

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



11 Publication number: **0 540 054 A1**

12

## EUROPEAN PATENT APPLICATION

21 Application number: **92118759.7**

51 Int. Cl.<sup>5</sup>: **C22C 45/08, C22C 21/00**

22 Date of filing: **02.11.92**

30 Priority: **01.11.91 JP 287918/91**

43 Date of publication of application:  
**05.05.93 Bulletin 93/18**

84 Designated Contracting States:  
**DE FR GB**

71 Applicant: **YOSHIDA KOGYO K.K.**  
**No. 1 Kanda Izumi-cho Chiyoda-ku**  
**Tokyo(JP)**

72 Inventor: **Kita, Kazuhiko**  
**3022, Butsuden**  
**Uozu-shi, Toyama(JP)**  
Inventor: **Nagahama, Hidenobu**  
**4018, Mikkaichi**  
**Kurobe-shi, Toyama(JP)**  
Inventor: **Terabayashi, Takeshi**  
**545, Kosurido, Nyuzen-machi**  
**Shimoniikawa-gun, Toyama(JP)**  
Inventor: **Kawanishi, Makoto**  
**4024, Mikkaichi**  
**Kurobe-shi, Toyama(JP)**

74 Representative: **Patentanwälte Leinweber &**  
**Zimmermann**  
**Rosental 7/II Aufg.**  
**W- 8000 München 2 (DE)**

54 **High-strength and high-toughness aluminum-based alloy.**

57 An alloy having a composition represented by the general formula,  $Al_aNi_bX_cM_d$ , wherein X is at least one element selected from the group consisting of La, Ce, Mm, Ti and Zr; M is at least one element selected from the group consisting of Fe, Co, Y, Nb, Hf, Ta and W; and a, b, c and d are, in atomic percentages,  $85 \leq a \leq 94.4$ ,  $5 \leq b \leq 10$ ,  $0.5 \leq c \leq 3$  and  $0.1 \leq d \leq 2$ . The aluminum-based alloy has a high strength and a high toughness and can maintain the excellent characteristics provided by quench solidification even when subjected to thermal influence at the time of working. In addition, the alloy material has a high specific strength due to minimized addition of elements having a high specific gravity.

EP 0 540 054 A1

BACKGROUND OF THE INVENTION1. Field of the Invention

5 The present invention relates to an aluminum-based alloy having a high strength and an excellent toughness which is produced by a quench solidification process.

2. Description of the Prior Art

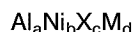
10 An aluminum-based alloy having a high strength and a high heat resistance has heretofore been produced by a liquid quenching process as disclosed in Japanese Patent Laid-Open No. 275732/1989. The aluminum-based alloy obtained by the liquid quenching process is an amorphous or microcrystalline alloy and is an excellent alloy having a high strength, a high heat resistance and a high corrosion resistance.

15 Although the above conventional aluminum-based alloy is an excellent alloy which exhibits a high strength, a high heat resistance and a high corrosion resistance and is also excellent in workability in spite of its being a high-strength material, it still admits of further improvement in toughness when used as the material required to have a high toughness. As a general rule, an alloy produced by a quench solidification process involves the problems that it is susceptible to thermal influence at the time of working and that it suddenly loses the excellent characteristics such as a high strength owing to the thermal influence. The above-mentioned aluminum-based alloy is not the exception to the aforesaid general rule and still leaves some room for further improvement in this respect.

SUMMARY OF THE INVENTION

25 In view of the above, an object of the present invention is to provide a high-strength and high-toughness aluminum-based alloy capable of maintaining its excellent characteristics provided by a quench solidification process as well as a high strength and a high toughness even if it is subjected to the thermal influence when working.

30 The present invention provides a high-strength and high-toughness aluminum-based alloy having a composition represented by the general formula



35 wherein X is at least one element selected from the group consisting of La, Ce, Mm (misch metal), Ti and Zr; M is at least one element selected from the group consisting of Fe, Co, Y, Nb, Hf, Ta and W; and a, b, c and d are, in atomic percentages,  $85 \leq a \leq 94.4$ ,  $5 \leq b \leq 10$ ,  $0.5 \leq c \leq 3$  and  $0.1 \leq d \leq 2$ .

BRIEF DESCRIPTION OF THE DRAWING

40 The single figure is a schematic illustration of one example of the apparatus well suited for the production of the alloy according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

45 In the alloy according to the present invention, the Ni element has a superior ability to form an amorphous phase or a supersaturated solid solution and serves for the refinement of the crystalline structure of the alloy including the intermetallic compounds and for the production of a high-strength alloy by a quench solidification process. The content of Ni in the above alloy is limited to 5 to 10 atomic % because a content thereof less than 5 atomic % leads to an insufficient strength of the alloy obtained by rapid quenching, whereas that exceeding 10 atomic % results in a sudden decrease in the toughness (ductility) of the alloy thus obtained.

55 The element X is at least one element selected from the group consisting of La, Ce, Mm, Ti and Zr and serves to enhance the thermal stability of the amorphous structure, supersaturated solid solution or microcrystalline structure as well as the strength of the alloy. The content of the element X in the above alloy is limited to 0.5 to 3 atomic % because a content thereof less than 0.5 atomic % leads to insufficiency of the above-mentioned effect, whereas that exceeding 3 atomic % results in a sudden decrease in the toughness (ductility) of the alloy thus obtained.

The element M is at least one element selected from the group consisting of Fe, Co, Y, Nb, Hf, Ta and W and serves to enhance the thermal stability of the rapidly solidified structure such as the amorphous structure, supersaturated solid solution or microcrystalline structure and to maintain the above-described characteristics even when the alloy is subjected to thermal influence. The addition of the element M in a slight amount to the alloy does not exert any adverse influence on the excellent toughness (ductility) of the Al-Ni-X-based alloy. The content of the element M in the above alloy is limited to 0.1 to 2 atomic % because a content thereof less than 0.1 atomic % leads to insufficiency of the above-mentioned effect, whereas that exceeding 2 atomic % results in the action of inhibiting the refinement of the aforesaid rapidly solidified structure and exerts evil influence on the toughness (ductility) of the alloy thus obtained.

The aluminum-based alloy according to the present invention is obtained by rapidly solidifying the melt of the alloy having the aforesaid composition through a liquid quenching process. The cooling rate of  $10^4$  to  $10^6$  K/sec in this case is particularly effective.

Now, the present invention will be described in more detail with reference to the Example.

#### Example

A molten alloy 3 having a given composition was prepared with a high-frequency melting furnace, introduced into a quartz tube 1 having a small hole 5 of 0.5 mm in diameter at the end thereof as shown in the figure, and melted by heating. Thereafter the quartz tube 1 was placed immediately above a copper roll 2. Then the molten alloy 3 in the quartz tube 1 was ejected onto the roll 2 from the small hole 5 of the quartz tube 1 at a high speed of the roll 2 of 3000 to 5000 rpm under a pressure of argon gas of  $0.7 \text{ kg/cm}^2$  and brought into contact with the surface of the roll 2 to obtain a rapidly solidified thin ribbon alloy 4.

There were obtained by the aforesaid production conditions, 25 kinds of thin ribbons of 1 mm in width and  $20 \mu\text{m}$  in thickness each having a composition by atomic % as given in Table 1. It was confirmed as the result of X-ray diffraction for each of the ribbons that both amorphous alloys and composite alloys composed of an amorphous phase and a microcrystalline phase were obtained as shown on the right end column in Table 1. The results of observation on the samples of the above composite alloys under a TEM (transmission electron microscope) gave the structure of a mixed phase in which the crystalline phase consisting of FCC (face-centered cubic) was homogeneously and finely dispersed in the amorphous phase. In Table 1, "amorph" and "microcryst" represent "amorphous" and "microcrystalline", respectively.

35

40

45

50

55

Table 1

	Composition (at%)				Phase structure
	Al	Ni	X	M	
Invention Ex. 1	balance	9	Zr=2.7	Fe=1.3	amorph.
Comp. Ex. 1	balance	9	Zr=2.7	-	amorph.
Invention Ex. 2	balance	8	Mm=1.2, Zr=0.5	W=0.3	amorph. + microcryst.
Comp. Ex. 2	balance	8	Mm=1.2, Zr=0.5	-	amorph. + microcryst.
Invention Ex. 3	balance	7	Mm=2.5	Nb=1.0	amorph.
Comp. Ex. 3	balance	7	Mm=2.5	-	amorph.
Invention Ex. 4	balance	7	La=1.0	W=1.6	amorph. + microcryst.
Comp. Ex. 4	balance	7	La=1.0	-	amorph. + microcryst.
Invention Ex. 5	balance	5	Mm=1.5	Ta=1.8	amorph. + microcryst.
Comp. Ex. 5	balance	5	Mm=1.5	-	amorph. + microcryst.

Table 1 (contd.)

	Composition (at%)				Phase structure
	Al	Ni	X	M	
5 Invention Ex. 6	balance	10	Mm=0.6	Fe=0.3 o	amorph. + microcryst.
10 Comp. Ex. 6	balance	10	Mm=0.6	-	amorph. + microcryst.
15 Invention Ex. 7	balance	10	Mm=1.5	Co=1.2	amorph. + microcryst.
Comp. Ex. 7	balance	10	Mm=1.5	-	amorph. + microcryst.
20 Invention Ex. 8	balance	10	Mm=2.5	Y=0.4	amorph.
Comp. Ex. 8	balance	10	Mm=2.5	-	amorph. + microcryst.
25 Invention Ex. 9	balance	9	La=1.3	Nb=0.2	amorph. + microcryst.
30 Comp. Ex. 9	balance	9	La=1.3	-	amorph. + microcryst.
Invention Ex. 10	balance	9	Ce=2.8	W=0.1	amorph.
35 Comp. Ex. 10	balance	9	Ce=2.8	-	amorph.
Invention Ex. 11	balance	9	Zr=2.5	Ta=1.0	amorph.
40 Comp. Ex. 11	balance	9	Zr=2.5	-	amorph. + microcryst.
45 Invention Ex. 12	balance	8	Ti=2.3	Hf=0.5	amorph.
Comp. Ex. 12	balance	8	Ti=2.3	-	amorph. + microcryst.

50

55

Table 1 (contd.)

	Composition (at%)				Phase structure
	Al	Ni	X	M	
5 10 Invention Ex. 13	balance	8	Ti=1.0, Zr=0.5	Fe=0.5	amorph. + microcryst.
15 Comp. Ex. 13	balance	8	Ti=1.0, Zr=0.5	-	amorph. + microcryst.
20 Invention Ex. 14	balance	8	Mm=2.5, Zr=0.4	Co=0.3	amorph.
25 Comp. Ex. 14	balance	8	Mm=2.5, Zr=0.4	-	amorph.
30 Invention Ex. 15	balance	8	Ti=2.3	Y=0.3	amorph. + microcryst.
35 Comp. Ex. 15	balance	8	Ti=2.3	-	amorph. + microcryst.
40 Invention Ex. 16	balance	7	Mm=2.2	Fe=0.2	amorph. + microcryst.
45 Comp. Ex. 16	balance	7	Mm=2.2	-	amorph. + microcryst.
50 Invention Ex. 17	balance	7	Zr=2.6	Fe=1.5	amorph. + microcryst.
55 Comp. Ex. 17	balance	7	Zr=2.6	-	amorph. + microcryst.
60 Invention Ex. 18	balance	7	Ti=2.3	Co=1.6	amorph. + microcryst.
65 Comp. Ex. 18	balance	7	Ti=2.3	-	amorph. + microcryst.

Table 1 (contd.)

	Composition (at%)				Phase structure
	Al	Ni	X	M	
5 10 Invention Ex. 19	balance	7	Mm=1.5	Y=1.5	amorph. + microcryst.
15 Comp. Ex. 19	balance	7	Mm=1.5	-	amorph. + microcryst.
20 Invention Ex. 20	balance	6	Mm=2.1	Ta=0.6	amorph. + microcryst.
25 Comp. Ex. 20	balance	6	Mm=2.1	-	amorph. + microcryst.
30 Invention Ex. 21	balance	6	Zr=1.0, Ti=1.2	Co=1.2	amorph. + microcryst.
35 Comp. Ex. 21	balance	6	Zr=1.0, Ti=1.2	-	amorph. + microcryst.
40 Invention Ex. 22	balance	6	Mm=2.6	W=1.2	amorph. + microcryst.
45 Comp. Ex. 22	balance	6	Mm=2.6	-	amorph. + microcryst.
50 Invention Ex. 23	balance	5	Zr=2.3	Nb=1.2	amorph. + microcryst.
55 Comp. Ex. 23	balance	5	Zr=2.3	-	amorph. + microcryst.
60 Invention Ex. 24	balance	5	Ti=1.6	Y=2	amorph. + microcryst.
65 Comp. Ex. 24	balance	5	Ti=1.6	-	amorph. + microcryst.
70 Invention Ex. 25	balance	5	Mm=1.9	Hf=1.6	amorph. + microcryst.
75 Comp. Ex. 25	balance	5	Mm=1.9	-	amorph. + microcryst.

50

Each of the samples of the above thin ribbons obtained under the aforementioned production conditions was tested for the tensile strength both at room temperature and in a 473K (200°C) atmosphere, and toughness (ductility). The results are given on the right-hand column in Table 2. The tensile strength in the 473 K atmosphere was tested at 473 K after the thin ribbon sample was maintained at 473 K for 100 hours.

55

As can be seen from Table 2, the aluminum-based alloy according to the present invention has a very high strength at both room temperature and an elevated temperature, that is, a tensile strength of 850 MPa or higher at room temperature and that of 500 MPa or higher in the 473 K atmosphere without a great

decrease in the strength at an elevated temperature; besides it has an elongation of 1% or greater at room temperature, rendering itself a material excellent in toughness.

Table 2

	Room temp. $\sigma_B$ (MPa)	473K $\sigma_B$ (MPa)
Invention Ex. 1	952	665
Comp. Ex. 1	847	597
Invention Ex. 2	837	567
Comp. Ex. 2	752	489
Invention Ex. 3	926	567
Comp. Ex. 3	860	502
Invention Ex. 4	923	665
Comp. Ex. 4	821	598
Invention Ex. 5	932	618
Comp. Ex. 5	861	563
Invention Ex. 6	947	643
Comp. Ex. 6	853	576
Invention Ex. 7	1067	636
Comp. Ex. 7	965	565
Invention Ex. 8	964	688
Comp. Ex. 8	856	523
Invention Ex. 9	916	656
Comp. Ex. 9	822	588
Invention Ex. 10	923	597
Comp. Ex. 10	823	523
Invention Ex. 11	1042	677
Comp. Ex. 11	933	600
Invention Ex. 12	883	579
Comp. Ex. 12	788	522
Invention Ex. 13	931	622

Table 2 (contd.)

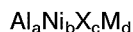
	Room temp. $\sigma_B$ (MPa)	473K $\sigma_B$ (MPa)	
5	Comp. Ex. 13	836	555
	Invention Ex. 14	965	618
10	Comp. Ex. 14	866	523
	Invention Ex. 15	914	556
	Comp. Ex. 15	826	489
	Invention Ex. 16	912	587
	Comp. Ex. 16	811	523
15	Invention Ex. 17	932	599
	Comp. Ex. 17	833	523
	Invention Ex. 18	888	687
	Comp. Ex. 18	789	521
	Invention Ex. 19	904	591
20	Comp. Ex. 19	802	512
	Invention Ex. 20	878	565
	Comp. Ex. 20	775	498
	Invention Ex. 21	923	686
	Comp. Ex. 21	823	522
25	Invention Ex. 22	887	623
	Comp. Ex. 22	800	566
	Invention Ex. 23	912	613
	Comp. Ex. 23	825	566
	Invention Ex. 24	851	602
30	Comp. Ex. 24	766	545
	Invention Ex. 25	876	565
	Comp. Ex. 25	789	508

35 As has been described hereinbefore, the aluminum-based alloy according to the present invention possesses a high strength and a high toughness and can maintain the excellent characteristics provided by quench solidification even when subjected to thermal influence at the time of working. In addition, it can provide an alloy material having a high specific strength by virtue of minimized amounts of elements having a high specific gravity to be added to the alloy.

40

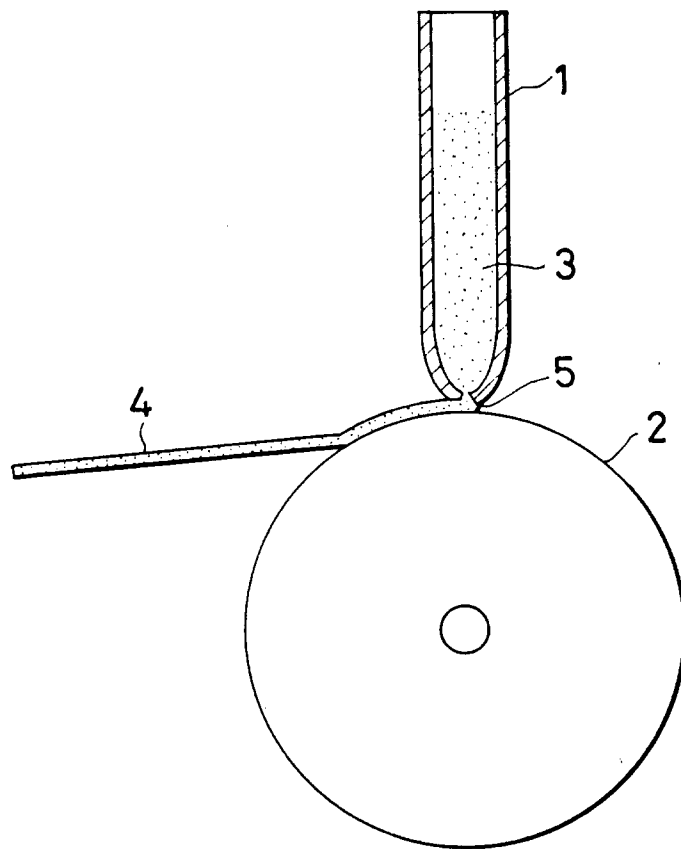
#### Claims

- 45 1. A high-strength and high-toughness aluminum-based alloy having a composition represented by the general formula



50 wherein X is at least one element selected from the group consisting of La, Ce, Mm (misch metal), Ti and Zr; M is at least one element selected from the group consisting of Fe, Co, Y, Nb, Hf, Ta and W; and a, b, c and d are, in atomic percentages,  $85 \leq a \leq 94.4$ ,  $5 \leq b \leq 10$ ,  $0.5 \leq c \leq 3$  and  $0.1 \leq d \leq 2$ .

55





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	CHEMICAL ABSTRACTS, vol. 118 Columbus, Ohio, US; abstract no. 10386, HORIMURA, HIROYUKI 'Manufacture of aluminum alloys having high strength and toughness' * abstract * & JP-A-4 154 933 (HONDA MOTOR CO., LTD.) 27 May 1992	1	C22C45/08 C22C21/00
P,X	EP-A-0 475 101 (YOSHIDA KOGYO K.K.) * claims 1,2; tables 1,2 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C22C
A	FR-A-2 651 246 (T. MASUMOTO ET AL) * claim 1; tables 1,2 *	1	
D,A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 43 (C-681)26 January 1990 & JP-A-12 75 732 ( T. MASUMOTO ) 6 November 1989 * abstract *	1	
A	EP-A-0 303 100 (YOSHIDA KOGYO K.K.) * claims 1-4; table 1 *	1	
A	EP-A-0 445 684 (YOSHIDA KOGYO K.K.) * claims 1,2; tables 1,2 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 FEBRUARY 1993	Examiner GREGG N.R.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ----- & : member of the same patent family, corresponding document	