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An agency of Industry Canada

CA 2327950 A1 2002/06/08

(21) 2 327 950

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2000/12/08

(41) Mise à la disp. pub./Open to Public Insp.: 2002/06/08

(51) Cl.Int.^{7}/Int.Cl.^{7} B22D 27/20, C22C 1/02, C22C 23/00, C22C 21/00

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(54) Titre : AGENT D'AFFINAGE DU GRAIN POUR DES PRODUITS MOULES A BASE D'ALUMINIUM OU DE MAGNESIUM

(54) Title: GRAIN REFINING AGENT FOR CAST ALUMINUM OR MAGNESIUM PRODUCTS

(57) Abrégé/Abstract:
The invention relates to a grain refining agent for cast aluminum or magnesium products, comprising particles having an average particle size of 0.1 to 30 µm and each formed of an agglomerate of grains with each grain comprising a nanocrystal of a transition metal boride or carbide of the formula: Me_aX_b (I) wherein Me is a transition metal, X is boron or carbon, a ranges from 1 to 10 and b ranges from 1 to 20. The grain refining agent according to the invention does not require to be formed into a master alloy prior to being added to the molten aluminum or magnesium to be cast.

ABSTRACT

The invention relates to a grain refining agent for cast aluminum or magnesium products, comprising particles having an average particle size of 0.1 to 30 μm and each formed of an agglomerate of grains with each grain comprising a nanocrystal of a transition metal boride or carbide of the formula:

$$Me_aX_b \qquad (I)$$

wherein Me is a transition metal, X is boron or carbon, a ranges from 1 to 10 and b ranges from 1 to 20. The grain refining agent according to the invention does not require to be formed into a master alloy prior to being added to the molten aluminum or magnesium to be cast.

GRAIN REFINING AGENT FOR CAST ALUMINUM OR MAGNESIUM PRODUCTS

The present invention pertains to improvements in the field of cast metals and metal alloys. More particularly, the invention relates to a grain refining agent for cast aluminum or magnesium products.

Grain refiners are widely used to reduce the grain size and to control the microstructure of cast metals and alloys. Adding grain refiners to molten metal or alloy during casting enhances the heterogeneous solidification and results in a fine-structured material with equiaxed grains. The resulting material shows improved mechanical properties such as high yield strength and toughness.

In the aluminum industry, different grain refiners are generally incorporated in the aluminum as master alloys which are added to the aluminum melt in solid form, for example, in the form of small ingots or a wire which is continuously fed into the melt. The master alloy can also be added in a molten state. The same applies to the magnesium industry.

Typical master alloys for use in aluminum or magnesium casting comprise from 1 to 10% titanium and from 0.1 to 5% boron or carbon, the balance consisting essentially of aluminum or magnesium, with particles of TiB_2 or TiC being dispersed throughout the matrix of aluminum or magnesium. Master alloys containing titanium and boron or carbon are normally produced by dissolving the required quantities of titanium and boron or carbon in an aluminum or magnesium melt at temperatures in excess of 1,200°C in the case of aluminum, and in excess of 800°C in the case of magnesium.

The production of master alloys is expensive since high operating temperatures are required.

It is therefore an object of the present invention to overcome the above drawback and to provide a grain refining agent for cast aluminum or magnesium products, which does not require to be formed into a master alloy prior to being added to the molten aluminum or magnesium to be cast.

According to one aspect of the invention, there is provided a grain refining agent for cast aluminum or magnesium products, comprising particles having an average particle size of 0.1 to 30 μm and each formed of an agglomerate of grains with each grain comprising a nanocrystal of a transition metal boride or carbide of the formula:

$$Me_aX_b \qquad (I)$$

wherein Me is a transition metal, X is boron or carbon, a ranges from 1 to 10 and b ranges from 1 to 20.

The term "nanocrystal" as used herein refers to a crystal having a size of 100 nanometers or less.

The expression "cast aluminum product" as used herein refers to a cast product comprising aluminum or an alloy thereof. Similarly, the expression "cast magnesium product" as used herein refers to a cast product comprising magnesium or an alloy thereof.

Typical examples of compounds of the formula (I) include TiB_2, Ti_3B, Ti_5B and TiC. TiB_2 and TiC are preferred.

The present invention also provides, in another aspect thereof, a method of preparing a grain refining agent as defined above. The method of the invention comprises the steps of:

a) providing a first reagent selected from the group consisting of transition metals and transition metal-containing compounds;

b) providing a second reagent selected from the group consisting of boron, boron-containing compounds, carbon and carbon-containing compounds; and

c) subjecting the first and second reagents to high-energy ball milling to cause solid state reaction therebetween and formation of particles having an average particle size of 0.1 to 30 μm, each particle being formed of an agglomerate of grains with each grain comprising a nanocrystal of a transition metal boride or carbide of formula (I) defined above.

The expression "high-energy ball milling" as used herein refers to a ball milling process capable of forming the aforesaid particles comprising nanocrystalline grains of the transition metal boride or carbide of formula (I), within a period of time of about 40 hours.

Examples of suitable transition metals which may be used as the aforesaid first reagent include titanium, chromium, zirconium and vanadium. Titanium is preferred. It is also possible to use a titanium-containing compound such as TiH_2, $TiAl_3$, TiB and $TiCl_2$.

Examples of suitable boron-containing compounds which may be used as the aforesaid second reagent include AlB_2, AlB_{12}, BH_3, BN, VB, H_2BO_3 and $Na_2B_4O_7$. It is also possible to use tetraboron carbide (B_4C) as either a boron-containing compound or a carbon-containing compound.

According to a preferred embodiment, step (c) is carried out in a vibratory ball mill operated at a frequency of 8 to 25 Hz, preferably about 17 Hz. It is also possible to conduct step (c) in a rotary ball mill operated at a speed of 150 to 1500 r.p.m., preferably about 1000 r.p.m.

According to another preferred embodiment, step (c) is carried out under an inert gas atmosphere such as a gas atmosphere comprising argon or nitrogen, or under a reactive gas atmosphere such as a gas atmosphere comprising hydrogen, ammonia or a hydrocarbon, in order to saturate dangling bonds and thereby prevent oxidation of the grain refining agent. An atmosphere of argon, nitrogen or hydrogen is preferred. It is also possible to coat the particles with a protective film or to admix a sacrificial element such as Mg or Ca with the reagents.

In the particular case of TiB_2 or TiC wherein titanium and boron or carbon are present in stoichiometric quantities, these two compounds can be used as starting material. Thus, they can be directly subjected to high-energy ball milling to cause formation of particles having an average particle size of 0.1 to 30 μm, each particle being formed of an agglomerate of grains with each grain comprising a nanocrystal of TiB_2 or TiC.

The high-energy ball milling described above enables one to obtain grain refining agents having either non-stoichiometric or stoichiometric compositions.

Since the grain refining agent according to the invention is in powder form, it may be difficult to handle. Consolidation is thus preferred to facilitate manipulations and also to ensure that the grain refining agent is homogeneously dispersed in the aluminum or magnesium melt to be cast. For example, the powder can be compacted to form pellets or bricks by uniaxial pressing, hot or cold isostatic pressing, with or without a suitable binder. The powder can also be formed into a cored wire by wrapping the powder with a suitable foil which is preferably made of the same metal or alloy to be cast or of an element having a melting point lower than that of the metal or alloy to be cast.

The following non-limiting examples illustrate the invention, reference being made to the accompanying drawing in which the sole figure shows the X-ray diffraction of the grain refining agent obtained in Example 1.

EXAMPLE 1.

A grain refining agent was prepared by ball milling 3.45g of titanium and 1.55g of boron in a hardened steel crucible with a ball-to-powder mass ratio of 4.5:1 using a SPEX 8000 (trademark) vibratory ball mill operated at a frequency of about 17 Hz. The operation was performed under a controlled argon atmosphere to prevent oxidization. The crucible was closed and sealed with a rubber O-ring. After 5 hours of high-energy ball milling, a TiB_2 structure was formed, as shown on the X-ray diffraction pattern in the accompanying drawing. The structure of TiB_2 is hexagonal with the space group P6/mmm (191). The particle size varied between 1 and 5 μm and the crystallite size, measured by X-ray diffraction, was about 30 nm.

EXAMPLE 2.

A grain refining agent was prepared according to the same procedure as described in Example 1 and under the same operating conditions, with the exception that the ball milling was carried out for 20 hours instead of 5 hours. The resulting powder was similar to that obtained in Example 1. The crystallite size, however, was lower (about 16 nm).

EXAMPLE 3.

A grain refining agent was prepared according to the same procedure as described in Example 1 and under the same operating conditions, with the exception that 3.5g of titanium hydride and 1.5g of boron were milled. The grain refining agent obtained comprised a mixture of TiB_2 and TiH_2.

EXAMPLE 4.

A grain refining agent was prepared according to the same procedure as described in Example 1 and under the same operating conditions, with the exception that 3.1g of titanium, 0.35g of titanium hydride and 1.55g of boron were milled. The grain refining agent obtained comprised a mixture of TiB_2 and TiH_2.

EXAMPLE 5.

A grain refining agent was prepared according to the same procedure as described in Example 1 and under the same operating conditions, with the exception that titanium, boron and graphite were milled. The main role of graphite is lubrication during milling; however, it may also act as a nucleating germ for titanium carbide or a protecting agent against oxidation. The grain refining agent obtained comprised a mixture of TiB_2 and TiC.

EXAMPLE 6.

A grain refining agent was prepared according to the same procedure as described in Example 1 and under the same operating conditions, with the exception that titanium and graphite were milled. The grain refining agent obtained comprised TiC.

EXAMPLE 7.

A grain refining agent was prepared according to the same procedure as described in Example 1 and under the same operating conditions, with the exception that titanium hydride and graphite were milled. The grain refining agent obtained comprised a mixture of TiC and TiH_2.

EXAMPLE 8.

A grain refining agent was prepared by ball milling titanium diboride under the same operating conditions as in Example 1, with the exception that the ball milling was carried out for 20 hours instead of 5 hours. The starting structure was maintained, but the crystallite size decreased to 15 nm.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A grain refining agent for cast aluminum or magnesium products, comprising particles having an average particle size of 0.1 to 30 μm and each formed of an agglomerate of grains with each grain comprising a nanocrystal of a transition metal boride or carbide of the formula:

$$Me_aX_b \qquad (I)$$

wherein Me is a transition metal, X is boron or carbon, a ranges from 1 to 10 and b ranges from 1 to 20.

2. A grain refining agent according to claim 1, wherein Me is a transition metal selected from the group consisting of titanium, chromium, zirconium and vanadium.

3. A grain refining agent according to claim 2, wherein Me is titanium.

4. A grain refining agent according to claim 3, wherein X is boron.

5. A grain refining agent according to claim 4, wherein a is 1 and b is 2.

6. A grain refining agent according to claim 4, wherein a is 3 and b is 1.

7. A grain refining agent according to claim 4, wherein a is 5 and b is 1.

8. A grain refining agent according to claim 4, wherein X is carbon.

9. A grain refining agent according to claim 8, wherein a is 1 and b is 1.

10. A grain refining agent according to claim 1, wherein said average particle size ranges from 1 to 5 μm.

11. A method of preparing a grain refining agent as defined in claim 1, comprising the steps of:

a) providing a first reagent selected from the group consisting of transition metals and transition metal-containing compounds;

b) providing a second reagent selected from the group consisting of boron, boron-containing compounds, carbon and carbon-containing compounds; and

c) subjecting said first and second reagents to high-energy ball milling to cause solid state reaction therebetween and formation of particles having an average particle size of 0.1 to 30 μm, each particle being formed of an agglomerate of grains with each grain comprising a nanocrystal of a transition metal boride or carbide of the formula (I) as defined in claim 1.

12. A method according to claim 11, wherein said first reagent comprises a transition metal selected from the group consisting of titanium, chromium, zirconium and vanadium.

13. A method according to claim 12, wherein said transition metal is titanium.

14. A method according to claim 11, wherein said first reagent comprises a titanium-containing compound selected from the group TiH_2, $TiAl_3$, TiB and $TiCl_2$.

15. A method according to claim 11, wherein said second reagent comprises boron.

16. A method according to claim 11, wherein said second reagent comprises a boron-containing compound selected from the group consisting of AlB_2, AlB_{12}, BH_3, BN, VB_2, H_2BO_3 and $Na_2B_4O_7$.

17. A method according to claim 11, wherein said second reagent comprises carbon.

18. A method according to claim 11, wherein said second reagent comprises tetraboron carbide.

19. A method according to claim 11, wherein step (c) is carried out in a vibratory ball mill operated at a frequency of 8 to 25 Hz.

20. A method according to claim 19, wherein said vibratory ball mill is operated at a frequency of about 17 Hz.

21. A method according to claim 11, wherein step (c) is carried out in a rotary ball mill operated at a speed of 150 to 1500 r.p.m.

22. A method according to claim 21, wherein said rotary ball mill is operated at a speed of about 1000 r.p.m.

23. A method according to claim 11, wherein step (c) is carried out under an inert gas atmosphere.

24. A grain refining agent according to claim 23, wherein said inert gas atmosphere comprises argon or nitrogen.

25. A grain refining agent according to claim 11, wherein step (c) is carried out under a reactive gas atmosphere.

26. A grain refining agent according to claim 25, wherein said reactive gas atmosphere comprises hydrogen, ammonia or a hydrocarbon.

27. A method according to claim 11, wherein step (c) is carried out for a period of time of about 5 hours.

28. A method of preparing a grain refining agent as defined in claim 5 or 9, comprising subjecting TiB_2 or TiC to high-energy ball milling to cause formation of particles having an average particle size of 0.1 to 30 μm, each particle being formed of an agglomerate of grains with each grain comprising a nanocrystal of TiB_2 or TiC.

29. A method according to claim 28, wherein said high-energy ball milling is carried out in a vibratory ball mill operated at a frequency of 8 to 25 Hz.

30. A method according to claim 27, wherein said vibratory ball mill is operated at a frequency of about 17 Hz.

31. A method according to claim 28, wherein said high-energy ball milling is carried out in a rotary ball mill operated at a speed of 150 to 1500 r.p.m.

32. A method according to claim 31, wherein said rotary ball mill is operated at a speed of about 1000 r.p.m.

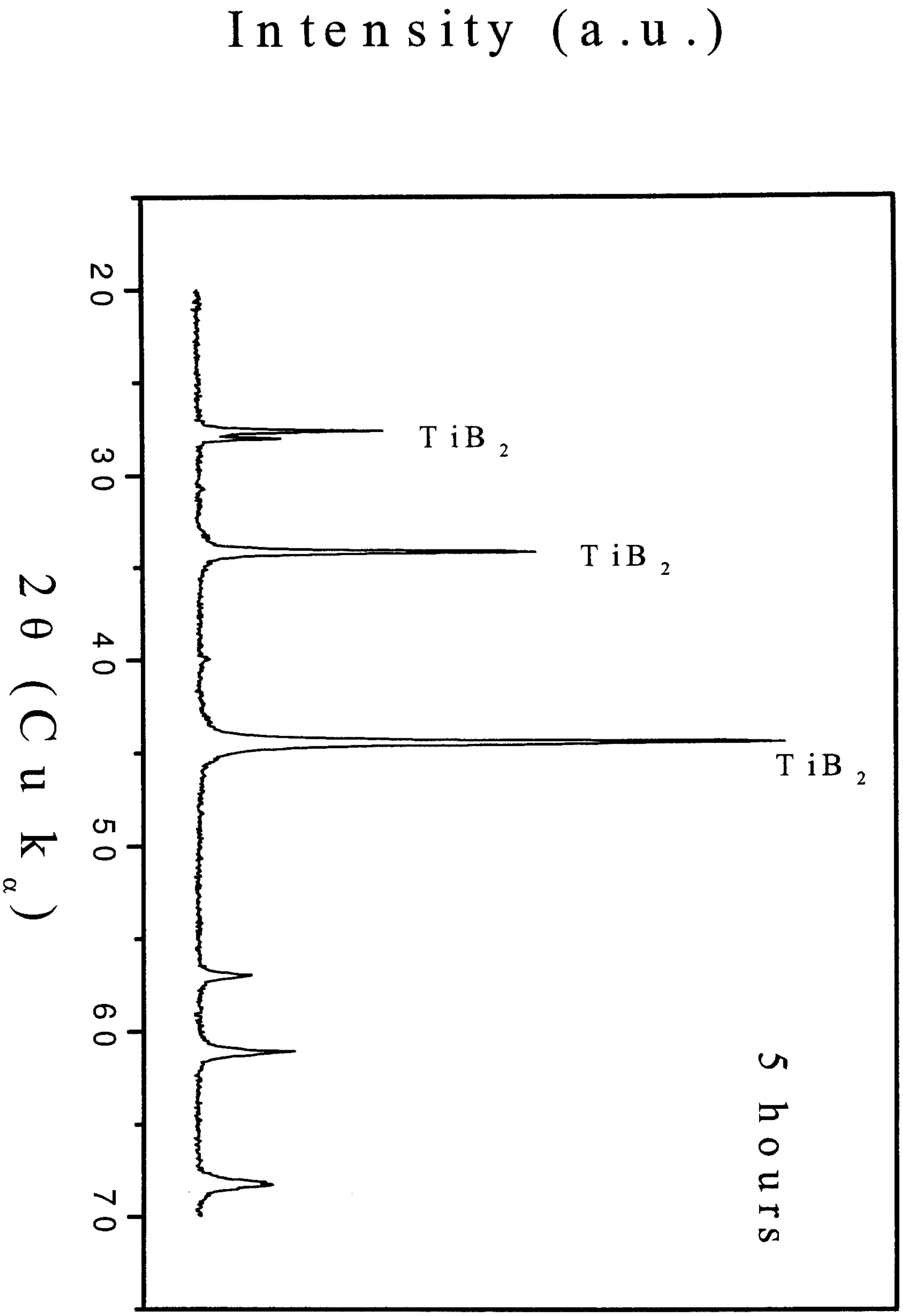
33. A method according to claim 28, wherein said high-energy ball milling is carried out under an inert gas atmosphere.

34. A grain refining agent according to claim 33, wherein said inert gas atmosphere comprises argon or nitrogen.

35. A grain refining agent according to claim 28, wherein said high-energy ball milling is carried out under a reactive gas atmosphere.

36. A grain refining agent according to claim 35, wherein said reactive gas atmosphere comprises hydrogen, ammonia or a hydrocarbon.

37. A method according to claim 28, wherein said high-energy ball milling is carried out for a period of time of about 20 hours.



Intensity (a.u.)
2θ (Cu kα)
20
30
40
50
60
70
TiB2
TiB2
TiB2
5 hours