

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 561 269 A2

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **93103890.5**(51) Int. Cl.⁵: **C22C 45/00**(22) Date of filing: **10.03.93**(30) Priority: **18.03.92 JP 62558/92**(43) Date of publication of application:
22.09.93 Bulletin 93/38(84) Designated Contracting States:
DE FR GB

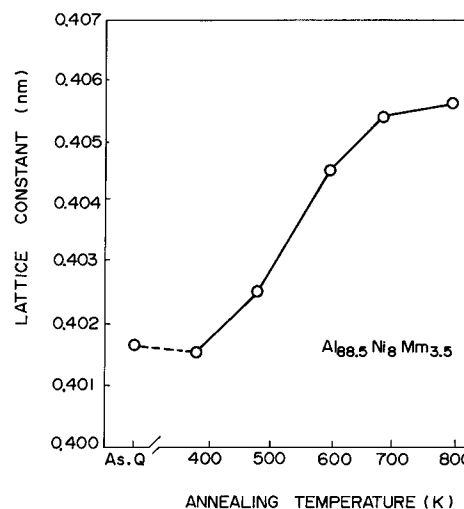
(71) Applicant: **Masumoto, Tsuyoshi**
3-8-22, Kamisugi Aoba-ku
Sendai-shi Miyagi(JP)
Applicant: **Inoue, Akihisa**
11-806, Kawauchijutaku, Mubanchi,
Kawauchi, Aoba-ku
Sendai-shi, Miyagi-ken(JP)
Applicant: **YOSHIDA KOGYO K.K.**
No. 1 Kanda Izumi-cho Chiyoda-ku
Tokyo(JP)

(72) Inventor: **Masumoto, Tsuyoshi**
3-8-22, Kamisugi, Aoba-ku
Sendai-shi, Miyagi(JP)
Inventor: **Inoue, Akihisa, 11-806,**
Kawauchijutaku
Mubahchi, Kawauchi, Aoba-ku
Sendai-shi, Miyagi(JP)
Inventor: **Nagahora, Junichi**
14-6, Sumiyoshidai, Midori-ku
Yokohama-shi, Kanagawa(JP)
Inventor: **Shibata, Toshisuke**
3105, Nogawa, Miyamae-ku
Kawasaki-shi, Kanagawa(JP)

(74) Representative: **Patentanwälte Leinweber &**
Zimmermann
Rosental 7/II Aufg.
D-80331 München (DE)

(54) **Amorphous alloy material and process for production thereof.**

(57) An amorphous alloy material consisting of a principal element and other additive elements and containing fine grains of perfect crystals having an average particle size of 2 to 100 nm that are formed by self-control and dispersed in an amorphous alloy matrix; and a method for self-controlling the average particle size of the crystal to be in the range of 2 to 100 nm through the stable phase of the amorphous phase or the stability corresponding to precipitation treatment temperature in the amorphous matrix by heating the amorphous material. Examples of the principal element include Al, Mg and Ni and those of the additive elements include rare earth elements. The alloy material has superior mechanical strength and toughness and exhibits precipitation-induced plastic flow.

FIG. 4

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an amorphous alloy material excellent in mechanical strength and toughness and a process for production thereof.

2. Description of the Prior Art

The present inventors invented an Al-based amorphous alloy and an Mg-based amorphous alloy that have superior strength and corrosion resistance and disclosed in Japanese Patent Laid-Open Nos. 47831/1989 and 10041/1991, respectively. These alloys disclosed in these applications were aimed at amorphous single phase. Thereafter, the present inventors found that the amorphous alloys can be improved in their strength and toughness by dispersing in an amorphous phase a crystal phase consisting of a fine supersaturated solid solution composed of a principal element and applied for a patent on the finding as Japanese Patent Application No. 59139/1990 (refer to Japanese Patent Laid-Open No. 260037/1991). They have also made a similar invention on an Ni-based amorphous alloy and applied for a patent as Japanese Patent Application No. 261263/1991. In addition, they found that an amorphous alloy exerts a high ductility when heated for the precipitation of a supersaturated solid solution composed of the principal element, and applied for a patent on the process for producing such an alloy as Japanese Patent Application No. 227184/1991.

It is known that in general an amorphous alloy is crystallized and embrittled when heated to a temperature (crystallization temperature) specific to the alloy. The present inventors found that by specifying an alloy composition, the strength and toughness of an amorphous alloy can be improved by dispersing fine crystalline grains in which additive elements form a supersaturated solid solution with a principal element which constitutes the alloy. As a result of further investigation on the crystallization process, it has been found by them that the crystallization mechanism constitutes the fundamental procedure capable of stably and efficiently dispersing fine crystalline grains in an amorphous matrix. The present invention has been accomplished on the basis of this finding.

SUMMARY OF THE INVENTION

The first aspect of the present invention relates to an amorphous alloy material consisting of a principal element and additive elements and containing fine grains of perfect crystals having an average particle size of 2 to 100 nm that are

formed by self-control and dispersed in an amorphous alloy matrix.

Basically, the following alloys pertain to the first aspect thereof.

5 One is an amorphous alloy material having high toughness and high strength and consisting 85 to 99.8 atomic % of Al as the principal element; and, as the additive elements, 0.5 to 5 atomic % of at least one element selected from among rare earth elements including Y and misch metal (Mm) 10 and 12 atomic % or less of at least one other element selected from among Ni, Fe, Co and Cu, the contents of the additive elements satisfying the relationship:
15 content of the rare earth elements $\leq$ content of other elements.

In this amorphous alloy material, Al may be replaced in part by at least one element selected from among Ti, Mn, Mo, Cr, Zr, V, Nb and Ta in the range of 0.2 to 3 atomic %. 20

Another one is an amorphous alloy material having high toughness and high strength and consisting of 80 to 90 atomic % of Mg as the principal element; and, as the additive elements, 1 to 5 atomic % of at least one element selected from among rare earth elements including Y and misch metal (Mm) and 8 to 15 atomic % of at least one other element selected from among Cu, Ni, Sn and Zn. In the Mg amorphous alloy material, Mg may be replaced in part by at least one element selected from among Al, Si and Ca in the range of 1 to 5 atomic %. 25

The remaining one is an amorphous alloy material having high toughness and high strength and consisting of 79 to 89 atomic % of Ni as the principal element; and, as the additive elements, 5 to 14 atomic % of Si and 6 to 15 atomic % of B; or the amorphous alloy material which comprises in addition to the aforesaid elements, 0.5 to 5 atomic % of at least one element selected from among Fe, Mn, Ti, Zr, Al, V, Mo and Nb. 30

These alloys are characterized by precipitating a supersaturated solid solution at a temperature lower than the temperatures at which the intermetallic compounds precipitate. Now, the crystallization mechanism will be considered in some detail. When a supersaturated solid solution precipitates at the crystallization temperature inherent in each alloy, the solute (additive elements) which is uniformly dissolved in a homogeneous solid solution in an amorphous phase is discharged outside the crystal grains for an attempt to attain the equilibrium concentration at the temperature (but in fact, no equilibrium state can be attained since it depends on the diffusion coefficient of the solute in the crystal consisting of the principal element). The discharge of the solute is accompanied by the tendency in which the lattice con- 35

stant of the crystal grains is changed towards the value of pure crystal grains. On the other hand, the discharge of the solute from the crystal grains increases the solute concentration in the amorphous phase which surrounds the crystal grains, thus raising the crystallization temperature of the amorphous phase. (The amorphous phase is thermally stabilized). As a result, the crystalline grains are inhibited in their growth and made into a substantially spherical form having a uniform partial size, which is regulated to 2 to 100 nm depending on the alloy species and treatment temperature.

The invention based on the above-mentioned consideration constitutes the process for producing the amorphous alloy material as the second aspect of the present invention.

Specifically, the second aspect of the present invention relates to a process for producing the above-defined amorphous alloy material which comprises;

producing an amorphous-phase alloy composed of the aforesaid principal element and additive elements; and

precipitating and dispersing fine crystal grains consisting of a supersaturated solid solution composed of the principal element and the additive elements in the amorphous matrix by heating to a temperature at which neither intermetallic compound nor other compound is formed, wherein the growth of crystalline grains is inhibited through the stability of the residual amorphous phase so that the average particle size of the grains is self-controlled to the range of 2 to 100 nm.

Further, the invention provides another process for producing the above-defined amorphous alloy material which comprises:

producing an amorphous-phase alloy composed of the above principal element and additive elements; and

precipitating and dispersing fine crystal grains consisting of a supersaturated solid solution composed of the principal element and the additive elements in the amorphous matrix by heating to a temperature at which neither intermetallic compound nor other compound is formed, wherein the average particle size of crystalline grains is self-controlled to the range of 2 to 100 nm through the stability corresponding to various precipitation treatment temperatures of the residual amorphous phase.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the result of differential scanning calorimetry for the thin ribbon as obtained in Example 1.

FIG. 2 is a graph showing the result of X-ray diffractometry for the thin ribbon as obtained in

Example 1.

FIG. 3 is a graph showing the change in the crystal size of an FCC phase due to isothermal heat treatment of the thin ribbon as obtained in Example 1.

FIG. 4 is a graph showing the change in the lattice constant of the FCC phase due to heating of the thin ribbon as obtained in Example 1.

FIG. 5 is a graph showing the result of measurement for internal friction of the thin ribbon as obtained in Example 2.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

An amorphous alloy is decomposed into crystals by heating to a temperature (crystallization temperature) specific to and depending on the alloy. All amorphous alloys necessarily have their own crystallization temperatures. When their crystallization, a crystal phase (supersaturated solid solution) in which additive elements form a supersaturated solid solution with a principal element, or a phase of intermetallic compounds or other compounds formed from the principal alloying element and the additive elements or/and formed from additive elements precipitates or both phases precipitate at the same time. The precipitation applicable to the present invention is that a supersaturated solid solution precipitates at a lower temperature in the case of continuously raising temperature and subsequently intermetallic compounds or other compounds precipitate at a higher temperature (two-stage crystallization). Among a variety of known alloy series including Al-based, Mg-based and Ni-based amorphous alloys, the alloys according to the present invention are those in which a supersaturated solid solution composed of a principal element containing supersaturated additive elements precipitates at a temperature lower than the precipitation temperature of the intermetallic compounds or other compounds. An FCC phase (Al phase) precipitates in an Al-based amorphous alloy, an HCP phase (Mg phase) in an Mg-based amorphous alloy and an FCC phase (Ni phase) in an Ni-based amorphous alloy. For the sake of the precipitation, the additive elements must be limited to a relatively low concentration, since an increased content of the additive elements causes the intermetallic compounds or other compounds to precipitate preferentially or simultaneously, thereby markedly embrittling the alloy and limiting the use thereof as the industrial material.

The amorphous alloy produced in such a way exerts an ideal composite structure consisting of two phases containing independent fine crystal grains homogeneously dispersed in the amorphous matrix.

A method of dispersing fine crystal grains in the amorphous alloy is also made possible by properly controlling the cooling rate of the alloy melt in the production step of the amorphous alloy. However, the control for the cooling rate is not easy in the conventional production apparatus for amorphous alloys. Thus, the present invention is excellent in efficiency and stability.

It may be presumed that the fine crystalline grains dispersed in the amorphous phase that are produced in the present invention are much smaller than the smallest particle size (Orowan size of about 1 μm) that causes dislocation and multiplication, thus forming perfect crystals. It may also be expected that such fine crystal grains hardly deform and are highly matched to the matrix. Specifically, the composite material having an ideal structure functions as a great reinforcing mechanism, which is primarily responsible for the improved strength of the composite-phase materials of an amorphous phase and a crystal phase as compared with amorphous single-phase materials.

The alloy of the present invention in the crystallization process manifests several functions as the functional material in addition to the effect on the inhibition of the self-growth of grains.

One of the above-mentioned functions is a large deformation in the high temperature region in spite of its amorphism. Every alloy of the present invention exhibits an elongation of about 20% or 30% or more under tensile stress in the precipitation temperature region of the supersaturated solid solution (Thus, consolidating-molding, joining and other plastic forming are made possible by processing amorphous thin ribbons, powders or the like, taking advantage of the above-mentioned phenomenon). It is believed by the present inventors that the phenomenon is not merely due to the viscous flow of the amorphous phase but also due to a dynamic action in some way of the precipitation of the supersaturated solid solution composed of the principal element. In general, an amorphous alloy forms a shear deformation zone on the maximum stress plane against external stress without a slip plane and, thus, fractures all at once above a given stress hardly showing deformation. However, the primary contributor to the large elongation in the region of precipitating a fine crystalline phase, although not yet established, can be described as follows: The slight propagation of the shear deformation zone causes a rise in the temperature at the end thereof due to the heat of deformation, thus precipitating there fine crystal grains of a supersaturated solid solution. Because of being perfect crystals, the precipitated grains hinder the propagation of the deformation zone and fix the zone. As further external stress is continued, new deformation zone develops, which is fixed by the

slight propagation. Numerous deformation zones develop in such a way and cause "precipitation-induced plastic flow" in which the integrated slight deformations appear as a large strain. The precipitation-induced plastic flow is an important phenomenon utilizable as the consolidating and forming method of the amorphous alloy to be produced as powder or thin ribbon.

Another function is the property of absorbing vibrational stress applied from outside at the time of precipitating a supersaturated solid solution composed of the principal element and containing the supersaturated additive elements from the amorphous phase. When an amorphous alloy is heated continuously from room temperature, a supersaturated solid solution composed of the principal element is precipitated at a temperature specific to the alloy (crystallization temperature), at which the atoms are provided with the mobility of such an extent that an atomic rearrangement is generated. When an external alternating stress such as vibration is applied to one side of the material in the aforementioned state, the vibration is absorbed there without being propagated to the other side. Specifically, the material can be said to be material exerting a vibration dampening function and is effective as vibrationproof, soundproof or shock-absorbing material.

The aforestated functions are those in which the material itself responds to the external stimulus intelligently and enable the material to be utilized as the intelligent material capable of self-hardening by detecting external stress, temperature or the like.

Exhibiting the precipitation-induced plastic flow, these materials can be utilized not only for consolidating-forming and joining of amorphous materials but also for stress sensors, temperature sensors, vibrationproof and soundproof materials, stress-sensing self-hardening materials, temperature sensing self-hardening materials and the like.

Example 1

A master alloy having a composition of $\text{Al}_{88.5}\text{Ni}_8\text{Mm}_{3.5}$ (suffixes representing atomic % of each element) was melted in an arc melting furnace and made into a thin ribbon with 20 μm thickness and 1.5 mm width by the use of a conventionally available single-roller liquid quenching apparatus (melt-spinning apparatus) having a copper-made roll of 200 mm in diameter at 4000 rpm in an argon atmosphere at a vacuum of 10^{-3} Torr or lower.

The thin ribbon thus prepared was analyzed for structure by X-ray diffractometry and measured for its decomposition temperature of the quenched phase with a differential scanning calorimeter. As a

result of X-ray diffraction, the thin ribbon proved to be composed of an amorphous single phase having a diffraction pattern of broad halo alone peculiar to an amorphous phase. The thin ribbon was analyzed with a differential scanning calorimeter at a temperature rise rate of 20 K/min. The result is given in FIG. 1. As seen from the figure, there exist the first peak with a rising point of 400 K (127 °C) and the second peak with a rising point of 570 K (293 °C). As seen from the result of X-ray diffraction in FIG. 2, the ribbon heated to the end point, 500 K (223 °C), of the first peak is composed of a crystalline phase of Al (FCC) and an amorphous phase and further, the diffraction peak of the FCC phase is considerably broad. The second peak observed in the differential scanning calorimetry indicates crystallization accompanied by the precipitation of intermetallic compounds. The amorphous thin ribbon thus prepared was isothermally heat-treated to measure the alteration in the crystal size of the FCC phase from the calculation of the half width of the X-ray diffraction peak. The result is given in FIG. 3. As seen from the figure, the crystal size is maintained at 10 nm or smaller at a temperature of 523 K or lower even after a retention time of 20 hours or longer. On the other hand, the FCC phase is grown to about 140 nm in crystal size at 580 K. It may be presumed that some intermetallic compounds have been precipitated in the amorphous phase existing around the FCC phase to cause a decrease in the concentration of the solute in the amorphous phase and grow the FCC grains or that the sum total of the interfacial energy between the two phases has participated in such growth. The alteration in the lattice constant of the FCC phase due to heating is given in FIG. 4. As seen from the figure, the crystal lattice constant of the FCC phase approaches the lattice constant of pure Al. The above fact is thought to result from the discharge of the solute from the FCC phase.

As can be seen from the above-mentioned results, the crystal size of the FCC phase is determined in connection with the stability of the amorphous phase.

Example 2

An $\text{Al}_{88}\text{Y}_2\text{Ni}_{10}$ alloy was made into an amorphous thin ribbon in the same manner as in Example 1. The amorphous alloy precipitated an FCC phase as is the case with Example 1, and the peak on the differential scanning calorimetry curve lies at 400 K. Measurement was made of the internal friction ($\tan \delta = E''/E'$ wherein E' is storage modulus of elasticity and E'' is loss modulus of elasticity) of the aforesaid amorphous thin ribbon by the use of a dynamic visco-elasticity automatic measuring instrument [dynamic mechanical thermal

analyzer (DMTA)] under the conditions including a temperature rise rate of 10 K/min, a frequency of 60 cycles/min and a load strain of 0.03%. The result is given in Fig. 5. As seen from the figure, the internal friction, $\tan \delta$, exhibits a sharp rise at 350 K and a peak at 400 K.

It is understood from the above-mentioned result that the alloy of the present invention has the effect on the absorption of vibration and impact applied from outside.

Example 3

A master alloy having a composition of $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ (suffixes representing atomic % of each element) was melted in an arc melting furnace and made into a thin ribbon with 20 μm thickness and 1.5 mm width by the use of a conventionally available single-roller liquid quenching apparatus (melt spinning apparatus) having a copper-made roll of 200 mm in diameter at 4000 rpm in an argon atmosphere at a vacuum of 10^{-3} Torr or lower.

The thin ribbon thus prepared was analyzed for structure by X-ray diffractometry and measured for the decomposition temperature of the quenched phase with a differential scanning calorimeter. As a result of X-ray diffraction, the thin ribbon proved to be composed of an amorphous single phase having a diffraction pattern of broad halo alone peculiar to an amorphous phase. It was analyzed with a differential scanning calorimeter at a temperature rise rate of 20 K/min. As a result, there existed the first peak with a rising point of 710 K and the second peak with a rising point of 780 K. It was seen that the ribbon heated to the end point (770 K) of the first peak was composed of a crystalline phase of Ni (FCC) and an amorphous phase and, further, the diffraction peak of the FCC phase was considerably broad. The second peak observed in the differential scanning calorimetry indicated crystallization accompanied by the precipitation of intermetallic compounds. The amorphous thin ribbon thus prepared was isothermally heat-treated to measure the alteration in the crystal size of the FCC phase. As a result, the crystal size was found to be maintained at 50 nm or smaller at a temperature of 770 K or lower even after a retention time of 20 hours or longer. On the other hand, the FCC phase was grown to about 140 nm in crystal size at 770 K. It may be presumed that some intermetallic compounds have been precipitated in the amorphous phase existing around the FCC phase to cause a decrease in the concentration of the solute in the amorphous phase and grow the FCC grains or that the sum total of the interfacial energy between the two phases has participated in such growth. The alteration in the lattice constant of the

FCC phase due to heating was examined. As the result, it was seen that the crystal lattice constant of the FCC phase approached the lattice constant of pure Ni. The above fact is thought to result from the discharge of the solute from the FCC phase.

As can be seen from the above-mentioned results, the crystal size of the FCC phase is determined in connection with the stability of the amorphous phase as in Example 1.

Example 4

A master alloy having a composition of $\text{Mg}_{85}\text{Zn}_{12}\text{Ce}_3$ (suffixes representing atomic % of each element) was melted in a high frequency melting furnace and made into a thin ribbon with 20 μm thickness and 1.5 mm width by the use of a conventionally available single-roller liquid quenching apparatus (melt spinning apparatus) having a copper-made roll of 200 mm in diameter at 4000 rpm in an argon atmosphere at a vacuum of 10^{-3} Torr or lower.

The thin ribbon thus prepared was analyzed for structure by X-ray diffractometry and measured for the decomposition temperature of the quenched phase with a differential scanning calorimeter. As a result of X-ray diffraction, the thin ribbon was found to be composed of a mixed phase of an amorphous phase and an Mg phase having a diffraction pattern of broad halo peculiar to an amorphous phase and hcp-Mg spot. It was analyzed with a differential scanning calorimeter at a temperature rise rate of 20 K/min. As a result, it was found that there existed the first peak with a rising point of 373 K and the second peak with a rising point of 483 K. Because of the low temperature at the first peak at the time of quenching, self-precipitation took place at room temperature, but it was suppressed by the heat treatment (383K, 20 sec) and water quenching, while the volume percentage of hcp-Mg of 50% was maintained. At a temperature of 373 K or lower, the crystal size changed from 3 nm to 20 nm, but the volume percentage of hcp was 10% or less remaining almost unchanged. However, at 383 K, the hcp phase sharply grew. The maximum strength was attained at a volume percentage of hcp of 50%. The thin ribbon that had been once heat treated did not exhibit crystal size growth even though allowed to stand at room temperature. It is conceivable that the self-precipitation of Mg continuously proceeds at the time of quenching, but the chain growth of grains is suppressed and the amorphous phase is stabilized by a single heat treatment with water quenching.

As can be seen from the above-mentioned results, the crystal size of the hcp phase is determined in connection with the stability of the amorphous phase due to heat treatment.

The alloys in the Examples 3 and 4 exhibited the same tendency as in Example 2.

According to the present invention, there are obtained alloy materials which have superior mechanical strength and toughness properties and exhibit precipitation-induced plastic flow. The above-obtained materials can be utilized not only for consolidating-forming and joining of amorphous material but also for stress sensors, temperature sensors, vibrationproof soundproof materials, stress sensing self-hardening materials, temperature sensing self-hardening materials and so forth.

Claims

1. An amorphous alloy material consisting of a principal element and additive elements and containing fine grains of perfect crystals having an average particle size of 2 to 100 nm that are formed by self-control and dispersed in an amorphous alloy matrix.
2. An amorphous alloy material according to Claim 1, wherein the amorphous alloy material has high toughness and high strength and consists of 85 to 99.8 atomic % of Al as the principal element; and, as the additive elements, 0.1 to 5 atomic % of at least one element selected from among rare earth elements including Y and misch metal (Mm) and 12 atomic % or less of at least one other element selected from among Ni, Fe, Co and Cu, the contents of said additive elements satisfying the relationship:
content of rare earth elements $\leq$ content of other elements.
3. An amorphous alloy material according to Claim 2, wherein Al as the principal element is replaced in part by at least one element selected from among Ti, Mn, Mo, Cr, Zr, V, Nb and Ta in the range of 0.2 to 3 atomic %.
4. An amorphous alloy material according to Claim 1, wherein the amorphous alloy material has high toughness and high strength and consists of 80 to 90 atomic % of Mg as the principal element; and, as the additive elements, 0.1 to 5 atomic % of at least one element selected from among rare earth elements including Y and misch metal (Mm) and 8 to 15 atomic% of at least one other element selected from among Cu, Ni, Sn and Zn.
5. An amorphous alloy material according to Claim 4, wherein Mg as the principal element is replaced in part by at least one element selected from among Al, Si and Ca in the

range of 1 to 5 atomic %.

6. An amorphous alloy material according to Claim 1, wherein the amorphous alloy material has high toughness and high strength and consists of 79 to 89 atomic % of Ni as the principal element; and, as the additive elements, 5 to 14 atomic % of Si and 6 to 15 atomic % of B. 5
7. An amorphous alloy material according to Claim 1, wherein the amorphous alloy material has high toughness and high strength and consists of 74 to 87.5 atomic % of Ni as the principal element; and, as the additive elements, 5 to 14 atomic % of Si, 6 to 15 atomic % of B and 0.5 to 5 atomic % of at least one element selected from among Fe, Mn, Ti, Zr, Al, V, Mo and Nb. 10 15 20
8. A process for producing an amorphous alloy material which comprises the steps of :
 producing an amorphous-phase alloy composed of a principal element and additive element; and 25
 precipitating and dispersing fine crystal grains consisting of a supersaturated solid solution composed of the principal element and the additive elements in the amorphous matrix by heating to a temperature at which neither intermetallic compound nor other compound is formed, wherein the growth of crystalline grains is inhibited through the stability of the residual amorphous phase so as to self-control the average particle size of the crystal grains to the range of 2 to 100 nm. 30 35
9. A process for producing an amorphous alloy material, which comprises:
 producing an amorphous-phase alloy composed of a principal element and additive elements; and 40
 precipitating and dispersing fine crystal grains consisting of a supersaturated solid solution composed of the principal element and the additive elements in the amorphous matrix by heating to a temperature at which neither intermetallic compound nor other compound is formed, wherein the average particle size of crystal grains is self-controlled to the range of 2 to 100 nm through the stability corresponding to various precipitation treatment temperatures of the residual amorphous phase. 45 50
10. A process according to Claim 8, wherein the principal element is any of Al, Mg and Ni, and the additive elements are at least one element selected from among rare earth elements in-

cluding Y and misch metal (Mm) and at least one other element.

11. A process according to Claim 9, wherein the principal element is any of Al, Mg and Ni, and the additive elements are at least one element selected from among rare earth elements including Y and misch metal (Mm) and at least one other element.

FIG. 1

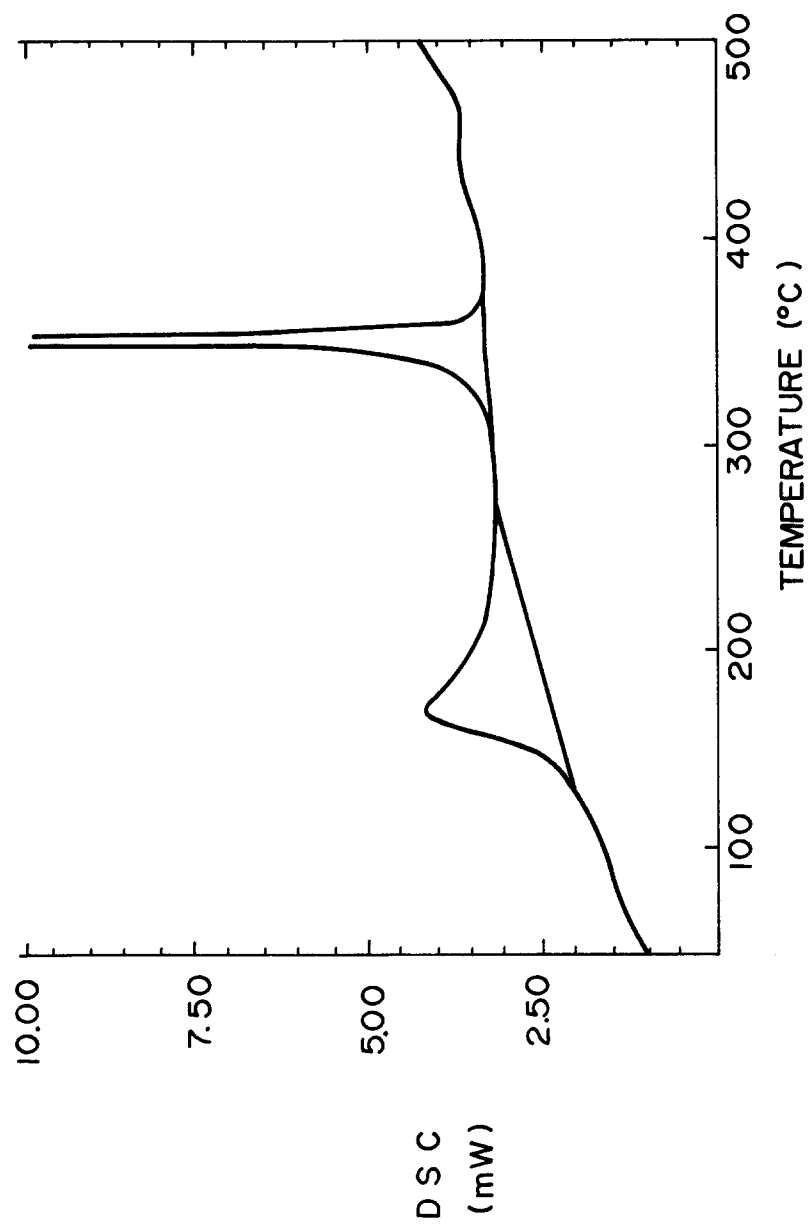


FIG. 2

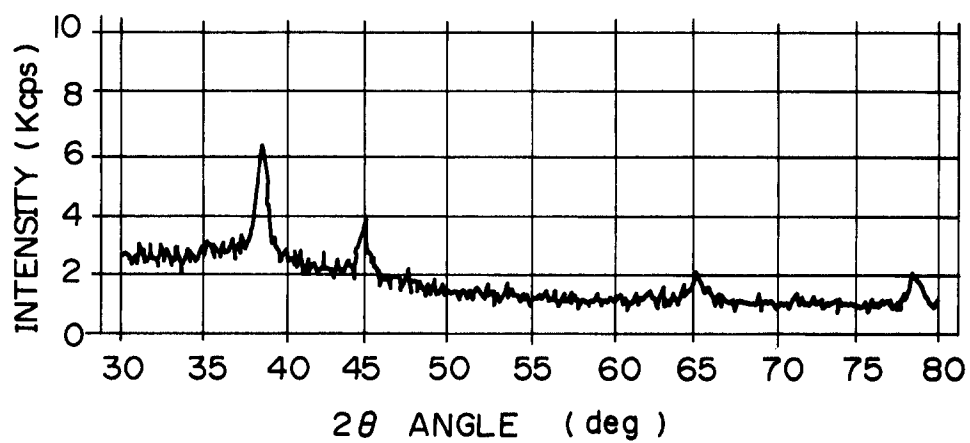


FIG. 3

Al_{88.5} Ni₈ Mn_{3.5}
CRYSTAL SIZE

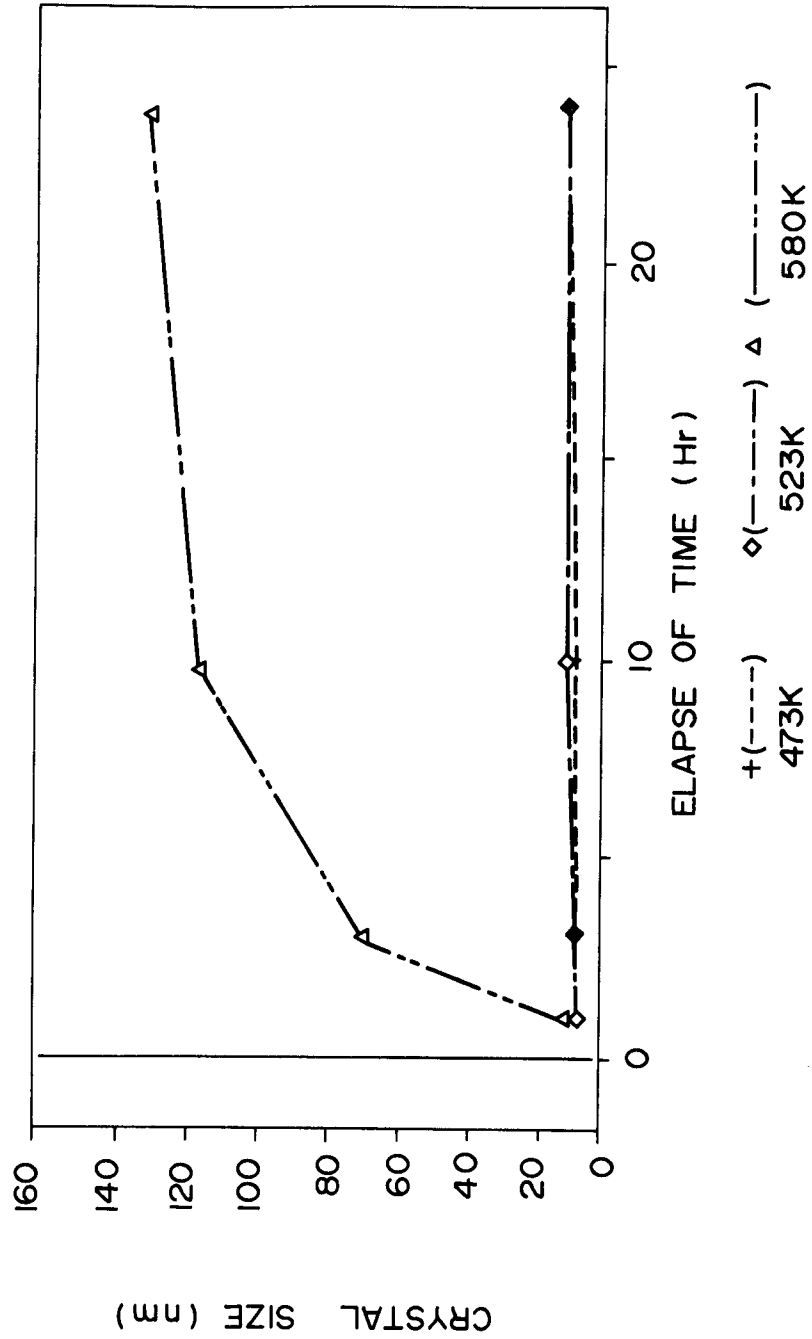


FIG. 4

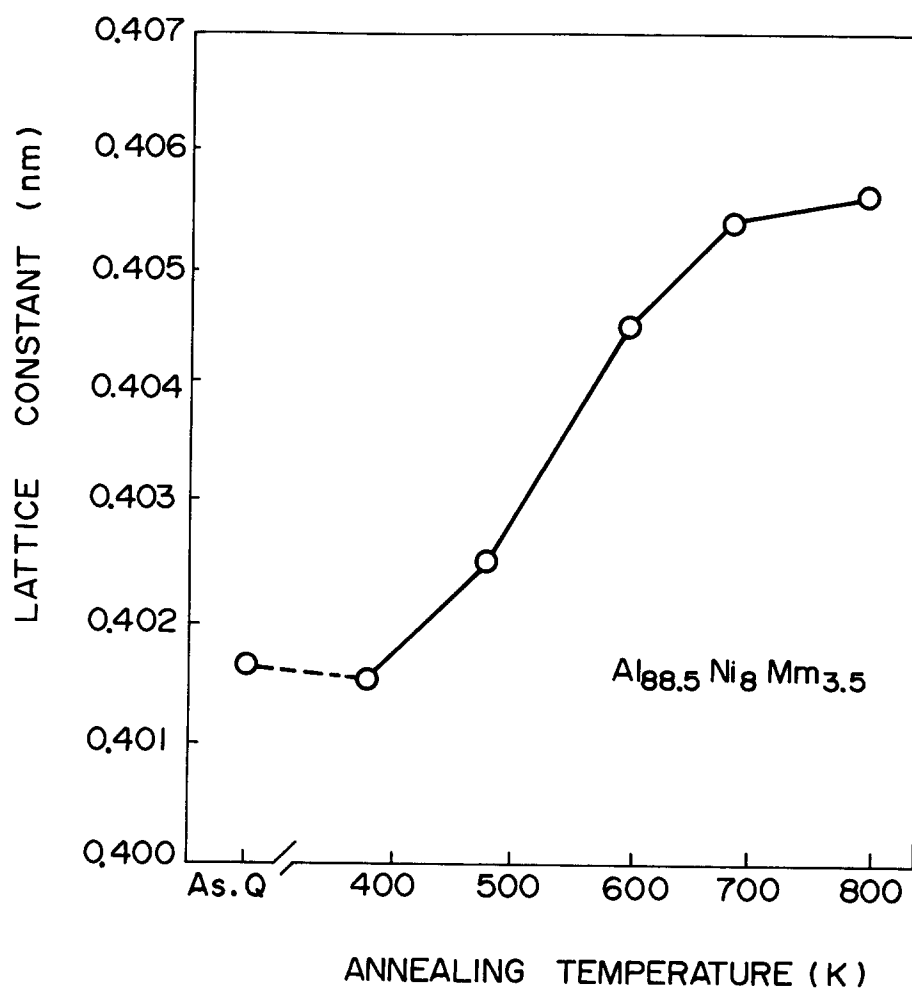


FIG. 5

