

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 668 806 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
**26.08.1998 Bulletin 1998/35**

(51) Int. Cl.<sup>6</sup>: **B22F 1/00**, C22C 1/04,  
C22C 28/00

(21) Application number: **94901077.1**

(86) International application number:  
**PCT/NO93/00171**

(22) Date of filing: **17.11.1993**

(87) International publication number:  
**WO 94/11138 (26.05.1994 Gazette 1994/12)**

(54) **SILICON ALLOY, METHOD FOR PRODUCING THE ALLOY AND METHOD FOR PRODUCTION  
OF CONSOLIDATED PRODUCTS FROM SILICON ALLOY**

SILIZIUMLEGIERUNG, VERFAHREN ZU DEREN HERSTELLUNG UND VERFAHREN ZUR  
HERSTELLUNG KONSOLIDierter PRODUKTE AUS DIESER LEGIERUNG

ALLIAGE AU SILICIUM, SON PROCEDE DE PRODUCTION ET PROCEDE DE PRODUCTION DE  
PRODUITS CONSOLIDES A PARTIR DUDIT ALLIAGE

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB IT LI NL PT SE**

• **SCHÜSSLER, Gunnar**  
**N-3000 Drammen (NO)**

(30) Priority: **18.11.1992 NO 924442**

(74) Representative:  
**Rees, David Christopher et al**  
**Kilburn & Strode**  
**20 Red Lion Street**  
**London WC1R 4PJ (GB)**

(43) Date of publication of application:  
**30.08.1995 Bulletin 1995/35**

(73) Proprietor: **Elkem ASA**  
**0377 Oslo (NO)**

(56) References cited:  
**GB-A- 404 463** **US-A- 4 402 905**  
**US-A- 4 830 820**

(72) Inventors:  
• **L'ESTRADE, Leif**  
**S-263 71 Höganäs (SE)**  
• **FORWALD, Karl**  
**N-4622 Kristiansand (NO)**

• **L.F. MONDOLFO, "Aluminum Alloys: Structure  
and Properties", 1976, Butterworth & Co,  
(London), page 614 - page 615**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 668 806 B1**

## Description

### Technical Field

5 The present invention relates to silicon based aluminium and titanium-containing alloys and powder-based products produced from such alloy. The invention further relates to a method for producing silicon based aluminium- and titanium-containing alloys and a method for producing shaped articles from such alloys.

### Background Art

10 Silicon has up till now been used as a raw material for producing silanes, electronic products and as an alloying element for steel and aluminium. When used as an alloying element for steel, silicon is normally added in the form of ferrosilicon in amounts normally below 4 % by weight of silicon. When used as an alloying element for aluminium and aluminium alloys silicon is added as elemental silicon. The content of silicon in aluminium alloys varies, but may, for aluminium-silicon alloys, be added in an amount of maximum 20 % by weight of the alloys.

15 Elemental silicon is very brittle and lacks ductility. Addition of silicon to for example aluminium alloys thus causes an increased brittleness of the alloys when the silicon content exceeds about 20 % by weight. As far as the inventors know, there does not exist silicon-based alloys which have such properties that the alloy can be used for structural purposes.

20 Silicon has, however, a number of properties which makes use of silicon-based alloys very interesting for structural applications. Thus silicon has a low density of 2.3 g/cm<sup>3</sup> and a high melting point of 1410°C. Silicon based alloys having a sufficient ductility and strength would thus have a number of advantages compared with other light metals such as for example Al, Ti, Mg and Be. This relates particularly to properties like high stiffness in relation to weight, low thermal expansion, high resistance to corrosion, high resistance against erosion, and use at higher temperatures than other light metals.

25 In the following table there is shown some properties for silicon compared to the same properties for Mg, Al, Ti, and stainless 18/8 steel.

30

|                                         | Si   | Mg   | Al   | Ti   | 18/8 steel |
|-----------------------------------------|------|------|------|------|------------|
| Density (g/cm <sup>3</sup> )            | 2.3  | 1.7  | 2.7  | 4.5  | 8.1        |
| E-module (GPa)                          | 113  | 44   | 71   | 106  | 200        |
| 35 Stiffness/density-ratio              | 4.8  | 2.1  | 2.6  | 2.4  | 2.5        |
| Melting point (°C)                      | 1410 | 650  | 660  | 1660 | 1400       |
| Thermal expansion (10 <sup>-6</sup> /K) | 2.5  | 26   | 23   | 10   | 18         |
| 40 Thermal conductivity (J/smK)         | 84   | 160  | 190  | 19   | 14         |
| Heat capacity (J/gK)                    | 0.71 | 1.03 | 0.90 | 0.53 | 0.48       |

### Disclosure of Invention

45 It is an object of the present invention to provide silicon-based alloys having such a ductility and strength that the alloys can be used for structural purposes and where the alloys still have the good properties of silicon.

Thus, according to a first aspect the present invention relates to a rapidly solidified silicon-based alloy, which alloy contains 2 - 40 % by weight Al, 2 - 45 % by weight Ti, 0 - 10 % by weight of one or more of the elements V, Cr, Mn, Fe, Ni, Co, 0 - 1 % by weight of one or more of the elements B, Sr, P, the rest, except for normal impurities, being silicon in an amount of at least 35 % by weight.

According to a preferred embodiment, the silicon alloy contains 10 - 30 % by weight Al and 3 - 15 % by weight Ti.

According to another preferred embodiment the silicon alloy contains 2 - 10 % by weight Al and 25 - 40 % by weight Ti.

55 The alloy according to the present invention contains preferably boron in an amount of 0.01 - 0,1 % by weight, and/or phosphorous in an amount of 0.01 - 0.05 % by weight and/or strontium in an amount of 0.05 - 0.5 % by weight. The content of the elements V, Cr, Mn, Fe, Ni and Co is preferably between 1 and 3 % by weight.

The rapidly solidified alloy has preferably a primary grain size of less than 50 micron and more preferred less than

10 micron. In order to obtain a highest possible strength and ductility it is particularly preferred that the solidified alloy and precipitated intermetallic phases have a primary grain size of less than 1 micron.

According to a second aspect, the present invention relates to a method for production of rapidly solidified silicon-based alloy, said method being characterized in that it is provided a molten alloy containing 2 - 40 % by weight Al, 2 - 45 % by weight Ti, 0 - 10 % by weight of one or more of the elements V, Cr, Mn, Fe, Ni and Co, 0 - 1 % by weight of one or more of the elements B, Sr and P, the rest, except for impurities, being silicon in an amount of at least 35 % by weight, which melt is solidified at a rate of at least  $10^3$  °C/second.

According to a preferred embodiment the melt is solidified at a rate of between  $10^4$  and  $10^6$  °C/second.

The solidification is preferably done by melt spinning or by gas atomization. It is, however, within the scope of the present invention to use other known methods to achieve a sufficiently high solidification rate.

According to a third aspect the present invention relates to a method for producing consolidated articles from rapidly solidified silicon-based alloy wherein rapidly solidified silicon-based alloy containing 2 - 40 % by weight Al, 2 - 45 % by weight Ti, 0 - 10 % by weight of one or more of the elements V, Cr, Mn, Fe, Ni, Co, 0 - 1 % by weight of one or more of the elements B, Sr and P, the rest, except for impurities, being silicon in an amount of at least 35 % by weight, is crushed and milled to a particle size below 500 microns and formed to articles by means of powdermetallurgical methods, whereafter the formed articles is hot consolidated.

According to a preferred embodiment the rapidly solidified silicon-based alloy is milled to a particle size below 200 microns before the articles are formed.

Forming of articles and consolidation of the formed articles are done by conventional powdermetallurgical methods. It is preferred to use hot isostatic pressing, but it is within the scope of the present invention to use for example cold isostatic pressing followed by sintering, hot single axial pressing, forging, extruding and injectioncasting followed by sintering.

It has surprisingly been found that the consolidated articles made from the silicon-based alloy according to the present invention have very high compression strength and a sufficiently high ductility in order that the products can be used for structural purposes.

By rapid solidification of the silicon-based alloy according to the present invention it is obtained a very fine grained material which has an exceptional good distribution of intermetallic phases in the material and very small grains. It is assumed that it is this combination which give the material its high ductility and high strength. By hot consolidation of the articles according to the present invention, it is important to use such a combination of temperature and pressure that the finished products become sufficiently dense and that grain growth during the consolidation process is not affecting the properties of the material.

#### Detailed description of preferred embodiments.

##### EXAMPLE 1

A silicon alloy containing 25 % by weight of Al, 5 % by weight of Ti, the rest except for normal impurities, being silicon, was melted in a vacuum furnace and cast in the form of rods. The rods were used as a raw material for melt spinning. By the melt spinning the rods were melted and cast to thin sheets or ribbons with a solidification rate of above  $10^4$  °C/second. The ribbons were milled in a closed mill to a particle size of less than 200 microns.

The alloy particles were thereafter filled into a cylinder-shaped mould having a diameter of 1 cm and a height of more than 1 cm. The alloy particles were thereafter pressed for two hours using single-axial pressure of 40 MPa and at a temperature of 700°C.

The produced articles were thereafter tested by compression. The ultimate strength was measured to 878 MPa and the change in length during compression was 7 %.

The results show that the produced alloy has a very high compression strength and a compression length comparable to fiber-reinforced aluminium.

##### EXAMPLE 2

Five alloys were made in powder form using the same procedure as described in Example 1.

Alloy 1: 25 % by weight Al, 5 % by weight Ti, 0.01 % Sr, the rest being silicon.

Alloy 2: 15 % by weight Al, 5 % by weight Ti, the rest being silicon.

Alloy 3: 35 % by weight Al, 5 % by weight Ti, the rest being silicon.

Alloy 4: 25 % by weight Al, 5 % by weight Ti, the rest being silicon.

Alloy 5: 5 % by weight Al, 35 % by weight Ti, the rest being silicon.

5 Alloys 1 through 5 were subjected to hot pressing and the fracture strength and compression length were measured. The results are shown in Table I.

Table I

| Alloy | Hot pressing parameters |             |           | Fracture Strength (MPa) | Compression Length % |
|-------|-------------------------|-------------|-----------|-------------------------|----------------------|
|       | Temp (°C)               | Time (min.) | Load (kg) |                         |                      |
| 1     | 700                     | 120         | 530       | 1196                    | 7.5                  |
| 2     | 700                     | 120         | 420       | 926                     | 5.4                  |
| 3     | 625                     | 120         | 420       | 723                     | 5.4                  |
| 4     | 700                     | 120         | 420       | 978                     | 7.7                  |
| 5     | 1125                    | 120         | 420       | 664                     | 5.9                  |

Table 2 shows that the hot pressed products obtained a very high strength and a good compression length.

### Claims

1. Rapidly solidified silicon-based alloy consisting of 2 - 40 % by weight Al, 2 - 45 % by weight Ti, 0 - 10 % by weight of one or more of the elements V, Cr, Mn, Fe, Ni, Co, 0 - 1 % by weight of one or more of the elements B, Sr and P, the rest, except for impurities, being silicon in an amount of at least 35 % by weight.
2. Silicon-based alloy according to claim 1, **characterized in** that it contains 10 - 30 % by weight Al and 3 - 15 % by weight Ti.
3. Silicon-based alloy according to claim 1, **characterized in** that it contains 2 - 10 % by weight Al and 25 - 40 % by weight Ti.
4. Silicon-based alloy according to claims 1 - 3, **characterized in** that it contains boron in an amount of 0,01 - 0,1 % by weight.
5. Silicon-based alloy according to claims 1 - 3, **characterized in** that it contains phosphorous in an amount of 0.01 - 0.05 % by weight.
6. Silicon-based alloy according to claims 1 - 3, **characterized in** that it contains strontium in an amount of 0.05 - 0.5 % by weight.
7. Silicon-based alloy according to claims 1 - 6, **characterized in** that it contains at least one of the elements V, Cr, Mn, Fe, Ni and Co in an amount of 1 - 3 % by weight.
8. Silicon-based alloy according to claims 1 - 7, **characterized in** that it has a primary grain size of less than 50 micron, preferably less than 10 micron.
9. Method for production of a rapidly solidified silicon-based alloy, **characterized in** that it is provided a melt containing 2 - 40 % by weight Al, 2 - 45 % by weight Ti, 0 - 10 % by weight of one or more of the elements V, Cr, Mn, Fe, Ni, Co, 0 - 1 % by weight of one or more of the elements B, Sr and P, the rest, except for impurities being silicon in an amount of at least 35 % by weight, which melt is solidified at a solidification rate of at least  $10^3$  °C/second.
10. Method according to claim 9, **characterized in** that the melt is solidified at a solidification rate between  $10^4$  and  $10^6$  °C/second.

11. Method for production of consolidated products from rapidly solidified silicon-based alloys, **characterized in** that it is provided a rapidly solidified silicon-based alloy containing 2 - 40 % by weight Al, 2 - 45 % by weight Ti, 0 - 10 % by weight of one or more of the elements V, Cr, Mn, Fe, Ni, Co, 0 - 1 % by weight of one or more of the elements B, Sr and P, the rest, except for impurities being silicon in an amount of at least 35 % by weight, crushing and milling the rapidly solidified alloy to a particle size below 500 micron, forming articles of the milled particles by powder-metallurgical methods and consolidating the formed articles.

12. Method according to claim 11, **characterized in** that the rapidly solidified silicon-based alloy is milled to a particle size below 200 microns before the articles are formed.

## Patentansprüche

1. Schnellhärtende Legierung auf Siliciumbasis, bestehend aus

2-40 Gew.% Al,  
2-45 Gew.% Ti,  
0-10 Gew.% eines oder mehrerer der Elemente V, Cr, Mn, Fe, Ni, Co,  
0-1 Gew.% eines oder mehrerer der Elemente B, Sr und P, und einem Rest, der außer den Verunreinigungen mindestens 35 Gew.% Silicium enthält.

2. Legierung auf Siliciumbasis nach Anspruch 1, gekennzeichnet durch einen Gehalt an 10-30 Gew.% Al und 3-15 Gew.% Ti.

3. Legierung auf Siliciumbasis nach Anspruch 1, gekennzeichnet durch einen Gehalt an 2-10 Gew.% Al und 25-40 Gew.% Ti.

4. Legierung auf Siliciumbasis nach Anspruch 1, gekennzeichnet durch einen Borgehalt von 0,01-0,1 Gew.%.

5. Legierung auf Siliciumbasis nach Ansprüchen 1 bis 3, gekennzeichnet durch einen Phosphorgehalt von 0,01-0,05 Gew.%.

6. Legierung auf Siliciumbasis nach Ansprüchen 1 bis 3, gekennzeichnet durch einen Strontiumgehalt von 0,05-0,5 Gew.%.

7. Legierung auf Siliciumbasis nach Ansprüchen 1 bis 6, dadurch gekennzeichnet, daß sie mindestens eines der Elemente V, Cr, Mn, Fe, Ni und Co in einer Menge von 1-3 Gew.% enthält.

8. Legierung auf Siliciumbasis nach Ansprüchen 1 bis 7, dadurch gekennzeichnet, daß sie eine primäre Korngröße von weniger als 50 µm, vorzugsweise von weniger als 10 µm aufweist.

9. Verfahren zur Herstellung einer schnellhärtenden Legierung auf Siliciumbasis, dadurch gekennzeichnet, daß eine Schmelze bereitgestellt wird, die

2-40 Gew.% Al,  
2-45 Gew.% Ti,  
0-10 Gew.% eines oder mehrerer der Elemente V, Cr, Mn, Fe, Ni, Co,  
0-1 Gew.% eines oder mehrerer der Elemente B, Sr und P, und einen Rest, der außer den Verunreinigungen mindestens 35 Gew.% Silicium enthält, und mit einer Erstarrungsgeschwindigkeit von mindestens 10<sup>3</sup> °C/sec gehärtet wird.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Schmelze bei einer Erstarrungsgeschwindigkeit zwischen 10<sup>4</sup> und 10<sup>6</sup> °C/sec ausgehärtet wird.

11. Verfahren zur Herstellung von konsolidierten Produkten aus schnellhärtenden Legierungen auf Siliciumbasis, dadurch gekennzeichnet, daß eine schnellhärtende Legierung bereitgestellt wird, die

2-40 Gew.% Al,  
2-45 Gew.% Ti,

0-10 Gew.% eines oder mehrerer der Elemente V, Cr, Mn, Fe, Ni, Co,  
 0-1 Gew.% eines oder mehrerer der Elemente B, Sr und P, und einen Rest, der außer den Verunreinigungen  
 mindestens 35 Gew.% Silicium enthält, die schnellhärtende Legierung durch Zerkleinern und Vermahlen auf  
 eine Partikelgröße von weniger als 500µm gebracht wird, die Produkte aus den vermahlenden Partikeln durch  
 Pulvermetallurgische Verfahren ausgeformt werden und die ausgeformten Produkte konsolidiert werden.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß die schnellhärtende Legierung auf Siliciumbasis vor  
 der Ausformung der Produkte auf eine Partikelgröße von weniger als 200 µm vermahlen wird.

## Revendications

1. Alliage à base de silicium solidifié rapidement comprenant 2-40 % pondéraux de Al, 2-45 % pondéraux de Ti, 0-10  
 % pondéraux d'un ou plusieurs des éléments V, Cr, Mn, Fe, Ni, Co, 0-1 % pondéraux d'un ou plusieurs des élé-  
 ments B, Sr et P, le reste sauf pour les impuretés étant du silicium représentant au moins 35 % pondéraux.

2. Alliage à base de silicium selon la revendication 1,  
 caractérisé en ce qu'  
 il contient 10-30 % pondéraux de Al et 3-15 % pondéraux de Ti.

3. Alliage à base de silicium selon la revendication 1,  
 caractérisé en ce qu'  
 il contient 2-10 % pondéraux de Al et entre 25-40 % pondéraux de Ti.

4. Alliage à base de silicium selon les revendications 1 à 3,  
 caractérisé en ce qu'  
 il contient du bore entre 0,1-0,1 % pondéraux.

5. Alliage à base de silicium selon les revendications 1 à 3,  
 caractérisé en ce qu'  
 il contient du phosphore entre 0,01-0,05 % pondéraux.

6. Alliage à base de silicium selon les revendications 1 à 3,  
 caractérisé en ce qu'  
 il contient du strontium entre 0,05-0,5 % pondéraux.

7. Alliage à base de silicium selon les revendications 1 à 6,  
 caractérisé en ce qu'  
 il contient au moins l'un des éléments V, Cr, Mn, Fe, Ni, Co selon une quantité de 1-3 % pondéraux.

8. Alliage à base de silicium selon les revendications 1 à 7,  
 caractérisé en ce que  
 la dimension des grains principaux est inférieure à 50 microns et de préférence inférieure à 10 microns.

9. Procédé de fabrication d'un alliage à base de silicium solidifié rapidement,  
 caractérisé en ce qu'  
 on réalise une fusion contenant 2-40 % pondéraux de Al, 2-45 % pondéraux de Ti, 0-10 % pondéraux d'un ou plu-  
 sieurs des éléments V, Cr, Mn, Fe, Ni, Co, 0-1 % pondéraux d'un ou plusieurs des éléments B, Sr, P) et le reste à  
 l'exception des impuretés étant du silicium représentant au moins 35 % pondéraux, et on fait solidifier le produit en  
 fusion à une vitesse de solidification d'au moins 10<sup>3</sup>°C/seconde.

10. Procédé selon la revendication 9,  
 caractérisé en ce que  
 le produit en fusion est solidifié à une vitesse de solidification comprise entre 10<sup>4</sup> et 10<sup>6</sup>°C/seconde.

11. Procédé de fabrication de produits solides à partir d'alliages à base de silicium solidifiés rapidement,  
 caractérisé en ce qu'  
 on réalise un alliage à base de silicium solidifié rapidement contenant entre 2-40 % pondéraux de Al, 2-45 % pon-  
 déraux de Ti, 0-10 % pondéraux d'un ou plusieurs des éléments V, Cr, Mn, Fe, Ni, Co, 0-1 % pondéraux d'un ou

plusieurs des éléments B, Sr et P, le reste sauf pour les impuretés étant du silicium représentant jusqu'à au moins 35 % pondéraux, on écrase et on broie l'alliage solidifié rapidement pour arriver à une dimension de particules inférieure à 500 microns, on forme des produits à partir des particules broyées selon les procédés de la métallurgie des poudres et on consolide les articles fabriqués.

5

- 12.** Procédé selon la revendication 11, caractérisé en ce qu' on broie l'alliage à base de silicium solidifié rapidement jusqu'à une dimension de particules inférieure à 200 microns avant de former les articles.

10

15

20

25

30

35

40

45

50

55