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⑤④ **Iron group transition metal-refractory metal-boron glassy alloys.**

⑤⑦ The invention deals with glassy alloys consisting essentially of about 5 to 12 atom per cent boron, one of the members selected from the group of 20 to 60 atom per cent molybdenum and about 13 to 40 atom per cent tungsten and the balance essentially one of the group consisting of cobalt, iron and nickel.

The invention also relates to glassy alloys containing all three iron, cobalt and nickel plus molybdenum and/or tungsten, together with low boron content. The latter glassy alloys of the invention consist essentially of about 5 to 12 atom per cent boron, about 5 to 15 atom per cent molybdenum and/or tungsten and the balance essentially iron, cobalt and nickel plus incidental impurities. The glassy alloys evidence hardness values of at least about 1000 Kg/mm<sup>2</sup>, ultimate tensile strengths of at least about 330 Kpsi and crystallization temperatures of at least about 445°C.

**EP 0 002 923 A1**

IRON GROUP TRANSITION METAL-REFRACTORY  
METAL-BORON GLASSY ALLOYS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to glassy alloys containing low boron content and molybdenum and/or tungsten in conjunction with at least one other metal of the group cobalt, iron and nickel.

2. Description of the Prior Art

Chen et al. in U.S.P. 3,856,513, issued December 24, 1974, have disclosed glassy alloys consisting essentially of about 60 to 90 atom percent of at least one element of iron, nickel, cobalt, vanadium and chromium, about 10 to 30 atom percent of at least one element of phosphorus, boron and carbon and about 0.1 to 15 atom percent of at least one element of aluminum, silicon, tin, germanium, indium, antimony and beryllium. Up to about one-fourth of the metal may be replaced by elements which commonly alloy with iron and nickel, such as molybdenum, titanium, manganese, tungsten, zirconium, hafnium and copper. Chen et al. also disclose wires of glassy alloys having the general formula  $T_i X_j$ , where T is a transition metal and X is an element selected from the group consisting of phosphorus, boron, carbon, aluminum, silicon, tin, germanium, indium, beryllium and antimony, and where "i" ranges from about 70 to 87 atom percent and "j" ranges from about 13 to 30 atom percent.

More recently, Masumoto et al. in U.S.P. 3,986,867 issued October 19, 1976, have disclosed iron-chromium glassy alloys consisting essentially of about 1 to 40 atom percent

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chromium, 7 to 35 atom percent of at least one of carbon, boron and phosphorus and the balance iron. Up to about 40 atom percent of at least one of nickel and cobalt, up to 20 atom percent of at least one of molybdenum, zirconium, titanium and manganese and up to about 10 atom percent of at least one of vanadium, niobium, tungsten, tantalum and copper may also be employed. Elements useful for improving mechanical properties include molybdenum, zirconium, titanium, vanadium, niobium, tantalum, tungsten, copper and manganese, while elements effective for improving the heat resistance include molybdenum, zirconium, titanium, vanadium, niobium, tantalum and tungsten.

Efforts to develop new compositions which are easily formed in the glassy state with superior mechanical properties and which at the same time retain high thermal stability are continuing. Substantial amounts of metalloid elements (typically 15 to 25 atom percent) are usually found most suitable for producing the glassy state under reasonable quenching conditions of at least about  $10^5$ °C/sec, consistent with forming a ductile product. However, such high metalloid content combined with a high refractory metal content also may result in increasing brittleness of the glassy alloy in the as-quenched state.

#### SUMMARY OF THE INVENTION

In accordance with the invention, substantially totally glassy alloys containing a low boron content as a first component, plus molybdenum or tungsten as a second component in conjunction with one of the metals cobalt, iron and nickel are provided. The glassy alloys of the invention consist essentially of about 5 to 12 atom percent boron, one only of the members selected from the group of 20 to 60 percent molybdenum and 13 to 40 atom percent tungsten and the balance essentially one of the group iron, cobalt and nickel. In a more specific embodiment glassy alloys containing all three of the metals cobalt, iron and nickel with the above specified boron and second component molybdenum, tungsten and mixtures thereof are provided wherein each of the metals cobalt, iron and nickel is present in an amount of at least

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about 5 atom percent, plus incidental impurities. The alloys of the invention evidence hardness values of at least about 1000 Kg/mm<sup>3</sup>, ultimate tensile strengths of at least about 330 Kpsi and crystallization temperatures of at least about 445°C.

#### DETAILED DESCRIPTION OF THE INVENTION

The glassy alloys of the invention consist essentially of (I) about 5 to 12 atom percent boron together with (II) one only of the group consisting of molybdenum (about 20 to 60 wt%) and tungsten (about 13 to 40 wt%) with the balance being one of the group iron, cobalt and nickel or (III) glassy alloys containing at least 5 atom percent of all three metals, cobalt, iron and nickel in amounts of at least 5 atom percent wherein the amount of molybdenum, tungsten or mixtures thereof, is used in lesser quantities of about 5 to 15 atom percent together with boron in specified amounts of 5 to 12 atom percent. Preferably the boron is present in amounts of 8 to 10 atom percent and the molybdenum and tungsten as component II in amounts of 30 to 50 atom percent and as component III in amounts of 8 to 12 atom percent. Examples of glassy alloys of the invention include

$\text{Ni}_{45}\text{Mo}_{45}\text{B}_{10}$ ,  $\text{Ni}_{55}\text{Mo}_{35}\text{B}_{10}$ ,  $\text{Ni}_{60}\text{W}_{30}\text{B}_{10}$ ,  $\text{Ni}_{70}\text{W}_{20}\text{B}_{10}$ ,  
 $\text{Fe}_{60}\text{Mo}_{30}\text{B}_{10}$ ,  $\text{Fe}_{55}\text{Mo}_{35}\text{B}_{10}$ ,  $\text{Fe}_{77}\text{W}_{15}\text{B}_{18}$ ,  $\text{Fe}_{77}\text{W}_{13}\text{B}_{10}$ ,  
 $\text{Co}_{50}\text{Mo}_{40}\text{B}_{10}$ ,  $\text{Co}_{55}\text{Mo}_{35}\text{B}_{10}$ ,  $\text{Co}_{60}\text{W}_{30}\text{B}_{10}$ ,  $\text{Co}_{70}\text{W}_{20}\text{B}_{10}$ ,  
 $\text{Fe}_{45}\text{Co}_{20}\text{Ni}_{15}\text{Mo}_{12}\text{B}_8$ ,  $\text{Ni}_{55}\text{Co}_{10}\text{Fe}_{15}\text{Mo}_{12}\text{B}_8$ ,  $\text{Co}_{55}\text{Fe}_{15}\text{Ni}_{10}\text{W}_6\text{Mo}_6\text{B}_8$ .

It is seen that the glassy metal alloys of the invention comprise three components: the first component is boron in amounts of from about 5 to about 12 atom percent; the second component is a refractory metal of the group molybdenum in amounts of 20 to 60 atom percent and tungsten in amounts of from about 13 to 40 atom percent; and the third component comprising the balance of the alloy is selected from the group cobalt, iron and nickel.

The low boron content, the refractory metal content and the third component are interdependent. When the boron content is less than about 5 atom percent and both the refractory metal content and the iron group metal content lie within the limits specified, rapidly quenched ribbons

are not totally glassy. Rather, the rapidly quenched ribbons contain crystalline phases, which may comprise a substantial fraction of the material, depending on specific composition. The rapidly quenched ribbons containing crystalline phases or mixtures of both glassy and crystalline phases have inferior mechanical properties, i.e., low tensile strength, and are brittle. Typically, such ribbons, having thicknesses up to 0.0015 inch, will fracture if bent to a radius of curvature less than 100 times the thickness.

5        When the boron content is greater than about 13 atom percent and both the refractory metal content and the iron group metal content lie within the limits specified, rapidly quenched ribbons, while remaining fully glassy are, nevertheless, more brittle than ribbons having compositions within the scope of the invention. Typically, such ribbons fracture when bent to a radius of curvature less than about 100 times the thickness.

10       Similarly, for refractory metal concentrations less than those listed above, compositions containing such low metalloid content do not form glassy alloys at the usual quench rates. For refractory metal concentrations greater than those listed above, compositions containing such low metalloid content form brittle glassy alloys. If the alloys do not contain these metals in the respective proportions then, in general, the alloys do not form fully glassy ductile ribbons.

15       In contrast, when the boron content ranges from about 5 to 12 together with the specified proportions of the refractory metal, molybdenum and/or tungsten, second component together with the third component of the group iron, cobalt and nickel, rapidly quenched ribbons are substantially totally glassy and possess superior mechanical properties, i.e., high tensile strength and ductility. For example, glassy ribbons of the invention can be bent without fracture to a radius of curvature about 10 times the thickness.

20       Use of refractory metal elements other than molybdenum and tungsten and use of metalloids other than boron in

the amounts given do not form ductile glassy alloys at the usual quench rates. For example, replacing boron by carbon or silicon results in the formation of crystalline, rather than glassy, phases.

5           The purity of all elements is that found in normal commercial practice. However, it is contemplated that minor additions (up to a few atom percent) of other alloying elements may be made without an unacceptable reduction of the desired properties. Such additions may be made, for exam-  
10       ple, to aid the glass-forming behavior. Such alloying elements include the transition metal elements (Groups IB to VIIB and VIII, Rows 4, 5 and 6 of the Periodic Table, other than the elements mentioned above) and metalloid elements (carbon, silicon, aluminum, and phosphorus).

15           The thermal stability of a glassy alloy is an important property in certain applications. Thermal stability is characterized by the time-temperature behavior of an alloy, and may be determined in part by differential thermal analysis (DTA). Glassy alloys with similar crystallization behavior as observed by DTA may exhibit different  
20       embrittlement behavior upon exposure to the same heat treatment cycle. By DTA measurement, crystallization temperatures  $T_c$  can be accurately determined by heating a glassy alloy (at about 20° to 50°C/min) and noting whether excess  
25       heat is evolved over a limited temperature range (crystallization temperature) or whether excess heat is absorbed over a particular temperature range (glass transition temperature). In general, the glass transition temperature is near the lowest, or first, crystallization temperature  $T_{cl}$  and, as is conventional, is the temperature at which the  
30       viscosity ranges from about  $10^{13}$  to  $10^{14}$  poise.

          The glassy alloys of the invention are formed by quenching an alloy melt of the appropriate composition at a rate of at least about  $10^5$ °C/sec. A variety of techniques are available, as is well-known in the art, for fabricating  
35       rapidly-quenched continuous filament. Typically, a particular composition is selected, powders of the requisite elements (or of materials that decompose to form the elements) in the desired proportions are melted and homogenized, and

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the molten alloy is rapidly quenched on a chill surface, such as a rapidly rotating cylinder.

The alloys of the invention are substantially totally glassy, as determined by X-ray diffraction. The term "glassy", as used herein, means a state of matter in which the component atoms are arranged in a disorderly array; that is, there is no long range order. Such a glassy alloy material gives rise to broad, diffuse diffraction peaks when subjected to electromagnetic radiation in the X-ray region (about 0.01 to 50 Å wavelength). This is in contrast to crystalline material, in which the component atoms are arranged in an orderly array, giving rise to sharp diffraction peaks. The term "substantially totally glassy" as used herein means a state of matter having crystalline and amorphous phases, the amorphous phase constituting at least about 80 percent of the combined phases. Thermal stability of the alloys improves as the degree of amorphousness thereof approaches 100%. Accordingly, totally glassy alloys, possessing a single, amorphous phase constituting 100% of the component atoms are preferred.

The glassy alloys of the invention evidence hardness values of at least about 1000 Kg/mm<sup>2</sup>, ultimate tensile strengths of at least about 350 Kpsi and crystallization temperatures of at least about 445°C. Preferred alloy compositions consist essentially of about 50 to 65 atom percent of one of the iron group metals of iron, cobalt and nickel, about 13 to 35 atom percent of the remaining two iron group metals, about 8 to 12 atom percent of at least one of molybdenum and tungsten and about 8 to 10 atom percent boron. The alloys having such preferred compositions are especially capable of being fabricated as good quality, ductile ribbons exhibiting high tensile strength.

The high mechanical strength and high thermal stability of the glassy alloys of the invention render them suitable for use as reinforcement in composites for high temperature applications.

#### EXAMPLES

Alloys were prepared from constituent elements of

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high purity (99.9%). The elements with a total weight of 30 g were melted by induction heater in a quartz crucible under vacuum of  $10^{-3}$  Torr. The molten alloy was held at 150° to 200°C above the liquidus temperature for 10 min and allowed to become completely homogenized before it was slowly cooled to the solid state at room temperature. The alloy was fractured and examined for complete homogeneity.

About 10 g of the alloys was remelted to 150°C above liquidus temperatures under vacuum of  $10^{-3}$  Torr in a quartz crucible having an orifice of 0.010 inch diameter in the bottom. The chill substrate used in the present work was beryllium-copper alloy in a heat-treated condition having moderately high strength and thermal conductivity. The substrate material contained 0.4 to 0.7 wt% beryllium, 2.4 to 2.7 wt% cobalt and copper as balance. The substrate was kept rotating at a surface speed of 4000 ft/min. The substrate and the crucible were contained inside a vacuum chamber evacuated to  $10^{-3}$  Torr.

The melt was spun as a molten jet by applying argon pressure of 5 psi over the melt. The molten jet impinged vertically onto the internal surface of the rotating substrate. The chill-cast ribbon was maintained in good contact with the substrate by the centrifugal force acting on the ribbon against the surface. The ribbon was ejected off the substrate by nitrogen gas at 30 psi, two-thirds circumferential length away from the point of jet impingement. During the metallic glass ribbon casting operation, the vacuum chamber was maintained under a dynamic vacuum of 20 Torr. The substrate surface was polished with 320 grit emery paper and cleaned and dried with acetone prior to the start of the casting operation. The as-cast ribbons were found to have good edges and surfaces. The ribbons had the following dimensions: 0.001 to 0.0012 inch thickness and 0.015 to 0.020 inch width.

The degree of glassiness was determined by X-ray diffraction. A cooling rate of at least about  $10^5$  °C/sec was attained by the quenching process.

Hardness was measured by the diamond pyramid technique using a Vickers-type indenter, consisting of a diamond in the form of a square-base pyramid with an included angle of 136° between opposite faces. Loads of 100 g were applied.

5 Crystallization temperature was measured by differential thermal analysis at a scan rate of about 20°C/min. Ultimate tensile strength was measured on an Instron machine using ribbons with unpolished edges. The gauge length of the specimens was 1 inch and the cross-head speed was 0.02  
10 in/min.

The following values of hardness in Kg/mm<sup>2</sup>, ultimate tensile strength in Kpsi and crystallization temperature in °C, listed in Tables I-IV below, were measured for a number of compositions falling within the scope of the  
15 invention.

TABLE I

Mechanical and Thermal Properties of Ni-Mo-B  
and Ni-W-B Glassy Alloys of the Invention

|    | Composition<br>(atom percent)                     | Hardness,<br>Kg/mm <sup>2</sup> | Ultimate Tensile<br>Strength, Kpsi | Crystallization<br>Temperature, °C |
|----|---------------------------------------------------|---------------------------------|------------------------------------|------------------------------------|
| 20 | Ni <sub>60</sub> Mo <sub>35</sub> B <sub>5</sub>  | 1186                            |                                    |                                    |
|    | Ni <sub>60</sub> Mo <sub>30</sub> B <sub>10</sub> | 1097                            |                                    |                                    |
|    | Ni <sub>57</sub> Mo <sub>35</sub> B <sub>8</sub>  | 1206                            | 490                                | 613,673                            |
|    | Ni <sub>55</sub> Mo <sub>35</sub> B <sub>10</sub> | 1246                            | 380                                | 610,655                            |
| 25 | Ni <sub>53</sub> Mo <sub>40</sub> B <sub>7</sub>  | 1310                            |                                    |                                    |
|    | Ni <sub>50</sub> Mo <sub>40</sub> B <sub>10</sub> | 1240                            | 390                                | 825                                |
|    | Ni <sub>45</sub> Mo <sub>45</sub> B <sub>10</sub> | 1330                            | 530                                | 850                                |
|    | Ni <sub>42</sub> Mo <sub>50</sub> B <sub>8</sub>  | 1401                            |                                    | 806,832,896                        |
|    | Ni <sub>35</sub> Mo <sub>55</sub> B <sub>10</sub> | 1452                            |                                    | 846                                |
| 30 | Ni <sub>33</sub> Mo <sub>55</sub> B <sub>12</sub> | 1465                            |                                    |                                    |
|    | Ni <sub>32</sub> Mo <sub>60</sub> B <sub>8</sub>  | 1505                            |                                    |                                    |
|    | Ni <sub>31</sub> Mo <sub>57</sub> B <sub>12</sub> | 1465                            |                                    | 860,890                            |
|    | Ni <sub>70</sub> W <sub>22</sub> B <sub>8</sub>   | 1246                            | 330                                | 562                                |
|    | Ni <sub>70</sub> W <sub>20</sub> B <sub>10</sub>  | 1159                            | 330                                | 546                                |
| 35 | Ni <sub>66</sub> W <sub>22</sub> B <sub>12</sub>  | 1287                            |                                    |                                    |
|    | Ni <sub>60</sub> W <sub>35</sub> B <sub>5</sub>   | 1032                            |                                    |                                    |
|    | Ni <sub>60</sub> W <sub>30</sub> B <sub>10</sub>  | 1222                            | 430                                | 544                                |

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TABLE II

Mechanical and Thermal Properties of Fe-Mo-B  
and Fe-W-B Glassy Alloys of the Invention

|    | Composition<br>(atom percent)                     | Hardness,<br>Kg/mm <sup>2</sup> | Ultimate<br>Tensile<br>Strength, Kpsi | Crystallization<br>Temperature, °C |
|----|---------------------------------------------------|---------------------------------|---------------------------------------|------------------------------------|
| 5  | Fe <sub>65</sub> Mo <sub>25</sub> B <sub>10</sub> | 1308                            | 475                                   | 615;680                            |
|    | Fe <sub>60</sub> Mo <sub>35</sub> B <sub>5</sub>  | 1354                            |                                       |                                    |
|    | Fe <sub>60</sub> Mo <sub>30</sub> B <sub>10</sub> | 1402                            | 486                                   |                                    |
|    | Fe <sub>55</sub> Mo <sub>40</sub> B <sub>5</sub>  | 1682                            |                                       |                                    |
| 10 | Fe <sub>55</sub> Mo <sub>35</sub> B <sub>10</sub> | 1532                            |                                       |                                    |
|    | Fe <sub>50</sub> Mo <sub>38</sub> B <sub>12</sub> | 1589                            |                                       |                                    |
|    | Fe <sub>77</sub> W <sub>15</sub> B <sub>8</sub>   | 1390                            | 420                                   | 658;867                            |
|    | Fe <sub>77</sub> W <sub>13</sub> B <sub>10</sub>  | 1330                            |                                       |                                    |
|    | Fe <sub>75</sub> W <sub>20</sub> B <sub>5</sub>   | 1465                            |                                       | 625;869                            |
| 15 | Fe <sub>75</sub> W <sub>13</sub> B <sub>12</sub>  | 1315                            |                                       |                                    |
|    | Fe <sub>67</sub> W <sub>25</sub> B <sub>8</sub>   | 1505                            |                                       |                                    |

TABLE III

Mechanical and Thermal Properties of  
Co-Mo-B and Co-W-B Glassy Alloys of the Invention

|    | Composition<br>(atom percent)                     | Hardness,<br>Kg/mm <sup>2</sup> | Ultimate Tensile<br>Strength, Kpsi | Crystallization<br>Temperature, °C |
|----|---------------------------------------------------|---------------------------------|------------------------------------|------------------------------------|
| 20 | Co <sub>70</sub> Mo <sub>20</sub> B <sub>10</sub> | 1266                            |                                    |                                    |
|    | Co <sub>66</sub> Mo <sub>26</sub> B <sub>8</sub>  | 1330                            | 395                                | 603;639                            |
|    | Co <sub>60</sub> Mo <sub>35</sub> B <sub>5</sub>  | 1131                            |                                    |                                    |
|    | Co <sub>58</sub> Mo <sub>39</sub> B <sub>12</sub> | 1402                            | 455                                | 670                                |
| 25 | Co <sub>55</sub> Mo <sub>35</sub> B <sub>10</sub> | 1450                            | 483                                | 684                                |
|    | Co <sub>50</sub> Mo <sub>40</sub> B <sub>10</sub> | 1510                            | 467                                | 785                                |
|    | Co <sub>40</sub> Mo <sub>50</sub> B <sub>10</sub> | 1560                            |                                    |                                    |
|    | Co <sub>77</sub> W <sub>15</sub> B <sub>8</sub>   |                                 |                                    | 570                                |
|    | Co <sub>70</sub> W <sub>20</sub> B <sub>10</sub>  | 1426                            |                                    |                                    |
| 30 | Co <sub>68</sub> W <sub>25</sub> B <sub>7</sub>   | 1410                            | 460                                | 641;665                            |
|    | Co <sub>63</sub> W <sub>25</sub> B <sub>12</sub>  | 1451                            |                                    | 683                                |
|    | Co <sub>60</sub> W <sub>30</sub> B <sub>10</sub>  | 1595                            | 515                                | 720;780;865                        |
|    | Co <sub>55</sub> W <sub>40</sub> B <sub>5</sub>   | 1309                            |                                    |                                    |

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TABLE IV

Mechanical and Thermal Properties of  
(Fe,Co,Ni)-(Mo,W)-B Glassy Alloys of the Invention

|    | Composition<br>(atom percent)                                                                    | Hardness,<br>Kg/mm <sup>2</sup> | Ultimate<br>Tensile<br>Strength, Kpsi | Crystal-<br>lization<br>Tempera-<br>ture, °C |
|----|--------------------------------------------------------------------------------------------------|---------------------------------|---------------------------------------|----------------------------------------------|
| 5  | Fe <sub>55</sub> Co <sub>20</sub> Ni <sub>15</sub> Mo <sub>12</sub> B <sub>8</sub>               | 1064                            | 396                                   | 445                                          |
|    | Fe <sub>55</sub> Co <sub>10</sub> Ni <sub>15</sub> Mo <sub>12</sub> B <sub>8</sub>               | 1159                            | 410                                   | 465                                          |
|    | Fe <sub>55</sub> Co <sub>10</sub> Ni <sub>15</sub> Mo <sub>6</sub> W <sub>6</sub> B <sub>8</sub> | 1186                            |                                       |                                              |
|    | Fe <sub>65</sub> Co <sub>10</sub> Ni <sub>10</sub> Mo <sub>4</sub> W <sub>3</sub> B <sub>8</sub> | 1048                            | 387                                   | 480                                          |
| 10 | Fe <sub>75</sub> Co <sub>5</sub> Ni <sub>5</sub> Mo <sub>4</sub> W <sub>3</sub> B <sub>8</sub>   | 1064                            |                                       |                                              |
|    | Fe <sub>67</sub> Co <sub>10</sub> Ni <sub>10</sub> Mo <sub>4</sub> W <sub>3</sub> B <sub>6</sub> | 1032                            |                                       | 450                                          |
|    | Fe <sub>57</sub> Co <sub>10</sub> Ni <sub>15</sub> Mo <sub>12</sub> B <sub>6</sub>               | 1114                            | 350                                   |                                              |
|    | Fe <sub>70</sub> Co <sub>10</sub> Ni <sub>8</sub> Mo <sub>5</sub> B <sub>7</sub>                 | 1000                            |                                       |                                              |
|    | Fe <sub>65</sub> Co <sub>10</sub> Ni <sub>10</sub> Mo <sub>10</sub> B <sub>5</sub>               | 1064                            |                                       | 463                                          |
| 15 | Fe <sub>65</sub> Co <sub>5</sub> Ni <sub>5</sub> W <sub>15</sub> B <sub>10</sub>                 | 1225                            |                                       | 553                                          |
|    | Fe <sub>57</sub> Co <sub>20</sub> Ni <sub>10</sub> W <sub>5</sub> B <sub>8</sub>                 | 1001                            |                                       | 472                                          |
|    | Ni <sub>45</sub> Co <sub>20</sub> Fe <sub>15</sub> W <sub>6</sub> Mo <sub>6</sub> B <sub>8</sub> | 1159                            |                                       | 478                                          |
|    | Ni <sub>55</sub> Co <sub>10</sub> Fe <sub>15</sub> Mo <sub>12</sub> B <sub>8</sub>               | 1114                            | 368                                   | 458                                          |
|    | Ni <sub>65</sub> Co <sub>10</sub> Fe <sub>10</sub> Mo <sub>7</sub> B <sub>8</sub>                | 1064                            |                                       |                                              |
| 20 | Ni <sub>57</sub> Fe <sub>10</sub> Co <sub>15</sub> Mo <sub>12</sub> B <sub>6</sub>               | 1120                            |                                       |                                              |
|    | Co <sub>45</sub> Ni <sub>20</sub> Fe <sub>15</sub> W <sub>12</sub> B <sub>8</sub>                | 1186                            | 403                                   |                                              |
|    | Co <sub>55</sub> Fe <sub>15</sub> Ni <sub>10</sub> W <sub>6</sub> Mo <sub>6</sub> B <sub>8</sub> | 1146                            |                                       | 505                                          |
|    | Co <sub>65</sub> Fe <sub>10</sub> Ni <sub>10</sub> Mo <sub>7</sub> B <sub>8</sub>                | 1080                            |                                       | 496                                          |
|    | Co <sub>57</sub> Ni <sub>10</sub> Fe <sub>15</sub> Mo <sub>12</sub> B <sub>6</sub>               | 1201                            |                                       |                                              |
| 25 | Co <sub>55</sub> Ni <sub>10</sub> Fe <sub>10</sub> Mo <sub>15</sub> B <sub>10</sub>              | 1225                            | 425                                   |                                              |

Table V sets forth compositions outside the scope of the invention and the results of structural analysis by X-ray diffraction in chill cast ribbons of these compositions prepared as above, and the brittleness of the ribbons.

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TABLE V

Results of Chill Casting of Alloy Compositions  
Outside the Scope of the Present Invention

|    | Composition<br>(Atom<br>percent)                                                                 | Structure<br>by X-ray<br>analyses<br>of Chill<br>Cast Ribbons | Elements<br>Outside<br>Scope of<br>Invention | Charac-<br>teristics<br>of the<br>Ribbons |
|----|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------|----------------------------------------------|-------------------------------------------|
| 5  | Fe <sub>50</sub> Ni <sub>20</sub> Co <sub>22</sub> B <sub>8</sub>                                | crystalline                                                   | Mo, W                                        | brittle                                   |
|    | Fe <sub>40</sub> Ni <sub>30</sub> Co <sub>22</sub> B <sub>8</sub>                                | crystalline                                                   | Mo, W                                        | brittle                                   |
|    | Ni <sub>50</sub> Fe <sub>20</sub> Co <sub>22</sub> B <sub>8</sub>                                | crystalline                                                   | Mo, W                                        | brittle                                   |
| 10 | Co <sub>50</sub> Ni <sub>20</sub> Fe <sub>22</sub> B <sub>8</sub>                                | crystalline                                                   | Mo, W                                        | brittle                                   |
|    | Fe <sub>70</sub> Ni <sub>10</sub> Co <sub>2</sub> Mo <sub>10</sub> B <sub>8</sub>                | 60% crystalline +<br>40% glassy                               | Co                                           | brittle                                   |
|    | Fe <sub>55</sub> Co <sub>20</sub> W <sub>15</sub> B <sub>10</sub>                                | 60% crystalline +<br>40% glassy                               | Ni                                           | extremely<br>brittle                      |
|    | Ni <sub>50</sub> Co <sub>30</sub> Mo <sub>10</sub> B <sub>10</sub>                               | crystalline                                                   | Fe                                           | brittle                                   |
| 15 | Fe <sub>50</sub> Co <sub>20</sub> Ni <sub>20</sub> Mo <sub>2</sub> B <sub>8</sub>                | 30% crystalline +<br>70% glassy                               | Mo or W                                      | brittle                                   |
|    | Fe <sub>70</sub> Ni <sub>10</sub> Co <sub>8</sub> W <sub>2</sub> B <sub>10</sub>                 | 60% crystalline +<br>40% glassy                               | Mo or W                                      | brittle                                   |
|    | Fe <sub>50</sub> Ni <sub>27</sub> Co <sub>15</sub> Mo <sub>5</sub> B <sub>3</sub>                | 50% crystalline +<br>50% glassy                               | B                                            | brittle                                   |
| 20 | Ni <sub>50</sub> Fe <sub>28</sub> Co <sub>10</sub> Mo <sub>5</sub> W <sub>5</sub> B <sub>2</sub> | crystalline                                                   | B                                            | brittle                                   |

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What is claimed is:

1. A substantially totally glassy alloy consisting essentially of (I) about 5 to 12 atom percent boron and (II) a member selected from the group consisting of about  
 5 20 to 60 atom percent molybdenum and about 13 to 40 atom percent tungsten with the balance being essentially a metal of the group consisting of cobalt, iron and nickel or (III) a member selected from the group consisting of about 5 to  
 10 15 atom percent molybdenum, tungsten or a mixture thereof and the balance being essentially iron, cobalt and nickel with each being present in an amount of at least 5 atom percent.
2. The glassy alloy of claim 1 wherein the boron is present in an amount of 8-10 atom percent, the molybdenum and tungsten in member II is present in amounts of  
 15 30 to 50 atom percent respectively and the molybdenum and tungsten in Member III is present in amounts of 8 to 12 atom percent.
3. A substantially totally glassy alloy consisting essentially of about 5 to 12 atom percent boron, a  
 20 member selected from the group consisting of about 30 to 60 atom percent molybdenum and about 20 to 35 atom percent tungsten and the balance essentially nickel plus incidental impurities.
- 25 4. The glassy alloy of claim 3 having a composition selected from the group consisting of  $\text{Ni}_{57}\text{Mo}_{35}\text{B}_8$ ,  $\text{Ni}_{55}\text{Mo}_{35}\text{B}_{10}$ ,  $\text{Ni}_{50}\text{Mo}_{40}\text{B}_{10}$ ,  $\text{Ni}_{45}\text{Mo}_{45}\text{B}_{10}$ ,  $\text{Ni}_{42}\text{Mo}_{50}\text{B}_8$ ,  $\text{Ni}_{70}\text{W}_{22}\text{B}_8$ ,  $\text{Ni}_{70}\text{W}_{20}\text{B}_{10}$  and  $\text{Ni}_{60}\text{W}_{30}\text{B}_{10}$ .
- 30 5. A substantially totally glassy alloy consisting essentially of about 5 to 12 atom percent boron, a member selected from the group consisting of about 25 to 40 atom percent molybdenum and about 13 to 25 atom percent tungsten and the balance essentially iron plus incidental impurities.
- 35 6. The glassy alloy of claim 5 having a composition selected from the group consisting of  $\text{Fe}_{60}\text{Mo}_{30}\text{B}_{10}$ ,  $\text{Fe}_{55}\text{Mo}_{35}\text{B}_{10}$ ,  $\text{Fe}_{77}\text{W}_{15}\text{B}_8$  and  $\text{Fe}_{77}\text{W}_{13}\text{B}_{10}$ .

7. A substantially totally glassy alloy consisting essentially of about 5 to 12 atom percent boron, a member selected from the group consisting of about 20 to 50 atom percent molybdenum and about 15 to 40 atom percent tungsten and the balance essentially cobalt plus incidental impurities.

8. The glassy alloy of claim 7 having a composition selected from the group consisting of  $\text{Co}_{66}\text{Mo}_{26}\text{B}_8$ ,  $\text{Co}_{55}\text{Mo}_{35}\text{B}_{10}$ ,  $\text{Co}_{50}\text{Mo}_{40}\text{B}_{10}$ ,  $\text{Co}_{70}\text{W}_{20}\text{B}_{10}$  and  $\text{Co}_{60}\text{W}_{30}\text{B}_{10}$ .

9. A substantially totally glassy alloy consisting essentially of about 5 to 10 atom percent boron, about 5 to 15 atom percent of at least one of molybdenum and tungsten and the balance essentially iron, cobalt and nickel, each present in an amount of at least about 5 atom percent, plus incidental impurities.

10. The glassy alloy of claim 9 consisting essentially of about 8 to 10 atom percent boron, about 8 to 12 atom percent of at least one of molybdenum and tungsten, about 50 to 65 atom percent of one of the iron group metals and about 13 to 35 atom percent of the remaining two of the iron group metals.

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## EUROPEAN SEARCH REPORT

Application number

EP 78 30 0851

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                   |                                                                                    |                                                | CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)                                                                                                                                                                                                                             |
|-------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Category                                                                                              | Citation of document with indication, where appropriate, of relevant passages      | Relevant to claim                              |                                                                                                                                                                                                                                                                            |
| P                                                                                                     | FR - A - 2 376 217 (ALLIED CHEMI-CAL)<br>* Claim 1 *<br>& DE - A - 2 756 921<br>-- |                                                | C 22 C 19/00<br>27/04<br>38/00                                                                                                                                                                                                                                             |
| P                                                                                                     | FR - A - 2 376 218 (ALLIED CHEMICAL)<br>* Claim 1 *<br>& DE - A - 2 756 920<br>--  |                                                | TECHNICAL FIELDS SEARCHED (Int. Cl. 7)                                                                                                                                                                                                                                     |
| A                                                                                                     | FR - A - 2 317 370 (ALLIED CHEMICAL)<br>* Claim 1 *                                |                                                | C 22 C                                                                                                                                                                                                                                                                     |
| A                                                                                                     | FR - A - 2 281 434 (ALLIED CHEMICAL)<br>* Claim 1 *                                |                                                |                                                                                                                                                                                                                                                                            |
| AD                                                                                                    | US - A - 3 986 867 (MASUMOTO et al.)<br>* Claim 1 *<br>-----                       |                                                | CATEGORY OF CITED DOCUMENTS                                                                                                                                                                                                                                                |
|                                                                                                       |                                                                                    |                                                | X: particularly relevant<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention<br>E: conflicting application<br>D: document cited in the application<br>L: citation for other reasons |
|                                                                                                       |                                                                                    |                                                | &: member of the same patent family, corresponding document                                                                                                                                                                                                                |
| <p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p> |                                                                                    |                                                |                                                                                                                                                                                                                                                                            |
| Place of search<br>The Hague                                                                          |                                                                                    | Date of completion of the search<br>05-04-1979 | Examiner<br>LIPPENS                                                                                                                                                                                                                                                        |