take place during the coulometric measurements.

2 Experimental

2.1 The samples

The samples analysed are SC strands for the LHC main dipole and quadrupole magnets with a nominal diameter $\varnothing$ of either $\varnothing = 0.825$ mm or $\varnothing = 1.065$ mm. The Sn-Ag coating is deposited onto the copper matrix of the SC strands by a hot dip process. For this purpose the strands are continuously fed through a bath of molten Sn95-Ag5 and directly afterwards through a so-called wiping die. The Sn-Ag coating thickness is controlled by the strand speed, the bath temperature and the diameter of the wiping die with respect to the uncoated strand diameter [2]. A Sn-Ag thickness of $0.5 \mu\text{m}$ is aimed for in order to obtain the desired R_C values during a reasonably long cable heat treatment time (about 8 hours at 200°C in air). During the coating deposition an interdiffusion of copper and tin occurs, producing a coating containing the intermetallic phases Cu_6Sn_5 (η -phase) and Cu_3Sn (ε -phase).

Several measurements that are presented in this article have been performed on strand samples that are considered to be identical (adjacent samples cut from one strand length, $\varnothing = 1.065$ mm). In the following these samples are referred to as reference strand samples. Some coulometry measurements have been done using uncoated OFHC Cu wires and Cu wires with a CuSn (Mirallloy®) coating, all with $\varnothing = 1.065$ mm. The nude

Cu wires were either used in the as-received state or after surface etching with different cleaners and fluxes.

2.2 Measurement of the coating mass

Coulometry measures the average coating mass per unit length of the strand sample dissolved while XRF averages the coating mass over the comparatively small surface area analysed. When assuming a constant coating density and a sharp interface between coating and substrate the coating mass can be expressed in terms of coating thickness.

In the present case of a hot dip coating with an extended Sn-Cu interdiffusion layer the coating composition and density are a function of coating depth. Despite this coating inhomogeneity a constant coating density of $\rho_{Sn} = 7.28 \text{ mg mm}^{-3}$ is in the following assumed for all thickness calculations. The Ag content in the coating is not taken into account for thickness calculations.

2.2.1 Coulometry

In coulometric coating thickness measurements [6] the electrical charge that is needed to dissolve the coating on a well-defined surface area is measured in order to determine the coating mass. In an ideal case the proportionality between the integrated cell current and the mass of the material analysed can be calculated from physical constants.

A self-made coulometry system is used, consisting of a working electrode (sample), a platinum counter electrode that is inert under the experimental conditions described, a reference electrode and a beaker containing the F12 electrolyte with a pH ≈ 1 from Helmut Fischer GmbH, Sindelfingen. According to the manufacturer this electrolyte contains about 4 % HCl.

The coating mass on the SC strands is measured by amperostatic coulometry, i.e. a constant current flow between the working electrode and the counter electrode is maintained. A current density of 10 mA cm^{-2} has been chosen in order to have measuring times that are sufficiently long for a precise integrated current measurement and at the same time maintaining an anodic current efficiency of 100 % (typical current densities in coulometry are higher, ranging between 100 and 400 mA cm^{-2} [6]).

For the measurement of the integrated current end points must be set at which the process of coating dissolution is assumed to be finished. For the determination of these end points anode potential changes are used that occur when the coating has been dissolved and the substrate material or a diffusion layer is exposed to the electrolyte [6]. Anode potentials have been measured against a saturated Calomel electrode (SCE).

When the measured cell current is entirely due to the transport of Sn^{2+} ions (anodic current efficiency $\eta = 100 \%$), the Sn mass m_{Sn} dissolved can be calculated from Faraday's law,

$$m_{Sn} = \frac{M_{Sn} \cdot Q}{z \cdot F} \quad (1)$$

with the molar Sn mass M_{Sn} , the integrated charge Q , the valence of the dissolved Sn ions ($z = 2$) and Faraday's constant ($F = 9.65 \times 10^4 \text{ C mol}^{-1}$). The charge Q is determined from the cell current and the dissolution time t_I . For a strand with $\varnothing = 1.065 \text{ mm}$ and an active length of 2 cm (surface area $A = 66.9 \text{ mm}^2$) the current density of 10 mA cm^{-2} is reached when a current of 6.69 mA is imposed.

Further assuming a pure Sn coating with a density $\rho_{Sn} = 7.28 \text{ mg mm}^{-3}$ the coating layer thickness d_{Sn} in μm can be calculated from the dissolution time t_I in s:

$$d_{Sn} = \frac{m_{Sn}}{A \cdot \rho_{Sn}} = \frac{118.7 \left[\text{g mol}^{-1} \right] \cdot 6.69 \cdot 10^{-3} \left[\text{A} \right] \cdot t_I \left[\text{s} \right]}{2 \cdot 9.65 \cdot 10^4 \left[\text{C mol}^{-1} \right] \cdot 66.9 \left[\text{mm}^2 \right] \cdot 7.28 \cdot 10^{-3} \left[\text{g mm}^{-3} \right]} \quad (2)$$

The current is adapted to each strand diameter such that the current density I/A is always 10 mA cm^{-2} . Hence, for all strand types d_{Sn} in μm is given by the relation:

$$d_{Sn} = t_I / 120 \text{ } \mu\text{m s}^{-1} \quad (3)$$

2.2.2 X-ray Fluorescence (XRF)

XRF measurements have been performed with a Xray-ComPact instrument from Röntgenanalytik Messtechnik. The instrument has been operated with collimator 2, resulting in an analysed spot size of $0.1 \text{ mm} \times 0.3 \text{ mm}$.

The measurement result obtained is the average coating mass per unit surface area, which is expressed in terms of coating thickness, assuming a constant coating density of $\rho_{Sn} = 7.28 \text{ mg mm}^{-3}$. The Ag content in the coating is not considered. For the case of Sn on Cu the minimum Sn thickness that can be measured by the instrument used is $0.25 \text{ } \mu\text{m}$. Since a suitable standard sample was not available the instrument has not been calibrated and, therefore, the thickness values presented must be considered as semi-quantitative results.

The Sn coating thickness has been measured on eight positions around the strand circumference by turning the strand sample in steps of 45° . Each thickness value given below is the average of five measurements that have been acquired along a 1 cm long line parallel to the strand axis. Hence, the total number of measurements per sample is 40. The minimum acquisition time for each measurement is 20 s. The entire measurement time needed for one strand sample, including sample positioning, is about 1 hour.

2.3 X-ray photoelectron spectroscopy (XPS)

All XPS measurements described have been carried out with a PHI ESCA 5400 instrument. The sample was exposed to air for about 1 hour before being introduced in the XPS vacuum system. Photoelectrons are excited by a non-monochromatic Mg K_α X-ray source operating at 350 W/15 kV. The PHI model 10-360 spherical sector electron spectrometer was operated with fixed pass energy of 89.45 eV for survey spectra and of 35.75 eV for high-resolution spectra. The analysed sample area has a diameter of about 1 mm^2 (aperture #2) and the electron take-off angle is 45° .

Atomic percent values (at.%) for the different elements detected have been calculated from the peak areas and the respective sensitivity factors published in [7]. Since the elements detected are not homogeneously distributed in the analysis volume the at.% values presented must be considered as semi-quantitative results. Peak areas are calculated after subtraction of a Shirley background [8].

The energy scale has been calibrated to the position of the Cu 2p^{3/2} and Au 4f^{7/2} peaks on sputter-cleaned samples. The reference peak positions used for chemical state analysis are listed in Table 1 together with the sources.

Table 1: Binding energy of the Cu 2p photoelectron peak and kinetic energy of the Cu-LVV Auger peak for different copper chemical states.

Chemical state	Cu 2p (eV)	Cu-LVV (eV)	Reference
Cu metal	932.5	918.6	7
CuCl	932.5	915.6	7
CuO	933.8	918.1	7,9
Cu ₂ O	932.5	916.2	10, 7
Cu(OH) ₂	934.4	916.2	10, 7

Due to charging effects all energies reported in the present work appear at about 0.5 eV lower kinetic energy than the reference values. Therefore, for the interpretation of the copper chemical state the energy difference between the Cu 2p photoelectron peak and the Cu-LVV Auger electron peak (Auger parameter) is used, which is not affected by surface charging.

2.4 Energy dispersive X-ray spectroscopy (EDS)

X-ray spectra were acquired with a Li-doped Si semi-conductor detector, ISIS 300 from Oxford Instruments. The energy dispersive spectrometer is attached to a scanning electron microscope Leo 430i. The primary electron beam energy was 20 keV.

In order to obtain a semi-quantitative result from the characteristic Sn and Ag X-ray peak intensities, the commonly used ZAF iteration method has been applied to take into account the influence of the atomic number on the excitation efficiency of the incident electron beam (Z), the absorption losses of characteristic X-rays (A) and fluorescent excitation (F) in the sample matrix [11]. Elements other than Sn and Ag have not been considered in the calculation of the Ag content.

2.5 Dynamic secondary ion mass spectroscopy (DSIMS)

A qualitative analysis of the elemental composition across a Sn-Ag hot dip coating has been obtained by DSIMS measurements, which have been performed by CSMA Ltd., Manchester, UK. Secondary ion mass spectra were acquired with a Cameca IMS 4f

instrument using a 10 keV Cs^+ primary ion beam (beam current = 10 nA). The depth scale has been calibrated by measuring the depth of the sputter crater by means of a profilometer [12]. The depth resolution of DSIMS is in the order of 10 nanometres.

The acquisition of fragment ions ($^{133}\text{Cs}^{63}\text{Cu}^+$, $^{133}\text{Cs}^{107}\text{Ag}^+$ and $^{133}\text{Cs}^{120}\text{Sn}^+$) is preferred over that of elemental ions since in this case secondary ion yields are less affected by matrix effects. However, since no standard samples are available the data shows only trends and cannot be quantified.

3 Results

3.1 Coulometry

3.1.1 Potential changes occurring during coating dissolution

When applying a current density of 10 mA cm^{-2} the potential of the Sn-Ag coated strand electrode remains for the time t_1 at a plateau of about -0.43 V versus a saturated calomel electrode (V/SCE). Afterwards on most strand samples three marked potential changes are observed during the sample dissolution in the F12 electrolyte. A typical potential versus dissolution time plot is shown in Figure 1.

Figure 1: Sample potential (versus saturated calomel electrode) as a function of the dissolution time t . Under the applied experimental conditions three potential plateaus are observed at -0.43 V/SCE, -0.05 V/SCE and +0.15 V/SCE.

The first potential change is from about -0.43 V/SCE to -0.05 V/SCE. This potential change is well reproducible on all kinds of strand samples and it does not depend on the degree of electrolyte agitation. When either a bare Cu wire or a Cu-Sn coated Cu wire is used as sample instead of a Sn-Ag coated strand and all experimental settings remain unchanged the -0.05 V/SCE potential is immediately established when the cell current is imposed.

The second marked potential change is to +0.15 V/SCE. After a few seconds this change is in most cases followed by a third change of a few volts to more positive potential. After the third change the anode potential is often not stable and shows strong fluctuations.

The potential changes to +0.15 V/SCE and to a few volts that are observed on Sn-Ag coated copper are also observed on bare copper. For both sample types these changes occur only when the F12 electrolyte is used without agitation. The 2nd and the 3rd change are often not well reproducible and the dissolution times t_2 (at -0.05 V/SCE) and t_3 (at +0.15 V/SCE) are strongly dependent on the current density.

On the Cu wire the dissolution time up to the potential change to +0.15 V/SCE is strongly dependent on the surface preparation. The dissolution time is significantly reduced when the native copper oxide is attacked prior to the sample insertion into the electrolyte, e.g. when treating the copper surface with a flux or a cleaner that etches the surface oxide.

3.1.2 Strand weight loss during coating dissolution

The sample weight loss of differently treated Cu wires and of Sn-Ag coated strand samples during the coulometric measurements has been measured in order to find out the kind of ions that are dissolved during the different sample dissolution steps. For the mass loss measurements the active strand length has been increased to 10 cm and the cell current has been adapted such that a current density of 10 mA cm⁻² is maintained. The samples were rinsed in an alcohol bath and thoroughly dried in air prior to the weight measurements. The weight loss measured for three different Sn-Ag coated strand samples during the dissolution at -0.43 V/SCE is shown in Table 2, together with the Sn mass calculated from $I \cdot t_l$ using Equation 1.

Table 2: Comparison between the weight loss measured with a precision balance during the dissolution time t_l and the mass m_{Snl} calculated from the integrated current $I \cdot t_l$ using Equation 1. The strand coating has been dissolved on an active strand length of 10 cm and the coating mass per cm strand is shown. The values presented are the average of at least 5 individual measurements.

Sample	Weight loss during t_l measured with balance (mg cm ⁻¹)	Sn mass calculated from $I \cdot t_l$ with 100 % Sn ²⁺ (mg cm ⁻¹)
01E	0.13 ± 0.01	0.12 ± 0.03
Strand reference	0.10 ± 0.01	0.10 ± 0.01
02C	0.051 ± 0.009	0.047 ± 0.002

The m_{Snl} values measured with the balance are in good agreement with the respective values that are calculated from the integrated cell current $I \cdot t_l$ when assuming that 100 % of the charge is transported by Sn²⁺ ions. The weight loss measurements of uncoated Cu wires indicate that, when dissolving a pure Cu wire at -0.05 V/SCE the cell current is entirely due to the transport of cupric ions (Cu²⁺).

Weight loss measurements on Sn-Ag coated strands during dissolution at -0.05 V/SCE were hampered by a significant material loss during sample rinsing in an alcohol bath. This effect was even stronger when samples were immersed in an ultrasonic bath. In this case the surface changed immediately from a greyish to a red, copper-like appearance, indicating the removal of a surface film. These observations indicate a substrate etching below the coating (undercutting) during sample dissolution at -0.05 V/SCE. The degree of undercutting depends on the current density [6], which may partly explain the strong influence of the current density on t_2 that is observed on certain strand types.

3.1.3 *The reproducibility of coulometry measurements and the influence of the electrolyte temperature*

The reproducibility of the coulometry measurements has been tested with ten reference strand samples. One sample was measured every day for ten successive working days, in order to consider fluctuations of experimental parameters such as concentration of metal ions in the electrolyte. The Sn mass dissolved during the time t_1 has been calculated using Equation 1 as $m_{Sn1} = 0.10 \pm 0.01 \text{ mg cm}^{-1}$ ($d_{Sn1} = 0.42 \pm 0.05 \text{ }\mu\text{m}$).

The influence of the electrolyte temperature has been investigated using 5 different strand samples. The electrolyte temperature was varied in steps between 12 °C and 28 °C while the other experimental parameters were kept constant. In this temperature range a significant influence of the electrolyte temperature on the dissolution time t_1 was not observed. However, already small changes of the electrolyte temperature influence the dissolution time t_2 . When the electrolyte temperature exceeds 25 °C t_2 increases dramatically. At 28 °C the t_2 value can be almost an order of magnitude higher than the value obtained for the same strand coating at an electrolyte temperature of 12 °C.

3.1.4 *Correlation between pure and total Sn thickness*

The total Sn mass in the strand coatings is determined by dissolving the entire coating in an acid, in which the Sn content is then analysed by atomic absorption spectroscopy (AAS) [13]. The total Sn mass is expressed in terms of AAS equivalent Sn thickness (d_{AAS}).

Figure 2: Pure Sn thickness (d_{SnI}) as a function of the total Sn thickness as determined by dissolving the entire coating in an acid and subsequent atomic absorption spectroscopy (AAS) analysis of the Sn content in the acid. All strand samples are from the same manufacturer. There is an approximately linear correlation between coulometry and AAS data.

In Figure 2 the pure Sn thickness (d_{SnI}) obtained so far for all samples of one manufacturer is plotted as a function of the total Sn thickness. It can be seen that there is an almost linear correlation between both values. Such a correlation is also found for the samples produced by other strand manufacturers. For the different sample types the average difference $d_{AAS} - d_{SnI}$ varies between 0.29 and 0.4 μm [5].

3.1.5 Influence of the Sn-Cu interdiffusion layer thickness on t_2

In Figure 3 the dissolution time t_2 (-0.05 V/SCE potential plateau) is plotted versus the Sn-Cu interdiffusion layer thickness ($d_{AAS} - d_{SnI}$). The results have been obtained for the same series of strand samples as those shown in Figure 2. Each data point is the average of two measurements. From Figure 3 it appears that t_2 and $d_{AAS} - d_{SnI}$ are not correlated.

Figure 3: Dissolution time t_2 (2nd potential plateau) versus the Sn mass in the interdiffusion layer. The Sn mass in the interdiffusion layer is expressed in terms of thickness, determined as the total AAS equivalent Sn thickness d_{AAS} minus the pure Sn thickness d_{SnI} . The dissolution time in seconds is scaled by a factor of 480.

3.1.6 Surface chemical analysis by XPS

XPS measurements have been performed in order to determine the surface composition and chemical state after the different dissolution steps during a coulometry measurement. Survey spectra were acquired on a Sn-Ag coated strand and on an uncoated Cu wire. In addition high resolution spectra were acquired on the Cu wire in order to determine the chemical state of the Cu surface. An uncoated Cu wire has been chosen for this purpose in order to avoid experimental problems due to coating inhomogeneity and coating undercutting.

Sn-Ag coated sample

The coating dissolution was stopped at the sample potential of -0.43 V/SCE, at -0.05 V/SCE and at +0.15 V/SCE and after oxidation in the electrolyte F 12 the sample was cleaned in an ultrasonic alcohol bath prior to the XPS analysis. The respective photoelectron spectra are shown in Figure 4.

Figure 4: Photoelectron survey spectra obtained after stopping the sample dissolution at a potential of -0.43 V/SCE (top), -0.05 V/SCE (middle) and at +0.15 V/SCE (bottom). Prior to surface analysis the samples have been cleaned in an alcohol bath. After dissolution at -0.43 V/SCE the only metal detected is Sn. In the spectrum “-0.05 V/SCE” a small Cu-LVV Auger and Ag 3d photoelectron peak appear but Sn is still the main metal present. In the “+0.15 V/SCE” spectrum the Sn and Ag peaks have vanished and instead strong Cu and Cl peaks can be seen.

In the photoelectron spectrum that was acquired after a short etch at -0.43 V/SCE (upper survey in Figure 4) the only metal detected is Sn. Carbon is omnipresent on air-exposed surfaces and is not considered further. When the dissolution process is stopped at -0.05 V/SCE potential some Cu and Ag is detected together with Sn. Cl is not detected. In the spectrum acquired after stopping the dissolution at +0.15 V/SCE (lower survey spectrum) an important quantity of Cl is found, indicating the adsorption of Cl ions from the electrolyte at this potential. Only traces of Sn are detected on this surface.

Uncoated Cu sample

The uncoated Cu samples were analysed when the dissolution was stopped just after establishing the -0.05 V/SCE potential, after reaching +0.15 V/SCE and after the last potential change to a few V. The surface composition of the Cu wire after the different dissolution steps, sample rinsing and the subsequent air exposure is shown in Table 3.

When stopping the sample dissolution at -0.05 V/SCE potential the only elements detected are copper, oxygen and carbon. The Cu 2p line-shape and energy position

indicate the presence of Cu^+ and/or metallic copper. The energy position of the Cu-LVV line, which has a larger probing depth than Cu 2p, is close to that of metallic copper. From these observations and the fact that a significant amount of oxygen is detected, one can conclude that the metallic substrate is covered by a thin layer of Cu_2O , which is presumably formed during the air exposure subsequent to the coulometry measurements.

Table 3: Surface composition in atomic % (at.%), Cu 2p binding energy and Cu-LVV kinetic energy obtained for a Cu wire after stopping sample dissolution at -0.05 V/SCE, +0.15 V/SCE and after passivation at a few volts. Due to surface charging all peak positions appear at approximately 0.5 eV lower kinetic energy than the reference values shown in Table 1.

Oxidation potential	Cu (at.%)	O (at.%)	C (at.%)	Cl (at.%)	Cu 2p ^{3/2} (eV)	Cu-LVV (eV)	Interpretation
-0.05 V/SCE	24.4	33.9	41.7	0	933.2	918.0	$\text{Cu}_2\text{O} + \text{Cu}$
+0.15 V/SCE	17.5	30.4	35.1	17.0	933.0 934.9	915.0	$\text{Cu}(\text{OH})_2 + \text{CuCl}$
passivation	29.3	16.3	25.7	28.7	933.0	915.0	CuCl

On the surface analysed after oxidation at +0.15 V/SCE, an equal amount of Cu and Cl is present on the sample surface, indicating the presence of a CuCl salt layer, which thickness exceeds the XPS probing depth. The line-shape of Cu 2p^{3/2} has two distinguishable components and a slight intensity at the satellite energy around 945 eV, which is related to the presence of Cu^{2+} . The Cu-LVV Auger peak energy position indicates additionally the presence of Cu^+ . These data and the surface composition shown in Table 3 indicate that the surface is covered by CuCl and some copper hydroxide.

Finally, the passivated surface has an unusually low content of oxygen. The Cu 2p^{3/2} and Cu-LVV line shape and position are characteristic for Cu^+ . Hence, this sample is almost entirely covered by a dense CuCl layer.

3.1.7 Surface morphology by scanning electron microscopy (SEM)

Variations of the strand surface morphology during the coulometry measurements have been investigated by SEM. The secondary electron images that were acquired in the as-received state and after coating dissolution during coulometry measurements at -0.05 V/SCE and +0.15 V/SCE are shown in Figure 5. It can be seen that the strand surface roughness increases strongly during the different coating dissolution steps. The surface morphology does not significantly change when the sample potential changes from +0.15 V/SCE to a few volts (surface passivation).

An elemental analysis of the outermost micrometer by EDS revealed the presence of Cl after oxidation at +0.15 V/SCE. Provided that the sample was properly cleaned before the EDS analysis no Cl was detected after oxidation at -0.43 V/SCE and at -0.05 V/SCE [14].

Figure 5: Morphology of the Sn-Ag hot dip coating in the as-received state before dissolution (left), after oxidation at -0.05 V/SCE (middle) and after oxidation at $+0.15$ V/SCE (right). For all images the magnification is 1500 (courtesy of J.-M. Dalin, CERN, EST-SM).

3.1.8 Sample aging

The thickness of a pure Sn layer on a Cu substrate may be significantly reduced within a few months storage due to the growth of a tin copper inter-diffusion layer [15]. It is therefore of interest to verify if the strand storage time at ambient conditions influences the coulometry results. For this reason a series of strand samples from different manufacturers was measured after reception at CERN and after further storage between 24 and 38 months.

For the 39 samples that have been tested the average d_{SnI} values (i.e. the pure Sn thickness) before and after prolonged storage are $0.31 \mu\text{m}$ and $0.28 \mu\text{m}$, respectively. This indicates that sample aging can slightly affect the d_{SnI} results. However, the aging of the present Sn-Ag layer is much less important than the aging for a pure Sn on Cu coating as it is reported in reference 15.

3.2 The variation of the coating composition as a function of depth as determined by DSIMS

In Figure 6: the intensity of $^{133}\text{Cs}^{63}\text{Cu}^+$, $^{133}\text{Cs}^{107}\text{Ag}^+$ and $^{133}\text{Cs}^{120}\text{Sn}^+$ ions is shown as a function of depth through a Sn-Ag strand coating. It can be seen that the Cu fragment ion intensity increases continuously while the Sn and Ag intensities decrease continuously with sputter depth. Despite the fact that the DSIMS results cannot be quantified this shows clearly that there are no discrete layers of the intermetallic phases Cu_6Sn_5 and Cu_3Sn . Instead the Sn content decreases gradually from the outer Sn layer towards the inner Cu substrate. This observation is also confirmed by Auger electron spectroscopy

(AES) and XPS sputter depth profiles that have been performed at CERN and elsewhere [16].

Figure 6: $^{133}\text{Cs}^{63}\text{Cu}^+$, $^{133}\text{Cs}^{107}\text{Ag}^+$ and $^{133}\text{Cs}^{120}\text{Sn}^+$ secondary ion intensities as a function of sputter depth. The continuous increase of Cu and decrease of Sn and Ag intensities shows that the Sn concentration within the coating decreases steadily towards the Cu substrate and that there are no discrete layers of Cu_6Sn_5 and Cu_3Sn .

3.3 Coating thickness variations as determined by XRF

In Table 4 the average coating thickness, calculated from the eight thickness values around the coating circumference, is plotted for different strand samples. In the same table the maximum and minimum values measured are shown together with the standard deviation calculated for the eight measurements. The standard deviation can be regarded as a measure for the coating thickness homogeneity. The repeatability of the XRF measurements has been tested by acquiring 10 successive thickness measurements on the same surface spot without moving the sample (measurement time 20 s). The measurement result was $0.69 \pm 0.04 \mu\text{m}$.

For the three samples analysed (all from the same manufacturer) the Sn thickness variations increase with the average coating thickness. The maximum and minimum thickness measured on one sample can vary by more than a factor of 5.

Table 4: Average, minimum and maximum coating thickness in μm and standard deviation calculated from the 8 mean values obtained by turning the coating in 45° steps. The standard deviation can be considered as a measure for the coating thickness homogeneity. The XRF values are compared with d_{SnI} determined by coulometry. For all measurements the presence of Ag is not considered.

Sample	d_{SnI} (μm)	Average thickness XRF (μm)	Minimum thickness (μm)	Maximum thickness (μm)	Standard deviation
01B00445A03SX	0.27	0.34	< 0.25	0.64	0.22
01B00563A04SA	0.31	0.58	0.33	0.90	0.27
Strand reference	0.42	0.72	< 0.25	1.28	0.39

3.4 The Ag content in the Sn-Ag coating as determined by EDS

An estimation of the Ag content in the Sn-Ag coating of a reference strand sample has been obtained by EDS. The sample was analysed on opposite faces of the strand, which respective relative thickness is $0.25 \mu\text{m}$ and $1.3 \mu\text{m}$, as determined by the XRF method described above. The Ag concentration averaged from five individual measurements is 2.9 wt.% and 4.4 wt.% on the thin and the thick coating side, respectively.

The ZAF method makes iterative corrections for fluorescence and absorption effects, but it assumes that the sample has a homogeneous composition in the excited sample volume. On the thinner coating side the excitation volume extends into the substrate material, as indicated by strong Cu peaks in the X-ray spectra, while on the thick coating side only a small Cu peak is visible.

4 Discussion

4.1 In depth composition of the Sn-Ag hot dip coatings

Hot dip Sn coatings are commonly applied to copper in order to prevent strong surface oxidation and to preserve a good surface wettability of substrates that need to be soldered (pre-tinning) [17]. Such coatings are often described as a sequence of 3 discrete layers, notably an outer pure Sn layer on top of a Cu_6Sn_5 layer (η -phase) and a Cu_3Sn layer (ε -phase).

In the present case of Sn-Ag strand coatings the sputter depth profiles through the coating reveal that there are no discrete intermetallic surface layers and that the Sn content in the coating decreases gradually from the outer Sn layer towards the inner Cu substrate. The reason for this discrepancy between the published results for Sn on Cu and the present Sn-Ag on Cu hot dip coatings may be related to the comparatively small coating thickness and/or the presence of Ag in the strand coatings.

4.2 Sn mass measurement by coulometry

A complication of the Sn mass measurement in the present case of a thin hot dip coating is the presence of an extended intermetallic Sn-Cu layer, in which an important amount of the total Sn coating mass is present. It is therefore important to evaluate if the coulometry method can be applied for the measurement of the Sn in the Sn-Cu layer as well as in the pure Sn.

4.2.1 Interpretation of the three potential plateaus

As outlined in 2.2.1, for coulometry measurements it is necessary to set end points at which a certain coating dissolution process is assumed to be finished. In order to find useful end points the origin for the different potential plateaus that are observed during the dissolution process need to be known. Based on the experimental results presented the three potential plateaus (-0.43 V/SCE, -0.05 V/SCE and +0.15 V/SCE) are interpreted as follows:

The -0.43 V/SCE potential is obtained for a pure Sn layer, containing up to a few per cent of Ag. The -0.05 V/SCE potential, which is found for Sn-Ag coated samples after the 1st potential change, is also found for uncoated and for Cu-Sn coated Cu wires. The 1st potential change from -0.43 V/SCE to -0.05 V/SCE is hence due to the entire consumption of the pure Sn layer, leaving a Sn-Cu layer, which Cu concentration can vary over a wide range. The presence of Sn on the strands after the potential change to -0.05 V/SCE is confirmed by XPS measurements (see Figure 4).

Surface analysis measurements reveal that during oxidation at +0.15 V/SCE a CuCl layer is present on the sample surface while no Sn is detected. The 2nd potential change from -0.05 V/SCE to +0.15 V/SCE is therefore assumed to be due to the adsorption and incorporation of Cl anions on the Cu surface from the electrolyte. The critical potential value at which a CuCl salt layer is formed on Cu anodes in HCl solutions [18] depends on the degree of electrolyte agitation, which may explain why the CuCl formation (and the 2nd potential change) is not observed when stirring the electrolyte during the coulometry measurements.

In most cases the 2nd potential change is followed by a 3rd change of a few volts, which is presumably due to the surface passivation [19]. Since the 3rd potential change is not related to the presence of Sn on the surface it is not relevant for coating thickness measurements.

This interpretation is partly in contradiction with other studies from which it was concluded that, under experimental conditions that differed from those described here, the 2nd and 3rd potential plateaus are characteristic for intermediate layers of the intermetallic phases Cu₆Sn₅ and Cu₃Sn, respectively [15].

4.2.2 Measurement of the pure Sn mass (1st potential plateau)

Weight loss measurements show that only Sn²⁺ ions are dissolved until the anode potential changes to -0.05 V/SCE. Hence, the Sn mass can be easily calculated from the Sn molar mass and the total accumulated charge $I \cdot t_L$.

Strong variations of the Sn coating thickness around the strand circumference seem not to perturb the m_{SnI} measurement. The m_{SnI} measurement is also rather robust against moderate variations of the experimental parameters and it is only slightly influenced by strand storage under ambient conditions of a few years. The comparatively moderate influence of the storage time on m_{SnI} might possibly be explained by the Ag content in the coating.

4.2.3 The usefulness of t_2 for the determination of the Sn mass in the Sn-Cu interdiffusion layer (2nd potential plateau)

The time t_2 needed to reach the +0.15 V/SCE potential change is longer for Sn coated Cu as it is for a bare Cu wire. This might indicate that the amount of Sn in the interdiffusion layer could influence the time t_2 by delaying the formation of the CuCl layer.

If t_2 would be correlated to the Sn mass in the interdiffusion layer it should be possible to determine the relative contribution of Sn and Cu ions to the cell current by combined weight loss and charge measurements, since the ion species that are dissolved have been determined (Sn^{2+} and Cu^{2+}) and the Sn and Cu molar masses vary by a factor of 1.9. However, reliable weight loss measurements were not possible because of the important material loss that takes place when taking out the samples of the electrolyte and during the subsequent sample rinsing. This material loss is caused by a preferential substrate etching below the coating (coating undercutting) at the -0.05 V/SCE potential.

While coating undercutting is probably the main reason why t_2 and the Sn mass in the interdiffusion layer ($d_{AAS} - d_{SnI}$) are not correlated (see Figure 3), the strong influence of experimental parameters like the current density, electrolyte composition and temperature on t_2 may be another cause. For uncoated Cu it has also been shown that the substrate surface preparation can have a strong influence on the time needed to form a CuCl layer.

It is hence concluded that, because of the variety of factors that influence t_2 , its practical use for Sn mass measurement in the Sn-Cu interdiffusion layer seems not to be possible.

4.3 Localised coating thickness measurements

The XRF measurements show that the strand coatings exhibit strong thickness variations around the circumference of the three SC strand samples tested. Thickness readings on one strand sample can vary by more than a factor of five (see Table 4). The localised thickness variations that are measured depend on the spatial resolution of the technique used, i.e. the better the spatial resolution of the technique the larger can be differences in the measured coating thickness. In the present case the thickness values are averaged over a surface area of 0.1 mm x 0.3 mm.

The strand curvature causes a further complication for the Sn coating thickness measurement on strands. The smaller the strand diameter the larger will be the influence of the curvature on the result. For this reason strands with 0.825 mm diameter were not tested.

Several analytical techniques with spatial resolution, such as XPS, AES or DSIMS can in principle be used directly to assess the localised coating thickness. However, measurement time and cost for these techniques are prohibitive for routine thickness

measurements. Compared to the previously mentioned techniques XRF measurements are simpler and less time consuming. The acquisition time with the instrument used (about 1 h including sample positioning when acquiring data on five points at eight different angles) may be reduced when using an instrument with higher sensitivity and an automatic sample positioning stage. Provided that a sufficiently large number of individual XRF measurements per strand sample can be acquired in a reasonable time and that useful standard samples are available XRF might also be used to determine the absolute Sn coating mass.

5 Conclusion

The three potential plateaus -0.43 V/SCE, -0.05 V/SCE and +0.15 V/SCE that are observed during the Sn-Ag coating dissolution are attributed to pure Sn, Cu (with or without the presence of Sn) and CuCl, respectively.

The measurement of the pure Sn mass in the Sn-Ag strand coatings by coulometry is well reproducible. Under the experimental conditions described, at -0.43 V/SCE a current efficiency $\eta = 100\%$ is obtained and, therefore, the Sn mass can be calculated from $I \cdot t_1$, i.e. no calibration is required.

Due to coating undercutting and the variety of parameters that influence t_2 , the use of $I \cdot t_2$ for the determination of the Sn mass in the Sn-Cu interdiffusion layer seems to be impossible. Therefore, the Sn mass in the interdiffusion layer has to be determined as the difference between the total Sn mass (determined by another technique) and m_{Sn1} .

Compositional depth profiles through the Sn-Ag coating reveal the absence of discrete intermetallic coating layers and XRF detects important thickness variations around the circumference of the strand coatings.

Acknowledgements

We would like to thank D. Leroy, D. Richter and T. Boutboul for fruitful discussions and a critical reading of the manuscript. We are also grateful to H. Krummenacher from Helmut Fischer AG for proposing the XRF method for measuring coating thickness variations, to L. Ferreira for helpful discussions concerning the coulometry measurements and to Z. Charifoulline for the setting up of the PC controlled data acquisition system. We are thankful to M. Grenard for performing the coulometry measurements, M. Carosone and D. Letant for the AAS measurements and to M. Malabaila for technical assistance during the XRF measurements. J.-M. Dalin we would like to thank for the SEM images.

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