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Lead-Free Conductors with a Surface Treatment Ensuring a Low Melting Temperature

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Abstract

In order to protect the environment and to ensure sustainability, it is prohibited to use lead materials in the production of automotive components. As part of soldering, busbars are used that usually have a copper core and a coating made of tin, but the melting point of such material is high, which poses a problem during soldering. This article discusses the case where a busbar is interconnected with another conductor in a sealable pressure vessel where high temperatures and pressures are reached. The product is heated to a certain temperature and the melting temperature of the given bus coating is exceeded, resulting in soldering and an ideal connection of the wires. The problem is that the temperatures reached by the processor during this operation are lower than the melting temperatures of the busbar with a tin coating. In the article, the authors focus on the production and development of new types of busbars with a coating consisting of tin, bismuth and indium and discuss possible formulations and their effect on the melting temperature of the busbars.

Keywords

lead-free soldering, environment, coating, conductors, tin

1 Introduction

Tungsten wire heated car windshields have strict regulations regarding maximum heating temperatures. According to the new legislation, it is also necessary to use lead-free materials for the processing of laminated glasses with tungsten wires. In the case of laminated samples, the sample overheats in the busbar area under the laboratory conditions.

Overheating is caused by imperfect contact between the conductors, which increases the transition resistances in the given place and increases the temperature. The objective of this study is to design lead-free materials suitable for soldering wires, busbars, and connectors within the automotive windshield (Zang et al., 2011). Front laminated glass is produced in the first step by floating the glass on a float line. Subsequently, the glass is cut into the required shapes and subsequently shaped, most often by gravity bending of the glass.

The glasses are then laminated with PVB foil. As part of the preparation of the PVB film, a tungsten wire is applied to the film itself, the busbar is glued to the PVB and connectors are usually soldered to the busbar (Pilkington et al., 1969).

The PVB is cut into sheets, first providing the first layer of busbars. This first busbar layer is either glued or soldered to the PVB. These busbars form the base layer and are in direct contact with the PVB. Subsequently, tungsten wires are applied over these busbars with a dedicated automatic device. As soon as they are applied, the connectors are soldered to the busbar set and the tungsten wire. Once the connectors are energized, the top layer of the busbar is applied, which is again either glued or soldered. The typical composition of conductors in the automotive glass industry is schematically indicated in Fig. 1 (Xu et al., 2018).

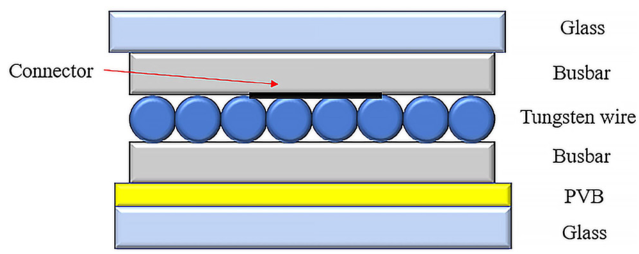

Fig. 1 Typical composition of conductors used in the automotive glass industry

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Optimal contact between all conductive connections is important, i.e. between the busbar, the wire and the connector. Imperfect contact between conductors is usually caused by their imperfect connection. Subsequently, vacancies are created in which the value of the transition resistance increases and the place heats up. In this case, the conductors conduct electric current more poorly. When the electric current flows, the power loss increases locally. This power loss manifests itself in increased heating and, depending on the intensity of the current flowing through the conductors and the size of the transition resistance ($P = I^2 \times R$), can cause ignition temperatures to be reached. A power loss of around 60 W already represents a very acute risk of fire. In professional circles, significantly lower values are often cited as fire hazards. Non ideal contact between the conductors is depicted in Fig. 2 (Mareška et al., 2022). In the framework of this study, it is mainly dealt with busbar material. Various coatings are applied to the busbar using dip coating technology and their effect on the formation of transition resistances is tested. It is thus applied to the so-called solder to the bus. Solder is a key element in the field of electronics and electrical engineering, which is used to solder connections. It creates the mechanical and electrical connection necessary to secure components in place in an electronic assembly. This can only be achieved if the material used, i.e. solder, conducts electricity well (Balabanova et al., 2016). Another requirement for the material from which the solder joint is made is that it should be easy to use. Unlike other alloys and pure metals, solder has the advantage of melting at a relatively low temperature. This means that it is most suitable for mounting electronic devices. The different melting point of different types of solders is a key parameter in their use. Some solders are activated at a lower temperature, i.e., < 200 °C, others at a higher temperature, for example > 200 °C. Various soldering technologies exist, some are contact methods, among which we can distinguish between mechanical and manual processes with the help of an operator, and so-called non-contact methods, where soldering takes place, for example, due to exceeding the melting temperature, e.g., in an autoclave. Solder is a material that can historically be understood as an alloy of tin and lead. However, there are different types of solder based on what they are used for. Solder for electronics contains 60% tin and 40% lead (Tu et al., 2001), which is generally referred to as "60/40 solder" (Zeng et al., 2002). In chemical terminology, it is a eutectic alloy – it melts at a lower temperature than its individual components (Fig. 3) (Zhang et al., 2021). The use of flux is often required to create quality joints. Flux is a chemical used as a cleaning agent to remove the oxidized layer. For soft soldering, rosin is most often used, or perhaps a soldering paste containing a mixture of zinc chloride and ammonium chloride with organic fats. Soldering joints up to 450 °C is referred to as soft soldering. Within various solders, the flux can be contained directly in the solder, or it can be used as a separate component (Alves et al., 2022). To reduce the amount of lead for reasons of environmental and health protection, lead-free solders have been used recently. The European directive states that lead solders must not be used for commercial purposes (Cheng et al., 2017). Lead-free solders have fully replaced traditional solders with lead. A wide variety of species are disposable in the market. One of them is a solder with a composition of 99.3% tin and 0.7% copper (Zhao et al., 2019), which has a melting point of 227 °C, which is close to the melting point of traditional lead solder. Other types available contain a small admixture of silver (Yassin et al., 2019). It is somewhat more expensive, but its melting point is 217 °C. It is sometimes called silver solder. However, it should be noted that the amount of silver contained is really small. Modern lead-free solders are often alloys of tin, copper and silver in different ratio like 99.3% Sn / 0.7% Cu (Fig. 4) or 96.5% Sn / 3.0% Ag / 0.5% Cu or 95.5% Sn / 3.8% Ag / 0.7% Cu (Fig. 5) (Ramli et al., 2020).

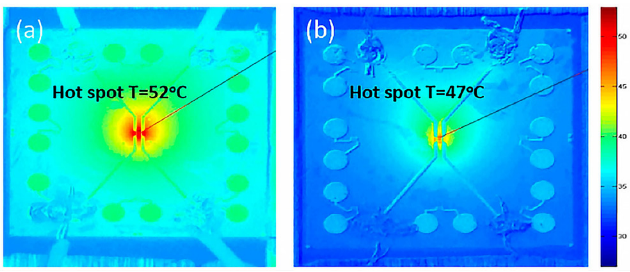

Fig. 2 Non-ideal contact between two conductors (Balabanova et al., 2016)

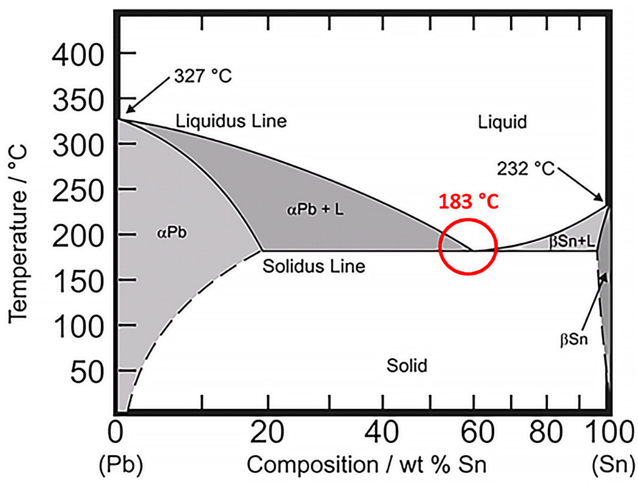

Fig. 3 Tin lead binary phase diagram (Tu et al., 2001)

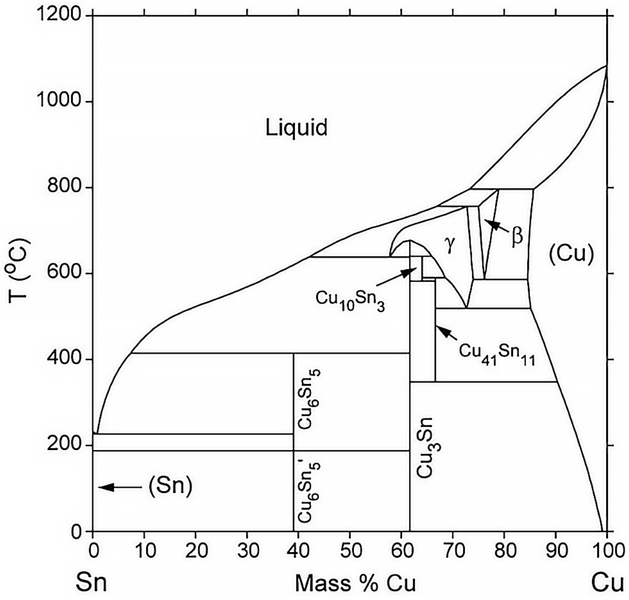

Fig. 4 Tin Copper binary phase diagram (Zhao et al., 2019)

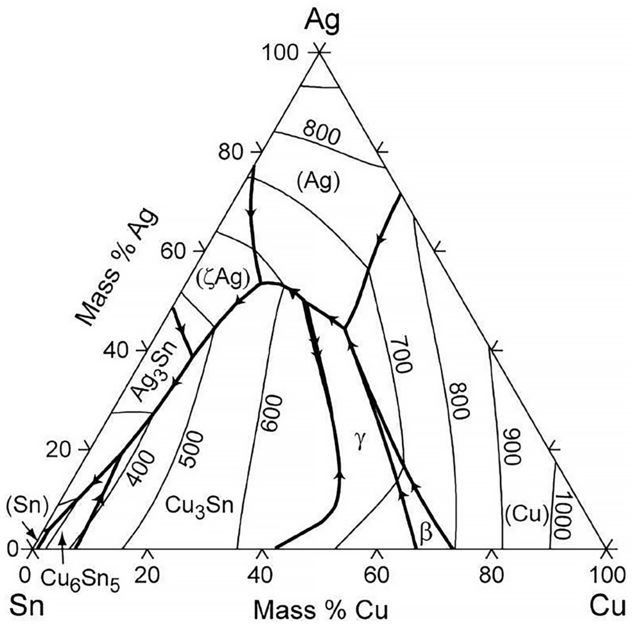

Fig. 5 Tin Copper Silver ternary phase diagram (Nousiainen et al., 2008)

Lead-free solders work similarly to traditional solders, except that longer soldering times must be used or the soldering temperature itself must be increased. This fact can cause problems especially for less experienced soldiers if it is referred to the manual soldering (Gao et al., 2023). The most commonly used busbars in the automotive glass industry are copper busbars with a diameter from 0.025 mm to 0.100 mm. They may or may not be coated with a layer of tin usually 0.005 mm to 0.025 mm thick (Nousiainen et al., 2008). This layer of tin allows hand soldering of joints. As a rule, the busbar can be automatically applied with or without a tin coating. However, the problem is the high soldering temperatures, which do not allow soldering as easily as in the case of lead materials. Partly due to better workability, and partly due to the improvement of the quality of the soldered joint, the use of busbars that have a melting temperature below 139 °C is recommended. This melting temperature is based on the maximum temperature of the autoclave cycle when processing laminated glass with PVB. As part of this requirement, the use of $Sn_{42}Bi_{58}$, a low-temperature alloy of tin and bismuth is proposed, the melting point of which is approximately 138 °C Fig. 6. In this case, it is not necessary to solder the busbar manually or automatically, but the busbar can only be secured on the PVB foil using acrylic glue and the activation will take place within the autoclave cycle (Nishikawa et al., 2022). Subsequently, the use of Bi_{57}–In_{26}–Sn_{17} bismuth-indium-tin solder is suggested Fig. 7 whose melting point is even below 100 °C, specifically around 79 °C, if lower maximum temperatures are set during the autoclave cycle (Manasijević et al., 2018).

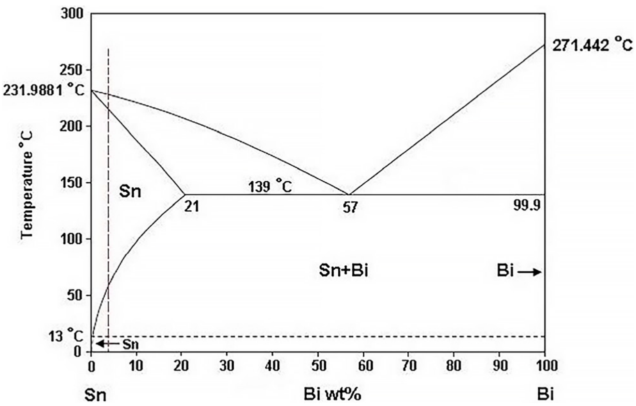

Fig. 6 Tin Bismuth binary phase diagram (Nishikawa et al., 2022)

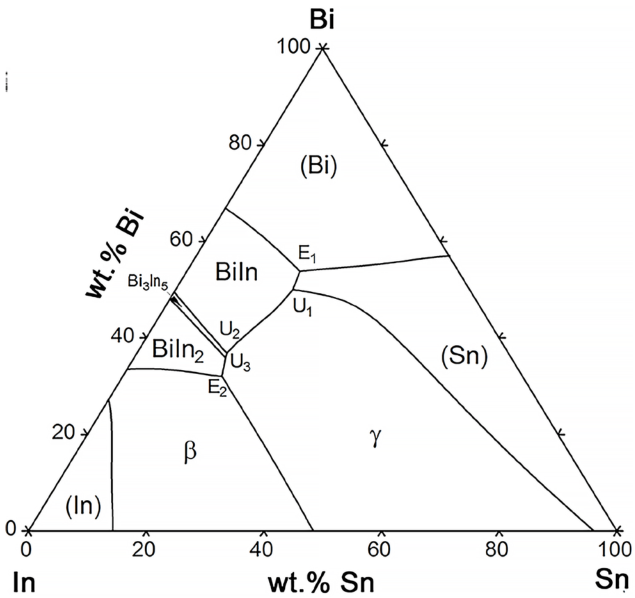

Fig. 7 Tin Bismuth Indium ternary phase diagram (Manasijević et al., 2018)

2 Analytical methods and samples preparation

2.1 Analytical methods

2.1.1 SEM-EDX

A Tescan Mira 3 LMH electron microscope with a Bruker Quantax 200 energy dispersive X-ray spectrometer with an XFlash 6/10 detector with a thermoemissive electron source is used for sample analysis. The selected accelerating voltage is 5 kV. Achieved resolution of 2 nm with magnification up to 1,000,000x. The achieved vacuum in the chamber is 9×10^{-3} Pa, while on the cathode it is up to 10^{-8} Pa. SEM is performed at the Institute of Metal Materials and Corrosion Engineering (Abdelaziz et al., 2017).

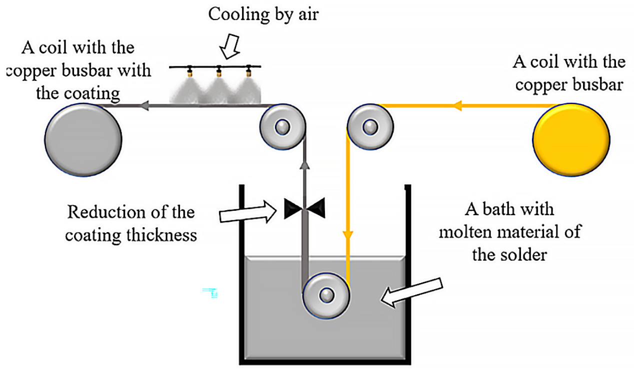

Fig. 8 Layout of dip coating technology

2.1.2 Differential scanning calorimetry

The principle of differential scanning calorimetry is the measurement of heat that is absorbed or released during a certain process, be it chemical, biological or physical, in the system under study. The result of the measurement are the values of the physical and thermal properties of the examined sample, such as heat capacity, temperature of phase transitions and others. Differential scanning calorimetry is used to determine the melting temperature of the busbar junction (El-Daly et al., 2019).

2.1.3 Measurement of electrical performance and temperature images of glasses

A Fluke Ti 300 thermal camera is used to measure temperature images, which is placed at a defined distance from the measured sample. The set emissivity of the measurement is 0.95. Fluke software is used to create an image with evaluation. The thermal imager and its distance from the glass is calibrated by placing white glass on the front side of the glass and laser targeting this white paper, thereby verifying the distance of the thermal imager from the glass (Fu et al., 2019).

2.2 Samples preparation

Laminated samples are prepared from two PVB glasses joined together, on which conductive components are placed according to the previous description in Section 1 – Introduction. Temperature properties are measured, which verified the contact between the conductors. Busbar samples are prepared using the dip coating method Fig. 8. The layout used in the given work to produce busbars with hot dip coating consists of unwinding the manufactured copper busbars from a roll, while the copper busbars themselves are produced by rolling copper wire into the shape of copper foil. The given film is cut to the required thickness, for example 0.075 mm and to the required dimension, for example the width of the busbar, e.g., 10 mm. Subsequently, the given copper tape is cooled, pickled, and degreased. Pickling is a process in which the busbar passes through an acid bath, where oxides and other impurities are removed from the surface of the busbar. This process will enable the subsequent application of coating layers on the surface of the busbar. The busbar is then coated with a layer of film in a so-called bath containing the given molten material. The temperature set in the molten bath is always 20–50 °C higher than the melting temperature of the material applied to the bus. The given busbar is pulled out of the bath and cooled by air. The speed of the line depends on the temperature of the bath, if the speed of the line is higher, the temperature of the molten bath must be increased. The speed of the line varies between 5–10 meters of coated busbar per minute. After cooling, the busbar is wound back onto the coil and the busbar is optically and visually inspected for the presence of possible defects. The busbar is then packed. The busbar can be rewound and cleaned primarily mechanically through a system of felts. As part of the study, various samples of busbars with coating were prepared. The goal was to apply a coating to the surface of the busbar and analyse the properties of the given busbar and discuss the quality of soldering connections. Samples were prepared, where the main elements were tin, lead, bismuth and indium. The aim was to prepare lead-free and leaded samples and compare their melting point. The applicability of lead-free coatings with tin-bismuth or tin-bismuth-indium composition in the automotive industry is further discussed in Table 1.

3 Results and discussion

Table 1 describes the busbar samples (a–f) used for the study. Busbars a–c are busbars containing basically three elements – tin, bismuth and indium – in a different

Table 1 Different samples of busbars with coating.

Element in mass %	Sample a	b	c	d	e	f
Bi	58.35	56.05	54.55	58.30	43.70	46.30
Sn	30.71	36.05	42.33	41.70	26.40	25.35
In	10.94	7.90	3.12	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00	29.90	28.35

ratio. Busbar d is a busbar containing bismuth and indium, busbars e–f are busbars containing three elements – tin, bismuth and indium. Different combinations of busbars were prepared and their melting point was measured. The main detail was devoted to busbars based on tin, bismuth, or tin, bismuth and indium – especially to samples d and a from the table below. Busbar d ($Bi_{58.3}$–$Sn_{41.7}$) was measured using SEM-EDX technology to determine the thickness of the coating layer and the distribution of individual component elements within the sample. The busbar was 50 micrometres thin, the coating on copper core consisted of tin and bismuth and was 20 microns thick at its widest point. Quantitatively, approximately the same amount of all metals was present in the busbar. There was an acrylic adhesive on the underside of the bus, which ensured optimal contact of the busbar with the substrate, for example with PVB Figs. 9 to 12. Fig. 13 shows the thickness profile of busbar d. Several measurements were made to make the result representative. The busbar sample was coated non-stoichiometrically. In the area where the busbar was in contact with tungsten wires

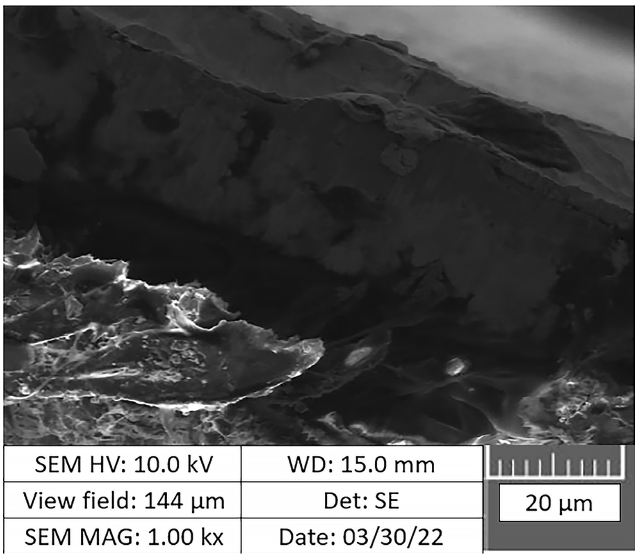

Fig. 9 Composition of busbar with Tin Bismuth coating – sample d by SEM-EDX

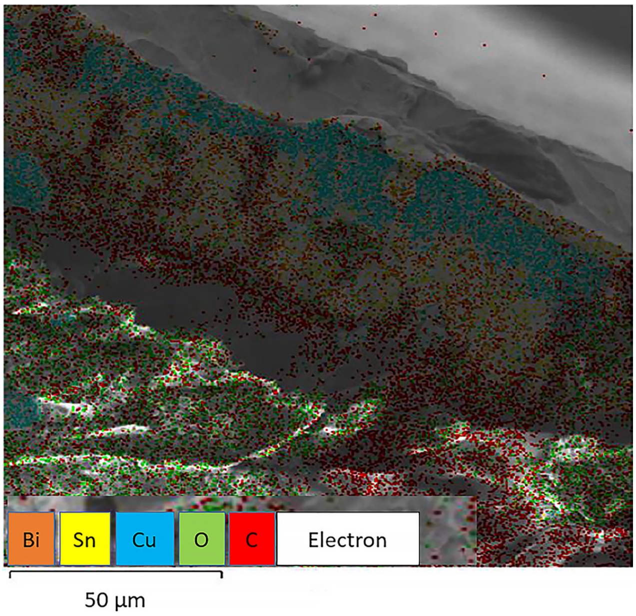

Fig. 10 Composition of busbar with Tin Bismuth coating – sample d by SEM-EDX – colour map by elements

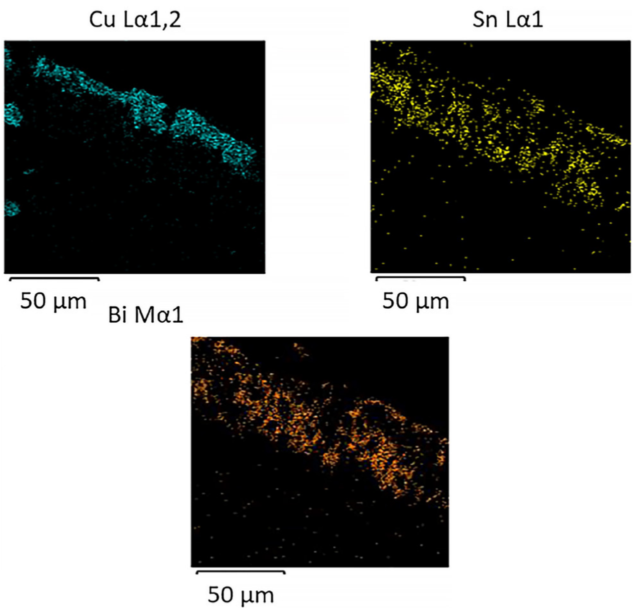

Fig. 11 Composition of busbar with Tin Bismuth coating – sample d by SEM-EDX – colour map by elements and their distribution within the sample – different colour is used to visualize where each concrete element is located in the sample.

or with another conductor, a higher coating thickness was applied, here approx. 0.03 mm. Onthe other hand, the thickness of the coating was lower than 0.01 mm, because on this side the busbar is glued to the underlying substrate, in this case the PVB foil, and the coating does not play any significant role. For DSC analysis, the temperature range from 25 °C to 200 °C was tested. The temperature step is 10 K min^{-1}. The surrounding environment

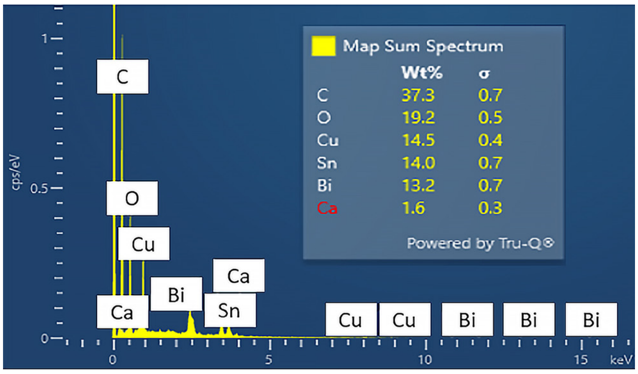

Fig. 12 Composition of busbar with Tin Bismuth coating – sample d by SEM-EDX

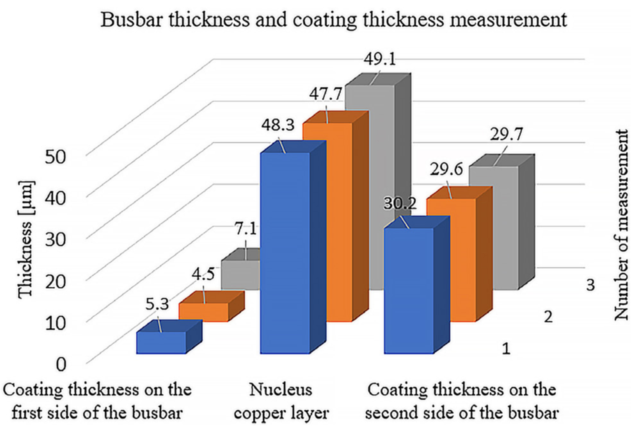

Fig. 13 Busbar thickness and coating thickness measurement

consisted of air and nitrogen. As a standard, it leached aluminium 40 μm. An 8 mg sample was taken for analysis. Sample d and its DSC spectrum is shown in Fig. 14 The melting point of this sample is determined to be 139 °C. This busbar can be used for applications where soldering is automatic during a thermal process where the temperature of the process exceeds 139 °C in all its locations. Lead-free samples a to d show different melting points depending on their composition (Table 2). Samples a to c contained different proportions of tin, bismuth and indium according to Table 1. In the case of samples a and b, the melting temperature of the samples is approximately the same and is around 100 °C. Sample c shows a higher melting point, around 120 °C. Sample d, which is the last lead-free sample, shows a melting point of 139 °C. Samples e to f are lead and show a melting point of 100 °C for sample e and 105 °C for sample f. Sample a containing 58.35 mass % bismuth, 30.71 mass % tin and 10.94 mass % indium shows that three peaks are detected at different temperatures, i.e., at 62.33 °C corresponding to the glass transition temperature, then at 81.10 °C, which corresponds to the Sn+Bi-In+Bi eutectic phase. At this temperature the Sn-Bi phase melts, then at a higher temperature Sn melts and at 100.02 °C Bi also melts. The entire system is above the liquid phase temperature of 100.02 °C Fig. 15.

4 Conclusion

This article discusses the use of lead-free busbar materials used for soldering joints in automotive production. Copper busbars are coated with a coating that consists of various elements. We applied these materials to the copper busbars using immersion. First, busbars with a coating consisting of tin and silver are discussed. The problem with these busbars is the high melting point of the coating, as discussed earlier in the article. Therefore, the addition of bismuth to the coating is subsequently discussed, which will cause the melting temperature of the busbar coating to decrease to 139 °C. These busbars are analysed using the SEM-EDX method, and the analysis revealed

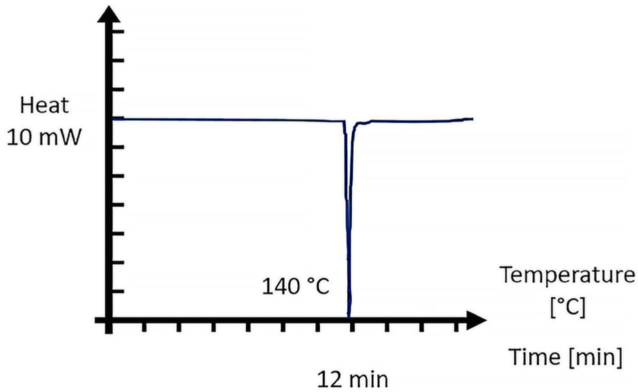

Fig. 14 DSC measurement of sample d → melting point of busbar corresponds with the peak at 139 °C

Table 2 Melting point of different samples determined by DSC analysis

Sample	a	b	c	d	e	f
Melting point by DSC (°C)	100	105	120	139	100	105

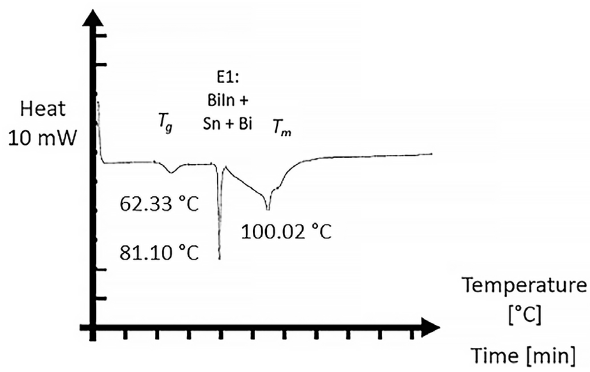

Fig. 15 DSC measurement of sample a

that the elements are homogeneously distributed within the bus coating and the composition meets the requirements. However, even this temperature, i.e., 139 °C, may not be sufficient for industrial applications. The manufactured bus coating sample consists of 58 wt. % bismuth and 42 wt. % tin. As the industry requires even lower bus melting temperatures, namely 120 °C, but also 100 °C, a different composition of the bus coating was discussed. Another part of the article is related to this, where the authors deal with a coating consisting of tin, bismuth and indium. Different ratios of these elements in the coating were discussed and the influence of the ratio on the melting temperature, which is verified by differential scanning calorimetry. Sample a, whose melting point is determined by DSC at 100 °C, has a composition of 58.35 wt. % of bismuth, 30.71 wt. % of tin and 10.94 wt. % of indium. Sample b, whose melting point is determined by DSC as 105 °C, has a composition of 56.05 wt. % of bismuth, 36.05 wt. % of tin and 7.90 wt. % of indium and finally sample c, whose melting point is 120 °C, has a composition of 54.55 wt. % of bismuth, 42.33 wt. % of tin and 3.12 wt. % of indium. Depending on the application and the temperature reached, the authors of the article recommended choosing a suitable ratio between tin, bismuth and indium so that the required melting point is achieved during industrial processing. The authors mentioned that this is the only way to optimally connect the given bus connections and another conductor. In the framework of the article, the authors produced new types of busbars with a coating consisting of tin, bismuth and indium for industrial applications as an alternative to lead busbars. At the same time, they discussed how the optimum melting temperature of the given bus can be achieved using a metal coating. These busbars have a wide range of uses. The authors discussed their use in the automotive industry.

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