

ALUMINIUM OXIDE GLASS COMPOSITION AND
MAGNETIC HEAD INCORPORATING SAME

FIELD OF INVENTION

5 This invention relates to a glass composition that is particularly useful for bonding metal alloys or metal oxides, and more specifically, for glass that can be used in the manufacture of magnetic heads for magnetic recording and reading.

10 BACKGROUND OF INVENTION

 A variety of products comprise glass bonded to metal alloys or metal oxides in a composite structure. A particularly useful example is a magnetic head for recording and reading signals.

15 Such a head typically comprises ferromagnetic cores containing a gap at the recording and reading site that is accurately joined by glass bonded to the cores. Such cores either comprise solid ferrite or they are ferrite provided with special plates forming

20 the gapping structure. The plates are a composite of metal alloy wafers laminated with alternating layers of a bonding composition, usually epoxy polymers, the composite being shaped and attached as tips to the cores of the head. In the past, it has not been

25 possible to bond such metal alloy structure with glass in a reliable manner. Glasses have obvious advantages over polymer adhesives. Such advantages include much higher mechanical modulus and a greater degree of thermal stability and hydrophobicity, which

30 improve the dimensional stability of the metal heads.

 Several problems have been encountered in the making of bonded metal alloy or metal oxide and glass products. One problem has been to provide a glass that has a coefficient of thermal expansion

35 that substantially matches that of the metal alloy or metal oxide. Failure to match such coefficient

creates thermal stress under varying temperature conditions and eventual cracking of the glass.

Another problem has been that certain glass ingredients are highly volatile, and create bubbles as the glass solidifies. Such bubbles in a magnetic head degrade the integrity of the head structure. If located at the magnetic tape contacting surface of the head, they may provide a sharp edge that causes damage to the tape.

Still another problem has been that certain ingredients used in glass formulations to substantially match the thermal expansion coefficients of the metal alloy or metal oxide, render the glass susceptible to chemical attack, for example, attack by caustic solutions. Magnetic heads often require cleaning using a caustic solution after they are machined. Accordingly, susceptibility to chemical attack by such caustic solutions cannot be tolerated. It has been suggested that significant amounts of aluminium oxide, i.e., at least 5 mole %, provides resistance to attack from caustic solutions. Unfortunately, such amounts of aluminium oxide do not readily dissolve into many useful glass networks which leads to an unacceptable non-uniform composition.

U.S. Patent No. 3,458,926, issued August 5, 1969, describes a glass composition that comprises up to 5.7 mole % Al_2O_3 . To solubilize this amount of aluminium oxide in a glass composition an excessive amount of SiO_2 has to be used as the glass former. Thus, the patent describes the use of 52.9 mole % of SiO_2 for this purpose. Such a large amount of SiO_2 imparts a coefficient of thermal expansion that is too low ($70.4 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$) to substantially match that of the head material. To

compensate for this mismatch, only an extremely thin layer of glass such as 0.5μ can be used. This in turn requires that the glass be applied by R.F. sputtering techniques, a very limited method of application.

Finally, many glass compositions have too high a softening temperature, e.g., a softening temperature greater than 500°C . Such glasses require special, expensive equipment to bond them to a metal oxide or metal alloy. The glass described in U.S. Patent No. 3,458,926, issued August 5, 1969, is such a glass.

Thus, there is a need in the art, for a glass composition that is not subject to the aforesaid problems. Specifically, there is a need for a glass composition that has a coefficient of thermal expansion that substantially matches that of the metal alloy or metal oxide to which it is to be bonded, and is resistant to attack by caustic solutions. Likewise, there is a need for such a composition with a softening temperature no greater than 500°C .

DESCRIPTION OF INVENTION

In accordance with this invention, 5 to 15 mole % of aluminium oxide is made to go into solution in glass to provide the needed resistance to caustics by using a glass former that is compatible with the need to maintain a coefficient of thermal expansion that matches the metal alloy or metal oxide to which the glass is bonded.

This invention provides a glass composition that is particularly useful for bonding to a metal alloy or metal oxide, which composition comprises:

- (1) an oxide of an alkali metal or alkaline earth metal,

(2) an oxide of a metal, which metal is both non-alkali and non-alkaline earth, in an amount sufficient to provide a coefficient of thermal expansion of 80 to 170 x $10^{-7}^{\circ}\text{C}^{-1}$,

(3) 5 to 15 mole % of an oxide of aluminium, and

(4) 10 to 35 mole % of a compatible glass former that renders the oxide of aluminium soluble in the composition.

This invention also provides a magnetic head comprising a metal alloy or metal oxide bonded to the glass composition.

A significant advantage of the glass compositions and magnetic heads of this invention is that they are substantially free of volatile components such as lead oxide and fluorine which frees the glass of bubble defects that could prevent formation of a smooth contact surface at the tape-head interface.

Another advantage of the glass compositions of this invention is that they soften at temperatures no greater than 500°C and do not require special high temperature equipment to bond them to metal alloys or metal oxides.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a perspective view of a magnetic head in an intermediate stage of manufacture, illustrating one use of the glass composition of this invention;

Fig. 2 is a section view of an alternative magnetic head of the invention; and

Fig. 3 is a section view taken along the plane of line III-III of Fig. 2, the spacings between parts being exaggerated for clarity.

MODES FOR CARRYING OUT INVENTION

As described in detail hereinafter, the glass compositions of this invention are particularly adapted for bonding to metal alloys or oxides useful in manufacturing magnetic heads. However, such glass compositions can be used to bond to metal alloys or oxides in the making of any end product. Also, P_2O_5 is most often used as the glass former for the aluminum oxide but, any other glass former capable of rendering soluble the amount of aluminum oxide of the composition without deleteriously affecting the coefficient of thermal expansion is suitable for the practice of this invention. Examples of such other glass formers include oxides of vanadium, antimony or germanium.

Two kinds of magnetic materials are often used in the manufacture of magnetic heads. These are a) magnetic oxides such as ferrites, and b) metal alloys. In either case, the heads are commonly formed by first forming two core elements that are joined together in such a way as to leave a magnetic gap. Glass is bonded to the joined cores at the gap, and the assembly is further machined as explained in detail, for example, in U.S. Patent No. 3,557,266, issued January 19, 1971. It is this material for which the composition of this invention is particularly useful.

If the cores are formed exclusively from a ferrite, a preferred procedure is to hot-press ferrite powder into a bulk shape followed by machining the elements to the exact shape. Suitable ferrite compositions are described in U.S. Patent No. 3,989,794, issued November 2, 1976, and have coefficients of thermal expansion that range from 80 to $120 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$.

If metal alloys are used to form magnetic heads, the typical procedure is to form the alloy into thin wafers which, when stacked and bonded together, comprise two laminate plates each attached to one of two core forms. The glass composition of this invention can be used as the bonding composition for the wafers, as well as the glass that is used to maintain the magnetic gap between the two laminate plates. Useful metal alloy compositions are described in U.S. Patent No. 3,999,216, issued December 21, 1976, at col. 9, and have from 6 to 12% Si, from 4 to 9% Al, and the remainder being essentially Fe. The alloy is further characterized by a resistivity of at least 100 micro-ohm-centimeters, a porosity of less than 1%, and a Vicker's hardness of greater than 600. Such an alloy has a coefficient of thermal expansion in the range of from 120 to 170 $\times 10^{-7}^{\circ}\text{C}^{-1}$.

The glass compositions of this invention have a coefficient of thermal expansion that spans the two ranges described in the preceding two paragraphs for the metal oxides and metal alloys. That is, the glass compositions of this invention have a coefficient of thermal expansion of 80 to 170 $\times 10^{-7}^{\circ}\text{C}^{-1}$. The specific value within that range for a specific composition can be selected to be consistent with the material to which such composition is to be bonded.

In the glass compositions of the invention, an oxide of an alkali metal or alkaline earth metal is included, along with a sufficient amount of a metal oxide of a non-alkali metal that provides the desired coefficient of thermal expansion. Typically, such metal oxides comprise an oxide of zinc, copper or boron. Optionally, an oxide of silicon is

included with such metal oxides. In amounts not exceeding 30 mole %, the SiO_2 imparts beneficial properties to the glass composition. For example, it can be used to regulate its flow temperature.

5 As previously indicated herein, 5 to 15 mole % of an oxide of aluminium is included in the composition of this invention to provide sufficient resistance to caustic solutions. A convenient test to establish whether a glass has sufficient
10 resistance to caustics comprises placing a weighed amount of a piece of the glass having a known surface area, into an aqueous 0.02N solution of a sodium salt having a pH of 10, for 6 hours at 80°C. After 6 hours, the glass is removed, rinsed, and re-weighed.
15 If the weight loss is no greater than about 0.7 mg per square centimeter of exposed surface area, the glass is sufficiently resistant to adequately withstand the caustic solutions commonly used to clean core elements of a magnetic head.

20 P_2O_5 has been determined to be an excellent compatible glass former for the large amounts of oxide of aluminium present in the compositions of this invention. Other glass formers, particularly germanium oxide, are also useful. Such
25 glass formers are considered to be "compatible" when they produce a coefficient of thermal expansion that falls within the range of 80 to $170 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$. Generally, the molar amount of the compatible glass former, e.g. P_2O_5 , is at least twice that of the
30 mole percent of the oxide of aluminium in the composition.

Preferred glass compositions of the invention are those that exclude substantially all amounts of volatile materials that cause bubbling in
35 the glass. Examples are PbO and F , as these materials are particularly volatile, even in amounts less than 1 mole %.

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An exemplary glass of this invention has the following composition, in mole %:

alkali metal or alkaline earth		
5	oxide	10-40%
	Al_2O_3	5-15%
	ZnO or CuO	0-25%
	B_2O_3	0-25%
	SiO_2	0-30%
10	P_2O_5	10-35%, provided
		that at least one
		of ZnO, CuO, or
		B_2O_3 is present
		in an amount that
15		provides the re-
		quired coefficient
		of thermal expansion.

As is apparent, this exemplary composition is substantially free of PbO and of F. Such a composition, in addition to being caustic-resistant, has a range of coefficients of thermal expansion from 80 to 170 X $10^{-7}^\circ\text{C}^{-1}$, and softens at a temperature no greater than 500°C. Not listed in the above composition, but useful nonetheless, are minor amounts of addenda such as pigments or coloring material, so long as they do not adversely affect the coefficient of thermal expansion or the resistance to caustics. Such addenda are also selected to not affect the glass softening temperature or cause bubble formation as occurs with PbO.

Variations within the ranges of concentration set forth in the aforementioned exemplary compositions are useful, depending, for example, upon the magnetic material to which the

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glass is to be bonded, and the glass flow or melt temperature that is desired. Thus, if the magnetic material is a ferrite, the alkali metal oxide is preferably 10 to 30 mole % Na_2O , to ensure that the coefficient of thermal expansion is from 80 to $120 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. For this range at least two metal oxides from the group ZnO , CuO and B_2O_3 are present. However, if the magnetic material is a metal alloy as described previously herein, then the alkali metal oxide is preferably 10 to 35 mole % K_2O , so as to ensure a coefficient of from 120 to $170 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. Within each of these ranges (80 to 120 or 120 to 170), the coefficient can be further reduced by increasing amounts of one or more of the following: ZnO , CuO , SiO_2 or B_2O_3 . In either case, up to 4 mole % Li_2O is useful to reduce thermal expansion and to increase chemical durability.

The alkaline earth oxides that can be used in the practice of this invention include e.g. BaO , CeO and CaO .

The specific mole % of SiO_2 , if any is used in the compositions of this invention, is dependent upon the flow temperature that is desired for the glass. The lower the mole % of SiO_2 within the range of 0-30 mole %, the lower will be the flow temperature of the composition. Similarly, whether CuO or ZnO is used depends upon the melt temperature and viscosity that is desired. CuO provides a lower melt temperature than does ZnO .

The glass compositions described in the following Table I give particularly good bonding results with the materials set forth:

Table I
Glass Compositions (Mole %)

	<u>Oxide</u>	<u>For Use With</u>	
		<u>For Use With Ferrite</u>	<u>Ferromagnetic Alloys</u>
5	Na ₂ O	10-30	—
	K ₂ O	—	10-35
	Li ₂ O	0-4	0-4
	Al ₂ O ₃	5-15	5-15
	ZnO or CuO	10-25	5-15
10	B ₂ O ₃	10-25	5-15
	SiO ₂	0-30	0-30
	P ₂ O ₅	10-30	10-30

Within the above, best results are generally obtained with compositions in which the amount of P₂O₅ is within 4 mole % of alkali metal oxide or alkaline earth metal oxide.

The glass compositions in Table I produce a loss of only 0.001 to 0.2 mg/cm² when they are tested for caustic resistance for 6 hours at 80°C, in a 1:9 mixture of (a) water and (b) a solution containing sodium chromate, monoethylamine, and about 8% sodium dodecylbenzenesulfonate ((b) being available under the trademark "Turco Cavaclean #2" from Turco, a division of Purex Industries, Inc., Lakewood, California, USA). This clearly demonstrates the superior resistance to caustic detergent solutions that is characteristic of the compositions of this invention. Compositions containing larger amounts of Al₂O₃, i.e., from 10 to 15 mole %, had the highest resistance, i.e., least weight loss.

The softening temperatures of all the glass compositions in Table I are lower than 500°C. The majority of them are between 350° and 450°C.

The concentrations of the various components of the glass compositions of this invention are

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obtained by adjusting the appropriate raw ingredients for the glass in the conventional manner. The proportions of the raw materials may have to be further adjusted for losses and gains during
5 founding, as is known in the art. Such raw ingredients are blended and melted together in a conventional manner to produce a glass frit. The frit is then either remelted and applied while molten, or is ground into a fine powder for
10 application to the bonding surface. In the latter case, the frit and bonding surface are heated to the flow temperature of the glass to bond the glass to such surface.

A suitable bonding technique is explained
15 with reference to the drawing. In Fig. 1, a magnetic head 5 comprises two core elements 8 and 10 prepared from a suitable ferrite, as described previously herein. Glass rods 15 and 16 formed from a composition of this invention, e.g., a composition of
20 Table 1 are placed at V-grooves 25 and 26 formed at the plane 27 defined by the facing surfaces of the two cores. The combination is heated to the flow temperature of the glass, which melts and bonds to the facing surfaces at plane 27. Upon cooling, the
25 glass hardens to join the core elements together and maintain the gap at portion 30, which becomes the portion that generates the magnetic field used in recording a magnetic recording element such as a magnetic tape. As is conventional, the joined core
30 elements are further machined and cleaned with a caustic solution to form the completed magnetic head for a magnetic recorder and reader.

If the core elements 8 and 10 are made of ferrite, they are prepared by hot-pressing and
35 machining an appropriate composition of Table I.

Alternatively, ferromagnetic alloys can be used to form a magnetic head, as illustrated in Figs. 2 and 3. (Parts the same or similar to those already described in Fig. 1 bear the same reference numeral to which the distinguishing suffix "a" has been appended.) Specifically, core elements 8a and 10a are ferrite, as described in Fig. 1. Portion 30a is modified in that two metal alloy laminates 90 are sealed by a glass composition of this invention, to the core elements at 200 and to each other at 210. Gap 210 is the recording and/or read gap, and the glass at this gap preferably comprises one of the compositions of Table I designed for use with ferromagnetic alloys. As illustrated in Fig. 3, each laminate 90 comprises a plurality of wafers 100, all having about the same two-dimensional shape. The wafers are bonded together by glass 110, such glass comprising a glass composition of Table I that is designed for use with the ferromagnetic alloys. Machining and cleaning is as previously described herein.

The following examples further illustrate the invention.

Example 1

The raw materials of Table II below were blended and melted together to form the glass composition of Table III. This was then ground, remelted and drawn into a fiber which was placed at a ferrite surface as in Fig. 1. The fiber bonded successfully to the ferrite surface.

Table II

<u>Raw Material</u>	<u>Wt. %</u>
Li_3PO_4	0.4
Na_2CO_3	23.0
5 $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$	31.6
ZnO	12.9
B_2O_3	13.7
$2\text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	16.6
10 $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$	1.8

Table III

Glass Composition

<u>Constituent</u>	<u>Mole %</u>
P_2O_5	18.5
Al_2O_3	10
15 Na_2O	21
ZnO	15.5
SiO_2	15
B_2O_3	19
Li_2O	1

20 The coefficient of thermal expansion was $125 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. This compared to a coefficient of $120 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ for the ferrite. The % weight loss when subjected to the caustic resistance test described herein was less than 0.01 mg/cm^2 .

25 Example 2

The raw materials of Table IV were blended and melted together to give the glass frit composition of Table V.

Table IV

<u>Raw Material</u>	<u>Wt. %</u>
K_2O_3	15.8
KH_3PO_4	34.1
$\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$	20.1
ZnO	5.6
35 B_2O_3	4.9
$2\text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	19.5

Table V

Glass Composition

<u>Constituent</u>	<u>Mole %</u>
P ₂ O ₅	27.5
5 Al ₂ O ₃	9.0
K ₂ O	27.5
ZnO	8.0
SiO ₂	20.0
B ₂ O ₃	8.0

10 The composition had a coefficient of thermal expansion of $157 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$, compared to a coefficient of $154 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ for the alloy. The % weight loss when subjected to the caustic resistance test described herein was less than
15 0.01 mg/cm².

The frit was then crushed and ball milled to yield a fine powder that was dispersed in an organic solvent/binder system comprising 15 g nitrocellulose, 40 ml butyl acetate, 50 ml toluene, 10 ml butanol,
20 and 5 ml acetone. This dispersion was then applied to magnetic alloy wafers using conventional coating techniques. The dispersion was allowed to dry and the binder was burned out at 375°C. Firing the glass powder and metal alloy wafers at 875°C melted the
25 glass, allowing it to flow and coat the metal with a continuous glass enamel. These glass coated metal wafers were then stacked and reheated to fuse the glass layers together giving a glass-metal-glass-metal laminate. Preformed glass wafers of the same
30 composition were placed on the top and bottom of the laminate and fused to form a uniform structure.

The uniform structure was then machined to the proper dimensions and used to form the tip plates of a magnetic recording head.

35 Comparable excellent bonding and caustic resistance are obtained with a glass composition

prepared using the procedure of this Example using appropriate raw materials but substituting a germanium compound for a phosphorus compound to obtain a composition containing a comparable amount of GeO_2 in place of P_2O_5 . Raw materials containing vanadium or antimony compounds can be similarly employed and provide comparable glass compositions containing oxides of these metals.

Example 3

The glass composition of Table V in Example 2 was melted and fined to remove all bubbles and then cast into a steel mold to form a sputtering target. This target was used in a sputtering system to form a thin continuous glass coating on magnetic alloy wafers as in Example 2. The wafers of glass coated metal were then stacked, heated and fused together to form a glass-metal laminate. Preformed glass wafers of the same composition were placed on the top and bottom of the laminate and fused to form a uniform structure.

Example 4

The raw materials of Table VI were blended and melted together to give the glass frit composition of Table VII:

25		<u>Table VI</u>	
	<u>Raw Materials</u>		<u>Wt. %</u>
	Na ₂ CO ₃		25.67
	Al ₂ O ₃ ·3P ₂ O ₅		32.50
	CuO		15.67
30	B ₂ O ₃		17.15
	Al ₂ O ₃ ·P ₂ O ₅		9.01

Table VII
Glass Composition

<u>Constituent</u>	<u>Mole %</u>
Na ₂ O	22.5
5 Al ₂ O ₃	10.0
CuO	20.0
B ₂ O ₃	25.0
P ₂ O ₅	22.5

10 This glass composition had a coefficient of thermal expansion of $120 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ and a % weight loss in the caustic resistance test described previously that was less than 0.001 mg/cm^2 .

15 The glass frit was remelted and applied to a ferromagnetic surface. It bonded successfully to the surface.

Example 5

The raw materials of Table VIII were blended and melted together to give the glass frit composition of Table IX:

20 Table VIII

<u>Raw Materials</u>	<u>Wt. %</u>
Na ₂ CO ₃	25.67
Al ₂ O ₃	32.50
ZnO	15.67
25 B ₂ O ₃	17.15
Al ₂ O ₃ ·P ₂ O ₅	9.01

Table IX
Glass Compositions

<u>Constituent</u>	<u>Mole %</u>
Na ₂ O	22.5
Al ₂ O ₃	10.0
ZnO	20.0
B ₂ O ₃	25
35 P ₂ O ₅	22.5

This glass composition had a coefficient of thermal expansion of $124 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ and a % weight loss in the caustic resistance test described herein that was less than 0.001 mg/cm². After
5 remelting, the glass frit was applied and bonded to a ferromagnetic surface.

Example 6

A glass frit was prepared using the procedure of Example 4 with the appropriate raw
10 materials. The composition was as follows:

Table X
Glass Composition

	<u>Constituent</u>	<u>Mole %</u>
	Na ₂ O	13.0
15	Al ₂ O ₃	10.0
	ZnO	19.2
	B ₂ O ₃	19.2
	SiO ₂	25.6
	P ₂ O ₅	13.0

20 This glass composition had a coefficient of thermal expansion of $85 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ and a % wgt. loss in the caustic resistance test described herein that was less than 0.001 mg/cm². This composition was found to exhibit excellent bonding to a ferrite
25 surface.

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Claims:

1. A glass composition that is particularly useful for bonding to a metal alloy or a metal oxide, which composition comprises:

- 5 (1) an oxide of an alkali metal or an alkaline earth metal,
- (2) an oxide of a metal, which metal is both non-alkali and non-alkaline earth, in an amount sufficient to provide a coefficient of thermal expansion of 80 to 170 x
- 10 $10^{-7}^{\circ}\text{C}^{-1}$,
- (3) 5 to 15 mole % of an oxide of aluminium, and
- (4) 10 to 35 mole % of a compatible glass former that renders the oxide of aluminium soluble
- 15 in the composition.

2. A composition according to claim 1, wherein the metal which is both non-alkali and non-alkaline earth is zinc, copper or boron.

3. A composition according to claim 1 or 2,

20 wherein the compatible glass former is an oxide of phosphorus, vanadium, antimony or germanium.

4. A composition according to claim 3, wherein the compatible glass former is an oxide of phosphorus or germanium.

25 5. A composition according to claim 1 comprising:

 10 to 35 mole % of oxide of potassium,

 5 to 15 mole % of oxide of zinc or copper,

 5 to 15 mole % of oxide of boron,

 5 to 15 mole % oxide of aluminium,

30 10 to 30 mole % oxide of phosphorus, and

 0 to 30 mole % of oxide of silicon.

6. A composition according to claim 1 comprising:

 10 to 30 mole % oxide of sodium,

 10 to 25 mole % oxide of zinc or copper,

35 10 to 25 mole % oxide of boron,

 5 to 15 mole % oxide of aluminium,

 10 to 30 mole % oxide of phosphorus, and

 0 to 30 mole % oxide of silicon.



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7. A composition according to claim 1 having a softening temperature no greater than 500°C.

8. Compositions according to claim 1 substantially as hereinbefore described.

5 9. A magnetic head comprising metal alloy or metal oxide bonded to a glass composition according to any one of claims 1 to 8.

10 10. A magnetic head according to claim 9 substantially as hereinbefore described with reference to, and as shown in, Figure 1 or Figures 2 and 3 of the accompanying drawings.

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