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(54) **Method for the manufacture of a ferromagnetic amorphous metal tape and such a ferromagnetic amorphous metal tape.**

(57) The invention relates to a method for the manufacture of a ferro magnetic amorphous metal tape having, at least on one side, an insulating silicon dioxide layer with favourable adhesive properties. In a way common in the art an amorphous metal tape is manufactured from an amorphous metal alloy comprising between 8 and 20 at. % of silicon. At least part of the surface of the metal tape is etched using an etching fluid thereby forming an insulating layer of silicon dioxide. The etching fluid comprises a solution of iron(III)-chloride in water.

The insulating layer, which preferably has a thickness of 0.05 μm to 1 μm, suppresses the development of eddy currents when the said amorphous metal tape is used, for example, in transformer cores.

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Method for the manufacture of a ferromagnetic amorphous metal tape and such a ferromagnetic amorphous metal tape.

The invention relates to a method for the manufacture of a ferromagnetic amorphous metal tape having, at least on one side, an insulating coating of silicon dioxide.

The invention also relates to a ferromagnetic amorphous metal tape manufactured by this method.

Such a metal tape is used, for example after winding or laminating to form a magnetic core, in transformer cores, magnetic heads or other inductive components.

Amorphous metal tapes having a high saturation magnetisation, for example, higher than 1 Tesla, may be used very advantageously at high frequencies, for example, frequencies over 16 kHz. However, this produces eddy current losses and the attendant development of heat. This problem is customarily obviated in the art by insulating the layers which form the magnetic core from one another. This can be achieved by means of well-known methods, such as applying a magnesium oxide layer from a suspension, applying a polymeric layer vapour-depositing aluminium oxide, phosphating, applying chromium oxide (possibly in combination with silicon dioxide powder) and thermally oxidizing the amorphous metal tape or a lacquer layer applied thereto.

In particular from Japanese Patent Application (Kokai) JP 57/204,104 (see Chemical Abstracts, Vol. 98, 1983, 100 077 X) a method is known to apply a silicon dioxide insulating layer to an amorphous iron alloy by means of a plasma vapour-phase reaction between SiH_4 and N_2O at a temperature between 100 and 150°C.

It is an object of the invention to provide a simple and inexpensive method of applying a silicon dioxide layer to an amorphous metal tape. It is desirable for the insulating layer to adhere readily to the metal tape. The temperature at which the method is carried out must not be so high that crystallisation of the amorphous metal alloy occurs. A further object of the invention is to provide a method in which the thickness of the silicon dioxide layer can be chosen within wide limits and can be adjusted.

These objects are achieved in accordance with the invention by a method in which, in a customary manner, an amorphous metal tape is manufactured from an amorphous metal alloy comprising between 8 and 20 at % of silicon, after which at least part of the surface of the metal tape is etched using an etching fluid, thus forming an insulating layer of silicon dioxide, which etching fluid comprises a solution of iron (III)-chloride in water.

During etching the main constituents of the metal tape (for example iron) dissolve at the surface. The silicon, however, does not dissolve and is oxidized to form silicon dioxide. To obtain a continuous insulating layer, at least 8 at.% silicon must be present in the amorphous metal alloy. The upper limit of 20 at.% of silicon is determined by the increasing tendency towards crystallisation when greater amounts of silicon are used.

Since the silicon dioxide layer is not deposited but instead forms part of the material, it adheres very well to the substrate. During winding the tape and impregnating the magnetic core formed in the winding proces, the insulating layer is found to be resistant to temperatures up to 450°C. An Auger analysis of the surface carried out in combination with ion etching shows that there is a gradual transition from the insulating layer to the base of the amorphous metal tape.

An additional advantage of the method in accordance with the invention is that, without any problems, an insulating layer can be applied to all sides of the amorphous metal tape.

The method in accordance with the invention may be applied to any suitable ferromagnetic amorphous metal alloy. Preferably, an amorphous metal alloy is used which is represented by the following composition $M_aR_bT_cSi_d$, where M is at least one of the metals selected from the group formed by Fe, Co and Ni, at least one of the elements selected from the group formed by said P, where T is at least one of the elements selected from the group formed by transition metals, rare earth metals and Be, Al, Ge, In, Sn and Sb, where a has a value from 70 to 86 at %, b from 7 to 22 at. %, c from 0 to 6 at. % and d from 8 to 20 at. %. Similar amorphous metal alloys are known per se, for example from German Patent Specification DE 3 326 556 which describes the manufacture of an insulating chromium oxide layer on an amorphous metal alloy.

In a preferred embodiment of the method in accordance with the invention, the amorphous metal alloy comprises at least 70 at. % of Fe. Such amorphous metal alloys have a surface layer of iron oxide/iron hydroxide which is quickly removed during etching, after which the metal tape is further etched, the insulating silicon dioxide layer being formed in the process.

In order to obtain a suitable etching rate, the iron(III)-chloride concentration in the etching fluid should preferably be between 200 and 750 g/l.

Particularly, in the case of high concentrations of silicon in the amorphous metal alloy, it is advantageous for the etching fluid to further comprise hydrochloric acid up to a concentration of 1 mol./l.

In a suitable embodiment of the method in accordance with the invention, the metal tape is etched at a temperature between 15 and 80°C. In the method in accordance with the invention, the etching rate is highest at a temperature between 70 and 80°C.

A particularly suitable embodiment of the method in accordance with the invention is characterized in that the amorphous metal alloy comprises at least 11 at. % of Si, that the amorphous metal tape is let through the etching fluid in a continuous operation and is moistered with the said fluid, after which the amorphous metal tape remains in contact with the etching fluid carried along for between 1 and 10 s. after which the amorphous metal tape is rinsed and dried.

In order, on the one hand, to obtain proper electrical insulation between the individual layers of the amorphous metal tape in a magnetic core but on the other hand to minimize the volume fraction of non-magnetic material in such a magnetic core, the insulating coating of silicon dioxide has a thickness between 0.05 μm and 1 μm in the ferro magnetic amorphous metal tape in accordance with the invention.

The required thickness of the insulating coating can be obtained by a suitable choice of the etching time, by renewing the etching fluid at the surface of the metal tape, for example, by stirring and by a suitable choice of the temperature, concentration and acidity of the etching fluid.

The invention will now be described in more detail with reference to the following embodiments.

Embodiment 1:

From a mixture of molten elements having the following composition $Fe_{70.2}Mn_2Si_{17.5}B_{10}C_{0.3}$, an amorphous metal tape is formed in a manner which is customary in the art, for example, by ejecting the molten mixture onto a quickly rotating cooled wheel, the melt being cooled at a rate of 10^5 to 10^6 °C/s. The tape thus formed has a thickness of, for example, 20 μm and a width of, for example, 12 mm.

The metal tape is led through a tank containing etching fluid, which fluid comprises 600 g/l of iron(III)-chloride and 0.1 mol/l of hydrochloric acid. After the metal tape is removed from the teching fluid, it will remain in contact with etching fluid carried along for 5 seconds at a temperature of 50°C. Subsequently, the metal tape is led through a rinsing tank containing water, after which it is dried in warm air, each of these steps taking between 5 and 10 seconds. Preferably, this method is performed in known manner as a continuous process. To enhance oxidation of the metal tape, air or oxygen may, for example, be led through the etching fluid.

An amorphous silicon dioxide layer having a thickness of 0.6 μm is obtained by etching away 1 μm thick layer from the surface of the amorphous metal tape. The oxide layer thus formed is very stable as appears from, for example, a test in which the metal tape is placed in nitrogen for 1 hour at a temperature of 450°C without any deterioration of the insulating properties of the oxide layer. The stability is far greater than that of the iron oxide/iron hydroxide skin which is present on the metal tape prior to etching and which is highly susceptible to ambient conditions.

The amorphous metal tape thus formed can suitably be worked into, for example, a transformer core, for which purpose the tape is wound or laminated and subsequently heated to relieve the mechanical stresses. The brittleness of the material is increased by the heating operation, but this of less importance than during etching which is, after all, carried out prior to winding or laminating. During heating the temperature is sufficiently low to avoid crystallization of the amorphous metal alloy. The intermediate product formed is impregnated, for example, using an epoxy resin and subsequently it is cut to shape. The amorphous metal tape in accordance with the invention exhibits very suitable wetting properties during impregnation. Impregnation serves to mechanically interconnect the individual layers, yet it can not by itself suppress to the required extent the eddy currents which develop in the product.

The eddy current losses which develop in the transformer core thus formed, depend amongst other things on the geometry of the winding, on the forces exerted during winding, on the surface roughness of the amorphous metal tape and on the manner of impregnation and the material used. The eddy current losses are particularly dependent on the insulating layers present between the magnetic layers. A silicon dioxide layer having a thickness of 0.05 μm suffices to largely suppress the eddy currents. A dioxide layer having a thickness of between 0.1 and 0.3 μm produces an almost optimal effect, because the additional effect of using a layer having a larger thickness is only marginal while it adversely affects the volume fraction of the magnetic material in the transformer core. A thickness up to 1 μm is tolerable, larger thicknesses leading to a strong decrease in mechanical strength.

The use of the amorphous metal tape as manufactured by a method in accordance with the invention has made it possible to reduce the interlaminary eddy current losses by a factor of 2 to 10.

<u>Embodiment 2</u>:

An amorphous metal tape which is manufactured as described in embodiment 1 and which has the same composition, is immersed at different temperatures (20, 35 and 50°C) in etching fluids having different compositions (0, 0.2 and 0.4 mol/l of hydrochloric acid and 250, 475 and 700 g/l of iron(III)-chloride). The results are listed in table 1.

TABLE I.

T °C	HCl mol/l	$FeCl_3$ 250 g/l	$FeCl_3$ 475 g/l	$FeCl_3$ 700 g/l
		time in seconds		
20	0	2	2	2
20	0.2	5	2	2
20	0.4	5	2	2
35	0	5	2	<1
35	0.2	2	2	<1
35	0.4	2	1	<1
50	0	2	<1	<1
50	0.2	2	<1	<1
50	0.4	2	<1	<1

Table 1 tabulates the time in seconds required to form a silicon dioxide layer having a thickness of approximately 0.3 /um. The etching rate and the oxidation rate increase as the temperature rises and particularly as the concentration of the iron(III)-chloride is increased. The influence of the hydrochloric-acid concentration is not very large in the present embodiment.

The etching rate can be slightly increased by making the etching fluid flow along or towards the metal tape, for example, by stirring. Too strong a current, however, will lead to a silicon dioxide layer which is less homogeneous and which does not adhere quite as well.

<u>Embodiments 3 to 8 and comparative examples IVto XI.</u>

A number of different ferromagnetic amorphous metal alloys are used to manufacture metal tapes in accordance with a method as described in embodiment 1. The said metal tapes were immersed at a temperature of 50°C in an etching fluid comprising 0.8 mol./l of hydrochloric acid and 250, 475 or 700 g/l of iron(III)-chloride. The results are listed in table II, examples 3 up to and including 8 being alloys having a composition in accordance with the invention and the alloys IX up to and including XI being compositions for comparison which are not in accordance with the invention.

TABLE II:

No.	composition	$FeCl_3$ 250 g/l	$FeCl_3$ 475 g/l	$FeCl_3$ 700 g/l
3	$Fe_{70.2}Mn_2Si_{17.5}B_{10}C_{0.3}$	++	++	++
4	$Co_{66}Fe_4Mo_{1.5}B_{12}Si_{16.5}$	+	+	+
5	$Fe_{73}Mn_2Si_{15}B_{10}$	+/-	+	++
6	$Co_{60}Mn_6Fe_{0.2}Nb_{0.2}Si_{11.6}B_{12}$	-	+/-	+/-
7	$Fe_{73}N_7Si_{10}B_{10}$	-	-	+
8	$Fe_{73}B_{13}Si_9$	-	-	+
IX	$Fe_{39}Ni_{39}Mo_4Si_6B_{12}$ *)	-	-	-
X	$Fe_{79}B_{16}Si_5$ *)	-	-	-
XI	$Fe_{81}B_{13.5}Si_{3.5}C_2$ *)	-	-	-

++ in less than 2 s
+ in less than 10 s
+/- in less than 60 s
- not within 60 s

*) not in accordance with the invention

Table 2 tabulates the time interval within which a 0.3 μm thick silicon dioxide layer is formed. In the case of the compositions 3 up to and including 6 which have a silicon content of more than 11 at.%, such a layer can be formed within 10 seconds. In the case of the compositions IX up to and including XI, which are not in accordance with the invention, no properly insulating silicon dioxide layer is formed.

1. A method for the manufacture of a ferromagnetic amorphous metal tape having, at least on one side, an insulating coating of silicon dioxide, characterized in that, in a curstomary manner, an amorphous metal tape is manufactured from an amorphous metal alloy comprising between 8 and 20 at. % of silicon, after which at least part of the surface of the metal tape is etched using an etching fluid, thus forming an insulating layer of silicon dioxide, which etching fluid comprises a solution of iron(III)-chloride in water.

2. A method as claimed in Claim 1, characterized in that the amorphous metal alloy is represented by the following composition $M_aR_bT_cSi_d$, where M is at least one of the metals selected from the group formed by Fe, Co, Ni, where R is at least one of the elements selected from the group formed by B, C and P, where T is at least one of the elements selected from the group formed by transition metals, rare earth metals and Be, Al, Ge, In, Sn and Sb, where a has a value from 70 to 86 at.%, b from 7 to 22 at. %, c from 0 to 6 at. % and d from 8 to 20 at. %.

3. A method as claimed in Claim 2, characterized in that the amorphous metal alloy comprises at least 70 at. % of Fe.

4. A method as claimed in Claim 1, characterized in that the concentration of iron(III)-chloride in the etching fluid is between 200 and 750 g/l.

5. A method as claimed in Claim 4, characterized in that the etching fluid further comprises hydrochloric acid up to a concentration of 1 mol./l.

6. A method as claimed in Claim 4 or 5, characterized in that the metal tape is etched at a temperature between 15 and 80°C.

7. A method as claimed in Claim 1, characterized in that the amorphous metal alloy comprises at least 11 at. % of Si, that the amorphous metal tape is led through the etching fluid in a continuous operation and is moistened with the said fluid, after which the amorphous metal tape remains in contact with the etching fluid carried along for between 1 and 10 seconds, after which the amorphous metal tape is rinsed and dried.

8. A ferro magnetic amorphous metal tape manufactured by the method in accordance with any one of the Claims 1 up to and including 7, characterized in that the insulating silicon dioxide layer has a thickness of 0.05 /um to 1 /um.

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EUROPEAN SEARCH REPORT

0 206 420

EP 86 20 1059

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
Y	US-A-4 310 381 (N. DE CRISTOFARO) * Claims 1,6; column 4, line 57 - column 5, line 1 *	1	H 01 F 1/18 C 23 F 1/28
Y	GB-A- 195 625 (ALUMINIUM CO. OF AMERICA) * Claims 1-5 *	1	
A,D	PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 58 (E-163)[1203], 10th March 1983; & JP-A-57 204 104 (SANYO DENKI K.K.) 14-12-1982 * Abstract *	1,8	
A	FR-A-2 240 963 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN) * Page 2; lines 2-11 *	1,4	TECHNICAL FIELDS SEARCHED (Int. Cl.4) H 01 F C 23 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30-09-1986	VITZTHUM N.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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