(19) DANMARK

(10) DK/EP 3259383 T3

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: *C 25 D 3/56 (2006.01)* *C 09 D 1/00 (2006.01)* *C 09 D 5/10 (2006.01)*
C 22 C 13/00 (2006.01) *C 25 D 3/60 (2006.01)* *C 25 D 5/50 (2006.01)*
C 22 C 19/03 (2006.01)

(45) Oversættelsen bekendtgjort den: **2019-10-28**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2019-10-02**

(86) Europæisk ansøgning nr.: **16705172.1**

(86) Europæisk indleveringsdag: **2016-02-18**

(87) Den europæiske ansøgnings publiceringsdag: **2017-12-27**

(86) International ansøgning nr.: **EP2016053452**

(87) Internationalt publikationsnr.: **WO2016131916**

(30) Prioritet: **2015-02-18 DE 102015202910**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **TIN-NIKKEL-LAG MED HØJERE HÅRDHED**

(56) Fremdragne publikationer:
JP-A- H0 734 296
JP-A- 2011 007 220
JP-A- 2014 227 602

Description

Tin-nickel layer with high value of hardness

The present invention concerns a tin-nickel layer having a high value of hardness, a method for producing same, and a coated component comprising as a coating such a tin-nickel layer.

Hard chromium layers are used for many technical applications. They are characterised by a high level of hardness and good tribological properties, such as low wear and low friction. Furthermore, hard chromium layers have good anti-adhesive properties, high corrosion resistance and good machineability.

Hard chromium layers are generally deposited electrolytically (electrodeposited) from chromic acid electrolytes containing chromic acid (e.g. 250 g/l), small amounts of sulfuric acid (e.g. 0.5 wt.%) and hexafluorosilicic acid (e.g. 1.5 to 4 g/l). The deposited layer thicknesses are usually in the range from 5 to 20 µm, but for special applications layers up to 150 µm thick can also be deposited.

Hard chromium layers can be machined by grinding, turning, milling and similar methods. Thus, components can first be chromium-plated to more than the required layer thickness and then uniformly reduced to the desired final dimension by machining. Worn chromium layers can be stripped away again without attacking the base material, enabling hard chromium-plated components to be repaired.

The problem is, however, that the chromic acid required for electrolytic deposition is classified as highly toxic and carcinogenic (category I) under the German Hazardous Substances Ordinance. The same is true of chromium(VI) compounds such as chromium trioxide, for example, which can be used as an alternative. Owing to these properties, chromic acid has been included in Annex XIV of Regulation 1907/2006/EC (known as the REACH Regulation), as a result of which it will be much more difficult to use this substance in future. There is thus a great need for alternative solutions to the deposition of hard chromium layers from chromic acid electrolytes.

One obvious alternative is chromium deposition from a chromium electrolyte based on chromium(III) salts. These compounds are less toxic and moreover they are not classed as carcinogenic. Chromium(III) electrolytes have been known since around 1970 and are also used - on a limited scale - in industry. The disadvantage of the first-generation processes, which were based on the use of chromium(III) chloride, was that the chromium layers obtained were markedly darker than those obtained with conventional chromic acid electrolytes. Since then, methods based on chromium(III) sulfate have been successfully developed, which overcome this decorative disadvantage because the layers deposited from chromium(III) sulfate electrolytes are visually almost indistinguishable from the layers deposited from chromic acid baths. However, only very thin layers of at most 0.5 µm can be deposited uniformly over the entire workpiece by the methods based on chromium(III) chloride or chromium(III) sulfate. The mechanism behind this restriction on layer thickness is unknown. It is argued that the deposition of Cr^{3+} ions to

form metallic chromium proceeds via the more unstable Cr^{2+} as an intermediate stage.

EP 2 054 539 B1 suggests separating the anode and cathode chambers by means of an anion-exchange membrane, which prevents Cr^{2+} ions formed at the cathode from reaching the anode and being oxidised back to Cr^{3+} ions there. Layer thicknesses of over 10 µm are said to be achieved with this method and the layers obtained can be used as hard chromium layers.

WO 2012/059473 A1 describes a method for depositing hard chromium layers from Cr(VI)-free electrolytes. The electrolyte solution contains Cr(II) or Cr(III) compounds or mixtures thereof and halide compounds, which trap the free halogen (particularly bromine or iodine) formed at the anode by complexation, thus preventing oxidation of the Cr(II) and Cr(III) compounds. It is said that chromium layers at least 10 µm thick and with Vickers hardness values of up to HV 1630 can be deposited in this way.

WO 2014/111624 A1 describes a method consisting of the deposition of a layer combination comprising a nickel-phosphorus alloy and a chromium layer deposited on top from a chromium electrolyte based on chromium(III) compounds. Vickers hardness values of HV 2000 and more can be achieved by this method.

Despite the methods described in the prior art for hard chromium deposition from chromium electrolytes based on chromium(III) compounds, these methods are rarely used in industry. Clearly the necessary process parameters cannot be

controlled accurately enough in practice to enable thick hard chromium layers to be deposited in a reproducible manner.

As an alternative to hard chromium coating, thermal spray application of ceramic materials can be used. Owing to the nature of the process, however, only exterior surfaces of the workpiece to be coated can be coated in this way. In hard chromium electroplating from chromic acid electrolytes, the use of auxiliary anodes means that interior component surfaces can be coated too. Since thermal spraying deposits only very rough layers initially, elaborate mechanical finishing is required, which in the case of the sprayed ceramic layers is often very difficult. Layers applied by thermal spraying are often brittle and as a consequence, despite very high hardness values, they have only poor tribological properties.

In addition, hard chromium alternatives such as titanium nitride (TiN), tungsten carbide (WC) or zirconium nitride (ZrN) can be deposited by vacuum processes such as PVD (physical vapour deposition) or CVD (chemical vapour deposition). The deposition rate of these processes is very low, so only thin layer thicknesses can be deposited. Owing to the high equipment cost, these methods can only be regarded as an alternative to hard chromium plating for special applications (niche technology).

There is thus still a great need for alternatives to hard chromium deposition.

Tin-nickel layers with a composition comprising approx. 65 wt.% Sn and approx. 35 wt.% Ni exhibit high corrosion resistance and in this respect satisfy an important property

of hard chromium layers. Methods based on tin-nickel electrolytes are also characterised by the fact that the alloy ratio of approx. 65 wt.% Sn and approx. 35 wt.% Ni is independent of the cathodic current density applied to the component. The methods also feature good throwing power, so even geometrically complex components can be coated uniformly. However, conventional tin-nickel layers have only a low hardness of approx. HV 450 to 500 (Vickers hardness) and thus cannot be used as an alternative to hard chromium layers.

JP 2014-227602 A concerns foils for shielding electromagnetic radiation. A thin base layer of nickel is first formed on a metal foil, said base layer being intended to suppress the diffusion of metal atoms into the layer consisting of a tin alloy that is arranged on top. The tin alloy layer can consist of tin, nickel and optionally further elements (P, W, Fe, Co, Zn, C, S, O) in a proportion of 1 to 40 wt.%. The tin alloy layer can be formed by vapour deposition. It has a thickness of 0.03 to 1.5 µm.

JP H07-34296 A describes an NiSn alloy film for lining a metal mould. The NiSn alloy film is electrodeposited together with particles of a fluorine-containing polymer having a diameter of 2 to 8 µm. The film obtained can then be heated under vacuum at 270 to 370°C. A hardness of HV 460 is described in the examples for a PTFE-containing tin-nickel layer with a layer thickness of 10 µm.

JP 2011-007220 A relates to a ball valve, for which a copper ball is electroplated with a thin tin-nickel layer. The tin-nickel layer is said to have high slippage. The layer thickness is 0.5 to 3 µm.

The problem addressed by the present invention is therefore that of providing alternatives to hard chromium layers which overcome the aforementioned disadvantages of the prior art. Further problems addressed are those of providing a production method for such alternatives and a coated component having such a layer as a coating.

These problems are solved by the tin-nickel layer, the method for producing same and the coated component, comprising as a coating such a tin-nickel layer, according to the independent claims. Dependent claims indicate further advantageous embodiments.

The invention comprises a tin-nickel layer having an NiSn phase, wherein the tin-nickel layer has a hardness of at least HV 750 (Vickers hardness) and a layer thickness of 5 to 250 µm.

The tin-nickel layer according to the invention thus has a much higher hardness than conventional tin-nickel layers. Moreover, it can have significantly improved tribological properties, expressed in particular in lower coefficients of friction, in comparison to conventional tin-nickel layers. The lower the coefficient of friction, the lower the wear on the layer. Furthermore, because of the tin/nickel composition, it has very high corrosion resistance and can be produced very uniformly even on geometrically complex substrates (components). Electrodeposition methods, for example, can be used for this purpose. The tin-nickel layer according to the invention is thus a technically valuable alternative to hard chromium layers.

The inventors discovered, surprisingly, that the tin-nickel layers according to the invention can be produced by the method described in more detail below, which involves annealing an electrodeposited tin-nickel layer at a temperature of at least 200°C, in particular at least 380°C. This discovery was surprising because tin-nickel layers are usually electrodeposited as a uniform NiSn phase, i.e. with a molar ratio of nickel to tin of 1:1. The deposition normally occurs in a single-phase and hence defined structure and leads to a very uniform composition of the layer. Since such a tin-nickel layer already has a defined structure, said NiSn phase, it would not be anticipated that the hardness and the tribological properties of the tin-nickel layer can be significantly improved by annealing.

An improvement in hardness was found for example in nickel-phosphorus layers deposited without current, which – in complete contrast to tin-nickel layers – are initially deposited in amorphous form. A heat treatment, at between 300°C and 600°C for example, leads to the formation of crystalline Ni_3P phases, which are assumed to be responsible for an increase in hardness to hardness values of up to HK 1000 (Knoop hardness).

Since, as has been explained above, tin-nickel layers are already electrodeposited in a defined phase, there was until now no reason for a person skilled in the art to assume that annealing a tin-nickel layer could lead to a significant improvement in hardness and also in tribological properties.

The tin-nickel layer according to the invention has an NiSn phase and is obtainable by means of electrodeposition and subsequent annealing, as described in more detail below.

Following electrodeposition, the molar ratio of nickel to tin is 1:1, which corresponds to 67 wt.% tin and 33 wt.% nickel, relative to the total content of tin and nickel (wt.% = percent by weight). Annealing is preferably carried out in such a way that a diffusion of tin or nickel out of the layer is prevented, and so there is a molar ratio of nickel to tin of 1:1 in the final tin-nickel layer too. To this end, annealing can be carried out at a temperature of 200°C to 750°C, preferably 380°C to 650°C. The annealing process can last for 20 to 240 minutes, in particular 25 to 200 minutes.

The composition of the tin-nickel layer is determined by X-ray fluorescence analysis in accordance with DIN EN ISO 3497 using a Fischerscope X-Ray XDAL X-ray fluorescence measuring instrument. The measuring accuracy is ± 2 wt.% or better.

The tin-nickel layer can consist entirely of tin and nickel and possibly unavoidable impurities originating from the electroplating bath that was used. It is possible, however, for further elements to be introduced into the tin-nickel layer by the annealing process. For example, atoms from a substrate may diffuse into the tin-nickel layer. It is also possible for atoms from the atmosphere to be introduced into the tin-nickel layer during annealing.

The tin-nickel layer has a hardness of at least HV 750. In particular, the tin-nickel layer can have a hardness in the range from HV 800 to 1050, for example in the range from HV 850 to 1000 or in the range from HV 850 to 950. In the context of this application, the Vickers hardness is determined in accordance with DIN EN ISO 4516. Details are described below in the methods section.

As already mentioned above, the high hardness value of the tin-nickel layers according to the invention is attributable to an annealing process. Hardness values of HV 900 for example can readily be obtained with a one-hour heat treatment in a range from 400°C to 520°C. The inventers assume that the development of further defined phases during the annealing process contributes to the increased hardness of the tin-nickel layers. Thus, in the X-ray diffractogram of an annealed tin-nickel layer, in addition to the original NiSn phase, new reflexes can possibly be observed, to which a composition of SnO_2 or $Ni_{48}Sn_{52}$ was able to be attributed.

Therefore, in addition to an NiSn phase, the tin-nickel layer can contain additional phases selected from SnO_2 and/or $Ni_{48}Sn_{52}$.

The tin-nickel layer is conventionally produced by electrodeposition onto a substrate, for example a component. Such a substrate can contain or consist entirely of one or more metals and/or one or more metal alloys, for example. The substrate can preferably comprise or consist entirely of steel, copper or brass. Examples of such substrates are metal sheets made of steel, copper or brass, for example.

According to a development of this embodiment, the substrate contains copper. It can also consist entirely of copper. During the annealing process copper-containing phases, for example an NiCuSn phase, can also form in the tin-nickel layer, as was able to be shown in the X-ray diffractogram of such a layer. The tin-nickel layer can thus contain an NiCuSn phase. Tin-nickel layers deposited on copper-containing substrates can have a high hardness value after annealing of around HV 900 (Vickers hardness) and sometimes more.

If required, a diffusion of copper atoms into the tin-nickel layer can be suppressed by creating a diffusion barrier consisting of nickel between the substrate and the tin-nickel layer. This can be produced by chemical deposition or electrodeposition of nickel, for example.

When the tin-nickel layer is formed on a substrate, it usually constitutes the final surface layer. A final surface layer is the outermost layer on the surface, on which no further layer is produced. Thus, analogously to the conventional use of a hard chromium layer, the tin-nickel layer constitutes a hard, outermost surface layer.

As already mentioned above, electrodeposition methods for tin-nickel layers have good throwing power, such that even geometrically complex substrates can be coated uniformly. A particular advantage of the tin-nickel layer according to the invention is that it can be electrodeposited in almost any layer thickness. Particularly when used for a similar purpose as a hard chromium layer, the tin-nickel layer has a layer thickness of 250 µm or less, specifically 5 to 250 µm. In particular, the layer thickness can be in the range from 5 to 200 µm, preferably in the range from 5 to 150 µm. The layer thickness is determined by X-ray fluorescence analysis in accordance with DIN EN ISO 3497.

As a further aspect of the invention, a method for producing the tin-nickel layers described above is specified. The method according to the invention comprises:

(A) electrodeposition of a tin-nickel layer having an NiSn phase and a layer thickness of 5 to 250 µm, and

(B) annealing of the deposited tin-nickel layer at a temperature of at least 200°C, such that the tin-nickel layer has a hardness of at least HV 750.

In the context of this application, electrodeposited tin-nickel layers which have not yet been annealed are also referred to as the "deposited tin-nickel layer". The annealing of such a deposited tin-nickel layer in step (B) then results in a tin-nickel layer according to the invention with a hardness of at least HV 750 (Vickers hardness). The method allows ready access to the tin-nickel layers according to the invention having a high hardness value.

The tin-nickel layers according to the invention as described above are obtained by the method according to the invention. Therefore, the statements made above in respect of the tin-nickel layers also apply to the method according to the invention. The electrodeposition can be carried out on a substrate comprising or consisting of one or more metals and/or one or more metal alloys. The substrate preferably comprises or consists of steel, copper or brass. The tin-nickel layer generally forms the final surface layer on the substrate. The tin-nickel layers are deposited in a layer thickness of 250 µm or less, specifically in a layer thickness in the range from 5 to 250 µm, in particular 5 to 200 µm, preferably 5 to 150 µm. As a result of the annealing process, the tin-nickel layer has a hardness of at least HV 750. During the annealing process, one or more of the phases described above can form in addition to the NiSn phase. If the tin-nickel layer is deposited on a substrate, it is generally annealed together with the substrate. Following electrodeposition, the molar ratio of nickel to tin is 1:1, which corresponds to 67 wt.% tin and 33 wt.% nickel, relative

to the total content of tin and nickel. Annealing is preferably carried out in such a way that a diffusion of tin or nickel out of the layer is prevented, and so there is a molar ratio of nickel to tin of 1:1 in the final tin-nickel layer too.

The tin-nickel layer is deposited in step (A) as a uniform NiSn phase. During the annealing process, as described above, further phases can form in the tin-nickel layer. Additional elements, from a substrate or from the atmosphere for example, can also be introduced into the tin-nickel layer by the annealing process.

As has already been mentioned above, particular importance is attached to the annealing of the deposited tin-nickel layer in terms of the improvement in the hardness and, depending on the process control, the tribological properties of the tin-nickel layer. To this end, annealing can be carried out for at least 20 minutes in step (B) at the specified temperatures. The annealing process does not generally last for more than 240 minutes. In particular, annealing can be carried out for 25 to 200 minutes, preferably for 30 to 120 minutes, particularly preferably for 35 to 90 minutes, for example for around 1 hour, at the specified temperatures.

With an annealing step at 200°C, in particular at least 300°C, for 120 minutes or 180 minutes for example, a significant increase in hardness is already observed in comparison to unannealed tin-nickel layers. However, an improvement in the tribological properties is usually only moderate. At temperatures of 380°C and more, improved hardness values and also significantly improved tribological properties could be observed. There is thus no direct

correlation between high hardness and good tribological properties in the tin-nickel layers. Therefore, a temperature of at least 380°C is preferably used for annealing in step (B). If the temperatures are too high, the hardness can fall again somewhat, such that the hardness is lower than under the particularly preferred conditions. The annealing step is preferably carried out at temperatures of 750°C and lower, in particular 650°C and lower.

Annealing can be carried out in particular at a temperature in the range from 390°C to 550°C, preferably 400°C to 520°C, particularly preferably 400°C to 450°C. Particularly advantageous tin-nickel layers are obtained if a combination of preferred time period and preferred temperature is used for annealing. If annealing is carried out for too short a time and/or at too low a temperature, a lower hardness value and/or poorer tribological properties are obtained.

The annealing step can be, but does not have to be, performed under protective gas. Rather, it has been found that annealing in an oxygen-containing atmosphere, in particular in air, can have an advantageous effect on the hardness and/or tribological properties of the tin-nickel layer. Thus, for example, one or more SnO_2 phases can form.

Methods known per se to a person skilled in the art can be used for the electrodeposition of the tin-nickel layer in step (A). An electrolyte solution containing tin ions and nickel ions is generally used for this purpose. This allows in particular a uniform deposition on substrates containing or consisting of one or more metals and/or one or more metal alloys.

In addition to tin salts, for example a tin(II) chloride, and nickel salts, for example a nickel(II) chloride, such an electrolyte solution can also contain additives. Such an additive can be, for example, a water-soluble fluorine salt, in particular ammonium fluoride and/or sodium fluoride. It is assumed that fluoride ions stabilise a binuclear complex consisting of tin and nickel, thereby ensuring a constant alloy ratio of the tin-nickel layers in the molar ratio 1:1.

Particularly suitable for electrodeposition is an acid electrolyte containing 40 to 60 g/l tin(II) chloride hexahydrate, 200 to 300 g/l nickel(II) chloride hexahydrate and 30 to 50 g/l fluoride ions, which are added as ammonium fluoride and/or sodium fluoride. The concentration of nickel is higher than that of tin here because it is less noble.

The electrodeposition preferably takes place at temperatures in the range from 60°C to 70°C. The pH of the electrolyte is preferably 2.5 to 3.5. The cathodic current densities used for deposition are preferably in the range from 2 to 4 A/dm^2. Deposition rates of approx. 0.8 µm/min can be achieved in this way.

Substrates or components can be provided with a tin-nickel layer according to the invention using the method according to the invention. A method for producing a coated component comprising as a coating one of the tin-nickel layers described above is thus also provided. The method comprises the following steps:

(A) electrodeposition of a tin-nickel layer having an NiSn phase and a layer thickness of 5 to 250 µm on a component, and

(B) annealing of the component with the deposited tin-nickel layer at a temperature of at least 200°C, in particular at least 300°C, preferably at least 380°C and/or at most 750°C, such that the tin-nickel layer has a hardness of at least HV 750.

The tin-nickel layer is thus generally speaking formed as a final surface layer on the component.

As a further aspect of the application, a coated component is specified which comprises as a coating a tin-nickel layer according to at least one of the embodiments described above. One of the substrates described above, for example, can be used as the component. The coated component can thus comprise or consist of a combination of substrate and tin-nickel layer. The entire surface of the component can be coated with the tin-nickel layer. The tin-nickel layer can in particular form the final surface layer on the component.

Examples

The following methods were used:

The hardness measurement was carried out by the Forschungsinstitut für Edelmetalle und Metallchemie (FEM), Schwäbisch Gmünd (Germany) in accordance with SOP 7 Met-0108: DIN EN ISO 4516 (October 2002), Metallic and other inorganic coatings - Vickers and Knoop microhardness tests. In the context of the application, the determination was carried out by the Vickers method only, on a transverse section in the case of layer thicknesses < 15 µm and on surfaces in the case of layer thicknesses < 80 µm.

The Vickers hardness is indicated by the symbol “HV”. After the hardness value, the following test conditions are specified:

a) the test force in newtons (N) (multiplied by a proportionality factor of 0.102), and
b) the exposure time in seconds (s) where it differs from 10 to 15 seconds.

Example 1: 640 HV0.1: Vickers hardness 640, determined with a test force of 0.9807 N acting for 10 to 15 s.

Example 2: 640 HV0.1/20: Vickers hardness 640, determined with a test force of 0.9807 N acting for 20 s.

Pursuant to DIN EN ISO 4516 (October 2002), the Vickers hardness is stated as a dimensionless value. The test force used in determining the Vickers hardness is included directly in the hardness value, so that even hardness values measured with different test forces can be compared directly with one another.

The tribology tests were carried out using a CSEM pin-on-disc tribometer. The counter body was a sphere of diameter 6 mm made from the alloy 100 Cr6, material number 1.3505.

Parameters for the tribology measurement:
Normal force: 5 N
Rotational speed: 500 rpm
Sliding speed: 52.4 mm/s
Temperature: 23 ± 2°C
Relative humidity: 50 ± 6%
Revolutions: 10,000

X-ray diffraction tests were carried out using a D8 GADDS X-ray diffractometer from Bruker AXS. The Cu-Kλ primary beam was aligned parallel using a Goebel mirror and limited by means of a 1 mm collimator and annulus for a spatially resolved measurement. Detection was carried out with a 2-dimensional Vantec 500 detector.

The layer thickness was measured in accordance with DIN EN ISO 3497 using a Fischerscope X-Ray XDAL X-ray fluorescence measuring instrument.

The composition of the alloys was also determined by X-ray fluorescence analysis using the aforementioned instrument, in accordance with DIN EN ISO 3497. The measurements were obtained with an accuracy of ± 2 wt.% or better.

For examples 1 and 2 below and comparative example 1, brass sheets measuring 50 x 50 x 5 mm were used as substrates. They were cleaned in an aqueous, alkaline cleaner and then pickled in an acidic solution consisting of sodium peroxodisulfate in sulfuric acid. The pretreatment was carried out as follows:

1) Alkaline ultrasonic degreasing in Slotoclean AK 160 degreaser:
Batch containing 30 g/l Slotoclean AK 161 degreaser salt, at 60°C for 1 minute.

Rinsing with distilled water.

2) Cathodic degreasing in Slotoclean DCG-F cleaner:
Batch containing 60 ml/l Slotoclean DCG-F degreaser concentrate, at 20°C for 1 minute.

Rinsing with distilled water.

3) Pickling in S 40 copper activating agent:
Batch containing 100 g/l S 40 copper salt and 100 ml/l sulfuric acid of density 1.84 g/cm^3,
at 20°C for 10 seconds to 1 minute, depending on the base material.

Rinsing with distilled water.

Slotoclean AK 161, Slotoclean DCG-F and S 40 copper salt are products manufactured by Dr.-Ing. Max Schlötter.

Example 1:

A 40 µm thick tin-nickel layer was electrodeposited onto a brass sheet pretreated in this way from a tin-nickel electrolyte at a current density of 1 A/dm^2 for a deposition period of 120 minutes. A SLOTOLOY NIT 10 tin-nickel alloy electrolyte from Dr.-Ing. Max Schlötter was used to produce the coating.

The batch contains:
48 g/l tin(II) chloride hexahydrate
243 g/l nickel(II) chloride hexahydrate
250 ml/l SLOTOLOY NIT 11 additive

The additive SLOTOLOY NIT 11 is a commercial product from Dr.-Ing. Max Schlötter.

Electrolyte temperature: 65°C
Current density: 1 A/dm^2

Deposition period: 120 minutes
Composition of deposited layer: 65 ± 2 wt.% tin and 35 ± 2 wt.% nickel
Layer thickness: 40 µm

The Vickers microhardness of the tin-nickel layer deposited in this way was measured using a microhardness tester. Immediately after deposition, a value of 630 HV0.02 was measured.

The specimen was then annealed for 1 hour at 500°C without protective gas and then the hardness measurement was repeated. The measured value was 920 HV0.02.

Example 2:

A tin-nickel layer having a highly textured structure was deposited on a brass sheet. Only one reflex was able to be detected in the X-ray diffractogram, specifically the reflex of a uniform NiSn phase.

The specimen was then heated in situ in 50°C increments up to 500°C, with a period of 25 minutes between each temperature increase. No phase change is detected up to 300°C. From 400°C upwards, new reflexes appear in the diffractogram. This new phase was able to be identified as tin oxide (SnO_2). Additional new reflexes were recorded, which were able to be attributed to a newly formed $Ni_{48}Sn_{52}$ phase.

Comparative example 1:

The production of a conventional hard chromium coating is used as a comparative example. The coating was deposited from hard chromium bath S from Dr.-Ing. Max Schlötter.

The batch contains:
220 g/l chromium trioxide
0.75 ml/l sulfuric acid, chemically pure, density 1.84 g/cm^3
40 ml/l hard chromium bath additive S1

Hard chromium additive S1 is a product manufactured by Dr.-Ing. Max Schlötter and contains 20% hexafluorosilicic acid.

Deposition conditions:
Current density: 50 A/dm^2
Deposition period: 10 minutes
Temperature: 54°C
Layer thickness: 10 µm

A hardness measurement for the hard chromium layer produced in this way resulted in a value of 890 HV0.015. The layer has a coefficient of friction (mean value) of 0.63228 and a wear mark depth (mean value) of 0.87 µm.

Example 3:

Tin-nickel layers were deposited on copper sheets in the manner described in example 1. The sheets were first pretreated in the same way as the brass sheets. Specimens 1 to 4 were annealed at 200°C, 350°C, 450°C and 550°C respectively for 3 hours in each case under an argon protective gas atmosphere. Tribology measurements were then

carried out. The results for hardness, friction and wear are summarised in table 1.

Table 1:

Spec.	Annealing	Vickers hardness HV0.015 (mean)	Coeff. of friction (mean)	Wear mark depth (mean, µm)
1	200°C	791	0.60667	5.32
2	350°C	890	0.65222	4.13
3	450°C	859	0.51169	1.56
4*	550°C	591	0.50809	4.74

*Reference example, not according to the invention.

Example 1 proves that the hardness is increased considerably by annealing a deposited tin-nickel layer. Vickers hardness values are obtained which are within the range of conventional hard chromium layers (see comparative example 1). Therefore, a tin-nickel layer according to the invention constitutes an alternative to hard chromium layers that is technically simple to achieve.

Example 3 shows that significantly improved hardness values are already observed with the method according to the invention with an annealing step at 200°C and 350°C. A higher temperature then led to significantly improved tribological properties of the tin-nickel layer. This example proves that tin-nickel layers having very good tribological properties can be obtained by the method according to the invention. The temperature in the annealing step clearly has a marked influence on the coefficient of friction of the surface. It was found that this value falls again as the temperature rises. In this example a rise in the annealing temperature from 450°C to 550°C led to a drop in the hardness value from

845 to 950 HV0.015 to 591 HV0.015. This temperature rise was also associated with a deterioration in the tribological properties.

Patentkrav

1. Tin-nikkel-lag med en NiSn-fase, hvor tin-nikkel-laget har en hårdhed på mindst HV 750 (Vickers-hårdhed) og en lagtykkelse, bestemt ved røntgenfluorescensanalyse i overensstemmelse med DIN EN ISO 3497, fra 5 til 250 µm.

2. Tin-nikkel-lag ifølge krav 1, hvor tin-nikkel-laget har en hårdhed i området fra HV 800 til 1050.

3. Tin-nikkel-lag ifølge krav 1 eller 2, hvor molforholdet mellem nikkel og tin i tin-nikkel-laget er 1:1.

4. Tin-nikkel-lag ifølge et af kravene 1 til 3, hvor tin-nikkel-laget er påført et substrat, som omfatter et metal og/eller en metallegering.

5. Tin-nikkel-lag ifølge krav 4, hvor substratet omfatter stål, kobber eller messing.

6. Tin-nikkel-lag ifølge krav 4 eller 5, hvor substratet indeholder kobber, og tin-nikkel-laget har en NiCuSn-fase.

7. Tin-nikkel-lag ifølge et af kravene 4 til 6, hvor tin-nikkel-laget danner slutoverfladelaget på substratet.

8. Tin-nikkel-lag ifølge et af kravene 1 til 7, hvor tin-nikkel-laget har en lagtykkelse fra 5 til 150 µm.

9. Fremgangsmåde til fremstilling af et tin-nikkel-lag ifølge krav 1, omfattende:

(A) galvanisk udfældning af et tin-nikkel-lag med en NiSn-fase og en lagtykkelse, bestemt ved røntgenfluorescensanalyse i overensstemmelse med DIN EN ISO 3497, fra 5 til 250 µm, og

(B) aducering af det aflejrede tin-nikkel-lag ved en temperatur på mindst 200°C, således at tin-nikkel-laget har en hårdhed på mindst HV 750.

10. Fremgangsmåde ifølge krav 9, hvor aducering udføres i mindst 20 min.

11. Fremgangsmåde ifølge krav 9 eller 10, hvor aducering udføres ved en temperatur på mindst 380°C og højest 750°C.

12. Coatet komponent, omfattende som coating et tin-nikkel-lag ifølge et af kravene 1 til 8.

13. Coatet komponent ifølge krav 12, hvor tin-nikkel-laget danner slutoverfladelaget på komponenten.