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(54) **Amorphous metals and articles made thereof.**

(57) An amorphous Fe–B–Si alloy and article made therefrom is provided having improved castability while maintaining good magnetic properties, ductility and improved thermal stability. The alloy consists of 73–80% Fe, 4–10% B and 14–17% Si, in atomic percentages, and no more than incidental impurities. A method of casting an amorphous strip material from the alloy is also provided.

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AMORPHOUS METALS AND ARTICLES MADE THEREOF

This invention relates to amorphous metal alloys. Particularly, the invention relates to iron-boron-silicon amorphous metals and articles made thereof having improved magnetic properties and physical properties.

Amorphous metals may be made by rapidly solidifying alloys from their molten state to a solid state. Various methods known in rapid solidification technology include spin casting and draw casting, among others. Vapour and electrodeposition can also be used to make amorphous metals. Amorphous metals provided by any of the above methods have distinctive properties associated with their non-crystalline structure. Such materials have been know, for example, to provide improved mechanical, electrical, magnetic and acoustical properties over counterpart metal alloys having crystalline structure. Generally, the amorphous nature of the metal alloy can be determined by metallographic techniques or by X-ray diffraction. As used herein, an alloy is considered "amorphous" if the alloy is substantially amorphous, being at least 75% amorphous. Best properties are obtained by having a (200) X-ray diffraction peak of less than 25.4mm (one inch) above the X-ray background level. This peak, in the case of body centered cubic ferrite (the hypoeutectic crystalline solid solution), occurs at a diffraction angle of 106^{O} when using $Cr_{K\alpha}$ radiation.

Unless otherwise noted, all composition percentages recited herein are atomic percentages.

There are various known alloy compositions of Fe-B-Si. For example, United States Patent No. 3,856,513, Chen et al, discloses an alloy and sheets, ribbons and powders made therefrom under the general formula $M_{60-90}Y_{10-30}Z_{0.1-15}$ where M is iron, nickel, chromium, cobalt, vanadium or mixtures thereof, Y is phosphorus, carbon, boron, or mixtures thereof and Z is aluminium, silicon, tin, antimony, germanium, indium, beryllium and mixtures thereof which can be made substantially amorphous. There are also known alloy compositions of Fe-B-Si which have shown promising magnetic properties and other properties for superior performance in electrical apparatus such as motors and transformers. United States Patent No. 4,219,355, Luborsky, discloses an iron-boron-silicon alloy with crystallization temperature (the temperature at which the amorphous metal reverts to its crystalline state) of at least 608°F (320°C), a coercivity of less than 0.03 oersteds, and a saturation magnetization of at least 174 emu/g (approximately 17,000 G). Generally, the alloy contains 80 or more atomic percent iron, 10 or more atomic percent boron and no more than about 6 atomic percent silicon. An amorphous metal alloy strip, greater than 1-inch (2.54 cm) wide and less than 0.003-inch (.00762 cm) thick, having specific magnetic properties, and made of an alloy consisting essentially of 77-80% iron, 12-16% boron and 5-10% silicon, all atomic percentages, is disclosed in United States Patent application Serial No. 235,064, by the common Assignee of the present application.

Attempts have been made to modify such amorphous materials by additions of other elements to optimize the alloy compositions for electrical applications. United States Patent No. 4,217,135, DeCristofaro, discloses an iron-boron-silicon alloy having 1.5 to 2.5 atomic percent carbon to enhance the magnetic properties.

United States Patent No. 4,190,438, Aso et al, discloses an iron-boron-silicon magnetic alloy containing 2-20 atomic percent ruthenium.

While such alloy compositions have provided relatively good magnetic properties, they are not without drawbacks. All of the above alloys are costly because of the relatively large amount of boron. A lower boron version is highly desirable. Also, higher crystallization temperatures are desirable in order that the alloys will have less tendency to revert back to the crystalline state. The composition should also be close to a eutectic composition so as to facilitate casting into the amorphous condition. Furthermore, the eutactic temperature should be as low as possible for purposes of improving castability. It is also desirable that the magnetic saturation should be high, of the order of at least 14,000 G. An object of this invention is to provide such an alloy which can compete with known conventional commercial nickel-iron alloys, such as AL 4750 which nominally comprises 48% Ni-52% Fe, by weight percentage.

In accordance with the present invention, an amorphous alloy and article are provided which overcome those problems of the known iron-boron-silicon amorphous metals. An amorphous metal alloy is provided consisting of 73-80% iron, 4-10% boron and 14-17% silicon, by atomic percentages, and no more than incidental impurities. This alloy is lower in cost than either the other known amorphous alloys, or the commercially available Ni-Fe alloys which the alloy disclosed herein is designed to displace.

An article made from the amorphous metal alloy of the present invention is also provided, being at least singularly ductile (as herein defined) and having a core loss competitive with commercial Ni-Fe alloys, such as AL 4750, and particularly, a core loss of less than 0.163 watts per pound (WPP) at 12.6 kilogauss (1.26 tesla) at 60 Hertz. The article of the alloy has a saturation magnetization measured at 75 oersteds (B_{75H}) of at least 14.0 kilogauss (1.40 tesla) and a coercive force (H_c) of less than 0.045 oersteds, and may be in the form of a thin strip or ribbon material product. The alloy and resulting product have improved thermal stability characterized by a crystallization temperature (T_x) of not less than 914°F (490°C).

The invention further provides a method of casting an amorphous strip material having a width of at least one inch (2.54cm), a thickness less than 0.003 inch (0.0762mm), a 60 Hertz core loss of less than 0.163 watts per pound at 12.6 kilogauss, saturation magnetization (B_{75H}) of at least 14 kilogauss, a coercive force of less than 0.045 oersteds and is at least singularly ductile, comprising the steps of:

melting an alloy consisting of 73-80% iron, 4-10% boron and 14-17% silicon, by atomic percentages, with no more than incidental impurities;

while maintaining the alloy molten, continuously delivering a stream of the molten alloy through a slotted nozzle and onto a casting surface disposed within 0.025 inch (0.635mm) of the nozzle;

continuously moving the casting surface past the nozzle at a speed of 200 to 10,000 linear surface feet per minute (61 to 3048m/minute).

at least partially solidifying the strip on the casting surface; and

separating the at least partially solidified strip from the casting surface.

The invention will be more particularly described with reference to the accompanying drawing, in which:-

Figure 1 is a termary diagram showing the eutectic line and composition ranges of the present invention.

Generally, an amorphous alloy of the present invention consists essentially of 73-80% iron, 4-10% boron and 14-17% silicon. In Figure 1, the compositions lying inside the lettered area defining the relationships expressed by points A, B, C, D and E, are within the broad range of this invention, The points A, F, G and H express relationships for compositions which lie within a preferred range of this invention. The line between points I and J, crossing through and extending outside the composition area relationships herein defined, represents the locus of eutectic points (lowest melting temperatures) for the eutectic valley in this region of interest in the Fe-B-Si ternary diagram.

The Fe-B-Si composition ranges of the invention shown in Figure 1 are close enough to the eutectic line or trough to be substantially amorphous as cast. The boron content is critical to the amorphousness of the alloy. The higher the boron content, the greater the tendency for the alloy to be amorphous. However, with increased boron content, the alloys become more costly. The preferred boron range is from 4% to less than 10% and more preferably is 7% to less than 10%. Lower cost alloys of less than 7% boron are included in the invention, but are more difficult to cast with good properties.

Silicon in the alloy primarily affects the thermal stability of the alloy and to a small degree affects the amorphousness. Silicon has much less effect on the amorphousness of the alloy than does boron. Preferably, silicon may range from more than 15% to 17%.

The alloy of the present invention is rich in iron. The iron contributes to the overall magnetic saturation of the alloy and preferably the iron content ranges from 73 to 78%.

The alloy composition of the present invention provides an optimization of the requisite properties of the Fe-B-Si alloys for certain electrical applications. Some properties have to be sacrificed at the expense of obtaining other properties, but the composition of the present invention is found to be an ideal balance between those properties. It has been found that the iron content does not have to exceed 80% to attain the requsite magnetic saturation. By keeping the iron content below 80%, the other major constituents, namely boron and especially silicon, can be provided in increased amounts. To obtain an article made of the alloy of the present invention having increased thermal stability, the silicon amount is maximized. Greater amounts of silicon raise the crystallization temperature, permitting the strip material to be heat treated at higher temperatures without causing crystallization. Being able to heat treat to higher temperatures is useful in releiving internal stresses in the article produced, which improves the magnetic properties. Also, higher crystallization temperatures extend the useful temperature range over which optimum magnetic properties are maintained for articles made therefrom.

In the alloy of the present invention, certain incidental impurities, or residuals, may be present. Such incidental impurities together should not exceed 0.83 atomic percent of the alloy composition. The following is a tabulation of typical residuals which can be tolerated in the alloys of the present invention.

Typical Residual Amounts (Atomic %)	Element
.0038	Tin
.0045	Aluminium
.0049	Titanium
.017	Molybdenum
.012	Phosphorus
.029	Nickel
.080	Manganese
.022	Copper
.0062	Sodium
.0012	Potassium
.055	Chromium
.0023	Lead
.006	Nitrogen
.020	Oxygen
.13	Carbon
.0032	Sulphur
.00036	Magnesium
.00049	Calcium
.00058	Zirconium
Less than .2	Others

Various known methods of rapid solidification may be used for casting the amorphous metal alloy of the present invention. Particularly, the alloy may be cast using draw casting techniques. Typically, a drawcasting technique may include continuously delivering a molten stream or pool of metal through a slotted nozzle located within less than 0.025 inch (0.635mm) of a casting surface which may be moving at a rate of about 200 to 10,000 linear surface feet per minute (61 to 3048 m/minute) past the nozzle to produce an amorphous strip material. The casting surface is typically the outer peripheral surface of a water-cooled metal wheel made, for example, of copper. Rapid movement of the casting surface draws a continuous thin layer of the metal from the pool or puddle. This layer rapidly solidifies at a quench rate of the order of 1 x 10^{5}°C per second into strip material. Typically, alloys of the present invention are cast at a temperature above about 2400°F (1315°C) onto a casting surface having an initial temperature that may range from about 35 to 90°F (1.6 to 32°C). The strip is quenched to below solidification temperature and to below the crystallization temperature and after being solidified on the casting surface it is separated therefrom. Typically, such strip may have a width of 1 inch (2.54 cm) or more and a thickness of less than 0.003 inch (0.0762mm), and a ratio of width-to-thickness of at least 10:1 and preferably at least 250:1.

From the alloys of the present invention, thin strip materials were made using such a draw casting technique for the alloy compositions which are shown in the following Table I.

Table I

	Composition Atomic Percent		
Heat No.	Iron	Boron	Silicon
158	75	9	16
671	75	9	16
600	76	10	14
610	73	10	17
621	73	7	20
622	74.5	8.5	17

Each strip was annealed in a 10 oersted DC magnetic field for four hours at 662°F (350°C). The amorphous character of each was confirmed by X-ray diffraction measurements. Furthermore, each was found to have at least singular ductility as determined by a simple bend test.

Ductility determined by bend tests include bending the strip transversely upon itself in a 180° bend in either direction to determine the brittleness. If the strip can be bent upon itself along a bend line extending across the strip (i.e., perpendicular to the casting direction) into a non-recoverable permanent bend without fracturing, then the strip exhibits ductility. The strip is double ductile if it can be bent 180° in both directions without fracture and single or singularly ducitile if it bends 180° only in one direction without fracture. Singular ductility is a minium requirement for an article made of the alloy of the present invention. Double ductility is an optimum condition for an article made of the alloy of the present invention.

The data of Table II (shown Below) demonstrates that the core loss, which should be as low as possible, of the alloy of the present invention is consistently less than the core loss of 0.163 WPP at 12.6 KG (1.26T) for a commercial alloy AL 4750 which nominally comprises 48% Ni-52% Fe. The AL 4750 alloy tested was 0.006-inch (0.015cm) thick and was prepared in accordance with recognized commercial practice for the alloy. The strips of the alloy of the present invention were about .0013-inch (.0033cm) thick.

TABLE II

	ALR 158	ALR 671	ALR 600	ALR 610	ALR 621	ALR 622	6 mil AL 4750 Ni-Fe Alloy (Reference)
D.C. B @ 1H	6500	10700	13200	13300	9100	11900	12600
Br	2300	7100	10600	11100	5100	8500	9200
H_c	.0925	.0449	.0392	.0301	.0487	.0368	.0361
B @ 10H	-	14000	14900	14500	12500	14300	15000
B @ 75H	14700	14900	15400	15000	13500	14800	15500
60 Hz WPP @ 1.0T	.138	.0363	.0565	.0422	.0748	.0583	.10
WPP @ 1.1T	-	.0440	.0725	.0541	.0818	.0695	.12
WPP @ 1.2T	-	.0531	.0863	.0697	.0994	.0816	.145
WPP @ 1.26T	.228	.0618	.0934	.0771	.105	.0900	.163
WPP @ 1.3T	-	.0644	.0992	.0821	.117	.0965	.175
WPP @ 1.4T	-	.0695	.115	.0954	-	.112	.21
60 Hz VAPP @ 1.0T	2.3	.203	.0659	.0446	1.14	.137	.15
VAPP @ 1.1T	-	.376	.104	.0644	2.17	.313	.25
VAPP @ 1.2T	-	.789	.237	.144	4.57	.703	.60
VAPP @ 1.26T	6.2	1.16	.428	.288	9.02	1.15	1.14
VAPP @ 1.3T	-	1.54	.623	.466	23.59	1.63	1.5
VAPP @ 1.4T	-	3.76	1.64	1.83	-	4.20	4.0
Crystalline Temp. T_x (^oC)	-	529	526	522	-	521	
(200) X-ray Peak Heights (inches)	>1	<1	<1	<1	>1	<1	<1

The magnetic data for Heat No. 158 is inconsistent with the other alloy data for the reason that the (200) X-ray diffraction peak is slightly larger than the 1.0" (2.54cm) max. above background level established for best properties. Heat 671 of the same composition was cast at a later date when casting techniques had improved allowing the alloy to be substantially amorphous by virtue of improved casting quench rate. The properties of Heat 158, however, demonstrate the capability of the alloy composition in providing magnetic saturation of the level required and useful articles made therefrom. By comparison, an alloy composition which is outside our invention, $Fe_{73}B_7Si_{20}$, Heat 621, having an extremely high silicon level, is still crystalline to a large extent and brittle when cast even under the best quenching conditions. Because the alloy is not substantially amorphous, it does not develop the desirable magnetic properties.

All of the heats, except ALR 621, are alloy compositions of the present invention. The data shown in Table II demonstrates that the alloys of the present invention have magnetic properties of magnetic saturation, coercive force, core loss (in WPP) and apparent core loss (in voltamperes per pound, VAPP) comparable to or better than the AL 4750 alloy.

The present invention provides alloys useful for electrical applications and articles made from these alloys having good magnetic properties. The alloys can be made less expensively because of the lower raw materials cost of boron. The alloys are amorphous and ductile and have a thermal stability greater than those iron-boron-silicon alloys having more than 10 atomic percent boron and less than 14 atomic percent silicon.

CLAIMS

1. An amorphous metal alloy characterised in constisting of 73-80% iron, 4-10% boron and 14-17% silicon, by atomic percentages, and no more than incidental impurities.

2. An alloy according to claim 1, characterised in including 4% to less than 10% boron, by atomic percentages.

3. An alloy according to claim 1 or 2 characterised in including more than 15% to 17% silicon, by atomic percentages.

4. An alloy according to claim 1, 2 or 3 characterised in including 7% to less than 10% boron, by atomic percentages.

5. An alloy according to any one of the preceding claims, characterised in including 73-78% iron, by atomic percentages.

6. An amorphous metal alloy characterised in consisting of 73-78% iron, 7% to less than 10% boron and more than 15% to 17% silicon, by atomic percentages, and no more than incidental impurities.

7. An alloy according to any one of the preceding claims, characterised in including no more than 0.83% incidental impurities, by atomic percentages.

8. An alloy according to any one of the preceding claims, characterised in further having improved thermal stability characterised by a crystallization temperature not less than 914°F (490°C).

9. An amorphous metal alloy article, characterised in said alloy consisting of 73-80% iron, 4-10% boron and 14-17% silicon, by atomic percentages, and no more than incidental impurities, said article being at least singularly ductile.

10. An article according to claim 9, characterised in including 4% to less than 10% boron, by atomic percentages.

11. An article according to claim 9 or 10, characterised in including more than 15% to 17% silicon, by atomic percentages.

12. An article according to any one of claims 9 to 11, characterised in including 7% to less than 10% boron, by atomic percentages.

13. An article according to any one of claims 9 to 12, characterised in said alloy including 73-78% iron, by atomic percentages.

14. An amorphous metal alloy article, characterised in said alloy consisting of 73-78% iron, 7% to less than 10% boron and more than 15% to 17% silicon, by atomic percentages, and no more than incidental impurities, said article being at least singularly ductile.

15. An article according to any one of claims 9 to 14, characterised in including no more than 0.83% incidental impurities, by atomic percentages.

16. An article according to any one of claims 9 to 15, characterised in having a relatively low core loss of less than 0.163 watts per pound at 12.6 kilogauss, at 60 Hertz, a saturation magnetization B_{75H} of at least 14 kilofauss, and a coercive force H_c of less than 0.045 oersteds.

17. An article according to any one of claims 9 to 16, characterised in being a thin strip material having a thickness of less than 0.003 inch (0.0762mm) and a ratio of width-to-thickness of at least 250 to 1.

18. An article according to any one of claims 9 to 17 characterised in having improved thermal stability characterised by a crystallization temperature of not less than 914°F (490°C).

19. A method of casting an amorphous strip material having a width of at least one inch (2.54cm), a thickness less than 0.003 inch (0.0762mm), a 60 Hertz core loss of less than 0.163 watts per pound at 12.6 kilogauss, saturation magnetization (B_{75H}) of at least 14 kilogauss, a coercive force of less than 0.045 oersteds and is at least singularly ductile, characterised in comprising the steps of:-

melting an alloy consisting of 73-80% iron, 4-10% boron and 14-17% silicon, by atomic percentages, with no more than incidental impurities;

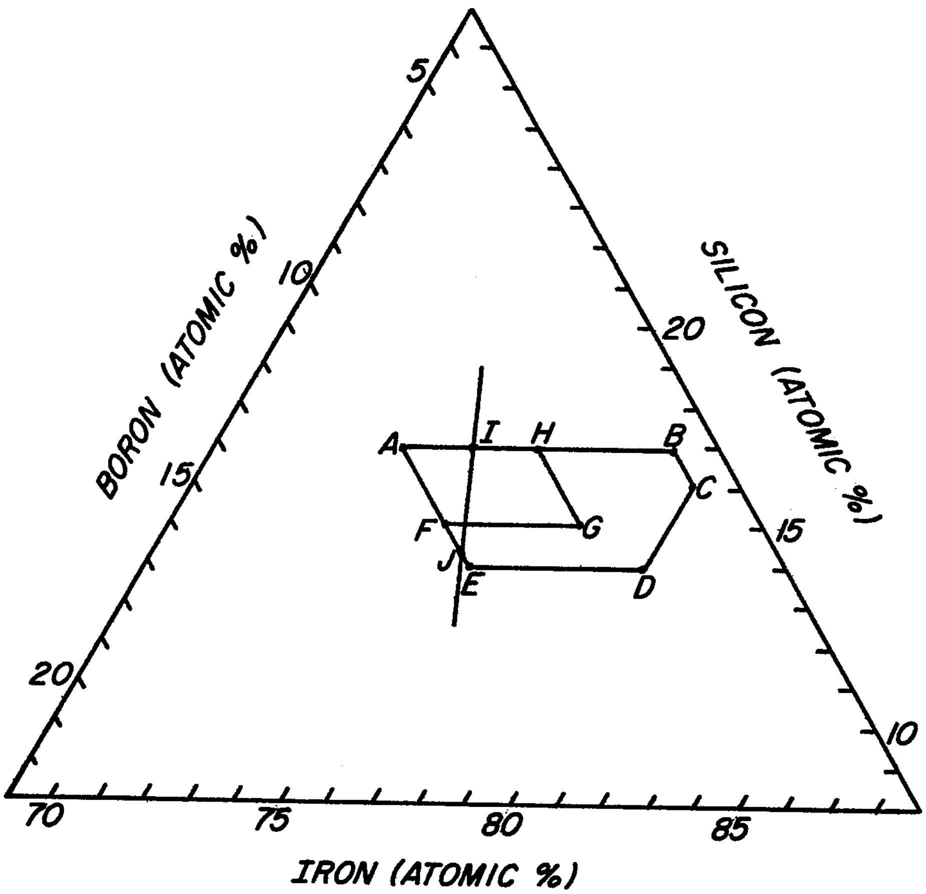
while maintaining the alloy molten, continuously delivering a stream of the molten alloy through a slotted nozzle and onto a casting surface disposed within 0.025 inch (0.635mm) of the nozzle;

continuously moving the casting surface past the nozzle at a speed of 200 to 10,000 linear surface feet per minute (61 to 3048m/minute);

at least partially solidifying the strip on the casting surface; and

separating the at least partially solidified strip from the casting surface.

20. A method according to claim 19 characterised in that said alloy consists of 73-78% iron, 7% up to less than 10% boron, from more than 15% up to 17% silicon, by atomic percentages, and no more than incidental impurities.



5
10
15
20
BORON (ATOMIC %)
20
15
10
SILICON (ATOMIC %)
70
75
80
85
IRON (ATOMIC %)
A
I
H
B
C
F
G
J
E
D

FIGURE 1