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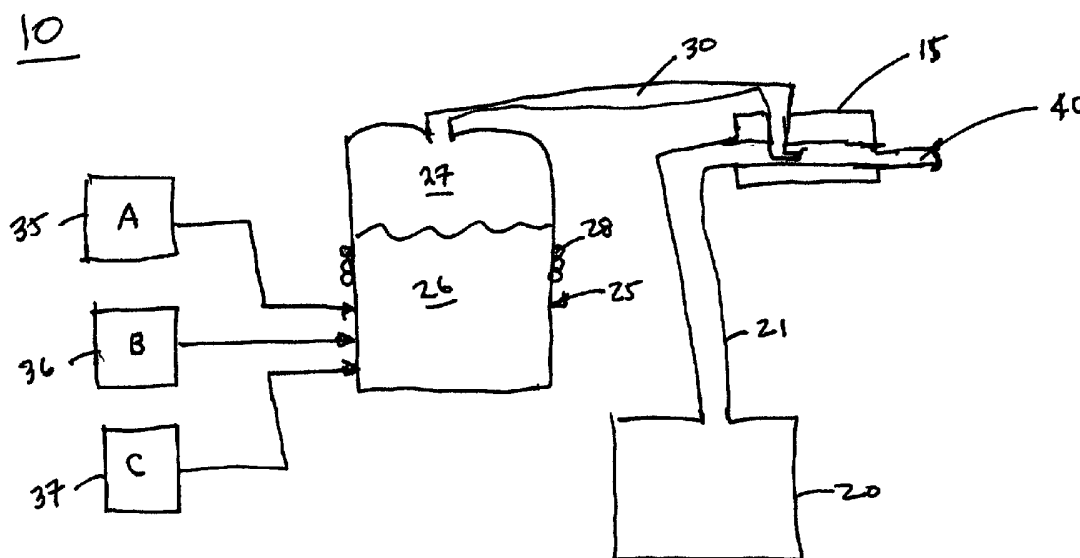
(43) International Publication Date
18 March 2004 (18.03.2004)

PCT

(10) International Publication Number
WO 2004/022797 A1

- (51) International Patent Classification⁷: C22B 34/12, B22F 9/28
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- (21) International Application Number: PCT/US2003/027390
- (22) International Filing Date: 3 September 2003 (03.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/408,934 7 September 2002 (07.09.2002) US
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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- Published:**
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
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(54) Title: PREPARATION OF ALLOYS BY THE ARMSTRONG METHOD



(57) Abstract: A method and apparatus for making alloys or ceramics by the subsurface injection of equilibrium mixed halide vapor of a boiling liquid of the ceramic or alloys constituents into liquid alkali or alkaline earth metals or mixtures thereof is disclosed. Various powders and products are disclosed.

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PREPARATION OF ALLOYS BY THE ARMSTRONG METHOD

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application U.S. Provisional Application Serial No. 60/408,934 filed September 7, 2002.

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in U.S. patents 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. As disclosed in the above-three patents, alloys or ceramics can be prepared by establishing a mixture of gases which are fed, as disclosed in the above-referenced patents, subsurface to a reducing metal thereby to initiate the reduction of the gas mixture to the corresponding alloy or ceramic. In general, the most obvious way to provide the mixed vapor is to introduce the constituent vapors in the required atomic ratio to a manifold and feed the mixed material to the reducing metal.

The present invention relates to another means for mixing the alloy or ceramic constituents prior to the introduction of the mixed vapor to the reducing metal. In the present invention, the various constituents of the alloy or ceramic are initially mixed as a liquid which is thereafter boiled. After the liquid is boiled and reaches equilibrium, the vapor coming off the liquid has the same atomic ratio as the feed liquid to the boiler, which may or may not be different than the liquid in the boiler. At steady state, the vapor from the boiler can be fed to the Armstrong process in the same manner as illustrated in the three referenced patents to produce an alloy or ceramic having a constant atomic ratio.

This invention simplifies the handling of materials, and particularly those materials such as aluminum chloride which sublimate rather than boil. For those materials, the solid is heated in a vessel under pressure so that a liquid is formed and that liquid is thereafter transmitted to a boiler, as will be shown. By way of example a boiler having feed streams of aluminum chloride and vanadium chloride and titanium chloride in atomic ratios of 6% Al and 4%V and the remainder Ti will produce at equilibrium a vapor of 6% Al, 4%V and 90% Ti, even if the atomic ratios of the

constituents of the liquid in the boiler differ. Using the equilibrium vapor as a feed in the process disclosed in the referenced patents produces a 6% Al, 4%V, titanium alloy.

The invention applies to a wide variety of alloys or ceramics and simplifies the materials handling of the constituent parts of each alloy produced in the Armstrong Process.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method and apparatus of producing an alloy or ceramic in which the liquid constituents thereof are fed into a boiler and the equilibrium vapor therefrom is thereafter used in the subsurface reduction with a liquid alkali or alkaline earth metal to form the alloy or ceramic.

Yet another object of the present invention is to provide a method of producing an alloy or ceramic by the exothermic subsurface reduction of a mixed halide vapor of the alloy or ceramic constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy or ceramic constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter introducing the equilibrium vapor into the liquid reductant metal to form an alloy or ceramic powder of the equilibrium vapor constituents in the preselected atomic ratio.

Still a further object of the present invention is to provide a method of producing an alloy by the exothermic subsurface reduction of a mixed halide vapor of the alloy constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter injecting the equilibrium vapor into the liquid reductant metal at greater than sonic velocity to form an alloy powder of the equilibrium vapor constituents in the preselected atomic ratio.

Another object of the present invention is to provide an apparatus for practicing the method hereinbefore discussed.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the

details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of the apparatus and system for practicing the method of the present invention.

DETAIL DESCRIPTION OF THE PREFERRED EMBODIMENT

Figure 1 illustrates a system 10 having a reactor 15 in communication with a source 20 of liquid reductant metal connected to the reactor by a pipe 21.

A boiler 25 has therein a liquid 26 which when boiled produces at equilibrium a vapor 27 which is introduced via pipe 30 into the pipe 21 preferably but not necessarily carrying a flowing stream the liquid metal from the source thereof 20, thereby producing a slurry 40 of the same type, consisting of excess liquid metal, ceramic or metal powder and a salt produced during the reaction as discussed in the above referenced Armstrong et al. patents.

The boiler 25 is provided with a heat source such as coils 28 and is connected or in communication with a plurality of sources of the constituents of the ultimately produced alloy or ceramic. Three such sources 35, 36, and 37 being illustrated.

The advantage of the present invention is that during the production of a ceramic or an alloy by the Armstrong method, liquid handling is frequently easier and more efficacious than handling vapors. To this end, representative constituent sources 35, 36 and 37 can each be a vessel (pressurized or not) in which the individual constituent halide is maintained as a liquid and thereafter transferred in a suitable predetermined atomic ratio into the boiler 25. The atomic ratio of the constituents from each of the sources 35, 36 and 37 determines the atomic ratio of the constituents in the vapor 27 at equilibrium with the liquid 26. Thereafter, the equilibrium vapor 27 in the preselected and predetermined atomic ratios is injected subsurface into a stream of liquid metal at

greater than sonic velocity, as is taught in the above-referenced Armstrong patents.

Although the reductant metal may be any suitable alkali or alkaline earth metal or mixtures thereof, the preferred reductant metal is sodium or magnesium, the most preferred reductant metal being sodium. Although a variety of halides may be used, the preferred halide is a chloride due to availability and cost. Although frequently described with respect to titanium, the invention is in fact applicable to a wide variety of alloys and ceramics, particularly ceramics including a nitride, a carbide, or a boride or mixtures thereof. In addition, many alloys may be produced by the method and apparatus of the subject invention, particularly those alloys or ceramics that include one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si. More preferably, alloys or ceramics are produced which include one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

Moreover, the powder ceramics or alloys produced by the method and apparatus of the present invention are useful in a wide variety of processes to make many different products. For instance, various powder metallurgy techniques may be used to produce product from the powder made by the method and apparatus of the present invention. Moreover, a wide variety of alloy and ceramic powders may be either melted or compressed to form a solid from the powder of the present invention. A particularly important alloy at the present time is the 6:4 alloy of titanium. This alloy is widely used in aerospace and defense and is substantially 6% aluminum and 4% vanadium with the remainder being substantially titanium.

As taught in the cited Armstrong et al. patents, the reductant metal is generally present in excess of the stoichiometric amount needed to reduce the mixed halide vapor injected subsurface of the reductant metal. More particularly, when the reductant metal is present in the range of from about 20 to about 50 times the stoichiometric amount, which enables the entire steady state reaction to be maintained at or around 400°C, an advantageous and mostly preferred temperature. The exact temperature at which the steady state reaction is maintained depends, in part, upon the ratio of halide to reductant metal, as well as the individual vapors being reduced and the reductant metals used to reduce same. It is within the skill of the art to calculate the exact ratios required to provide a predetermined steady state operating temperature for the process producing any of the wide variety of ceramics or alloys made by the method and

apparatus of the present invention.

As previously stated, although the examples herein are discussed with respect to titanium or titanium alloys, a wide variety of alloys and ceramics may be made by the present invention and it is intended to cover in the claims appended hereto, all such alloy and ceramics particularly, but not exclusively, the nitride, boride or carbide ceramics. Representative alloys of the present invention are those which include one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si and most preferably one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A method of producing an alloy or ceramic by the exothermic subsurface reduction of a mixed halide vapor of the alloy or ceramic constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy or ceramic constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter introducing the equilibrium vapor into the liquid reductant metal to form an alloy or ceramic powder of the equilibrium vapor constituents in the preselected atomic ratio.

2. The method of claim 1, wherein the reductant metal is Na or Mg.

3. The method of claim 2, wherein the halide is a chloride.

4. The method of claim 3, wherein the alloy is principally Ti.

5. The method of claim 4, wherein the alloy is principally Ti and includes Al and V.

6. The method of claim 5, wherein the alloy is substantially 6% Al and 4% V with the remainder substantially Ti.

7. The method of claim 1, wherein the reductant metal is present in excess of the stoichiometric amount.

8. The method of claim 7, wherein the reductant metal is present in the range of from about 20 to about 50 times the stoichiometric amount.

9. The method of claim 7, wherein the reductant metal is present as a flowing stream.

10. The method of claim 1, wherein the vapor is introduced into the liquid metal by subsurface injection at greater than sonic velocity.

11. The method of claim 1, wherein the ceramic is one or more of a nitride or a carbide or a boride mixture thereof.

12. The method of claim 1, wherein the alloy includes one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.

13. The method of claim 12, wherein the alloy includes one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

14. The method of claim 1, wherein at least some of the liquid halides are under pressure prior to forming the liquid mixture of halides.

15. A powder produced by the method of claim 1.

16. A solid produced from the powder of claim 15.

17. A method of producing an alloy by the exothermic subsurface reduction of a mixed halide vapor of the alloy constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter injecting the equilibrium vapor into the liquid reductant metal at greater than sonic velocity to form an alloy powder of the equilibrium vapor constituents in the preselected atomic ratio.

18. The method of claim 17, wherein the reductant metal is Na or Mg.

19. The method of claim 18, wherein the halide is a chloride.

20. The method of claim 19, wherein the alloy is principally Ti.

21. The method of claim 20, wherein the alloy is principally Ti and includes Al and V.

22. The method of claim 21, wherein the alloy is substantially 6% Al and 4% V with the remainder substantially Ti.

23. The method of claim 22, wherein the reductant metal is present in excess of the stoichiometric amount.

24. The method of claim 23, wherein the reductant metal is present in the range of from about 20 to about 50 times the stoichiometric amount.

25. The method of claim 24, wherein the reductant metal is present as a flowing stream.

26. The method of claim 17, wherein the reductant metal is Na and the halide is a chloride and the alloy includes one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.

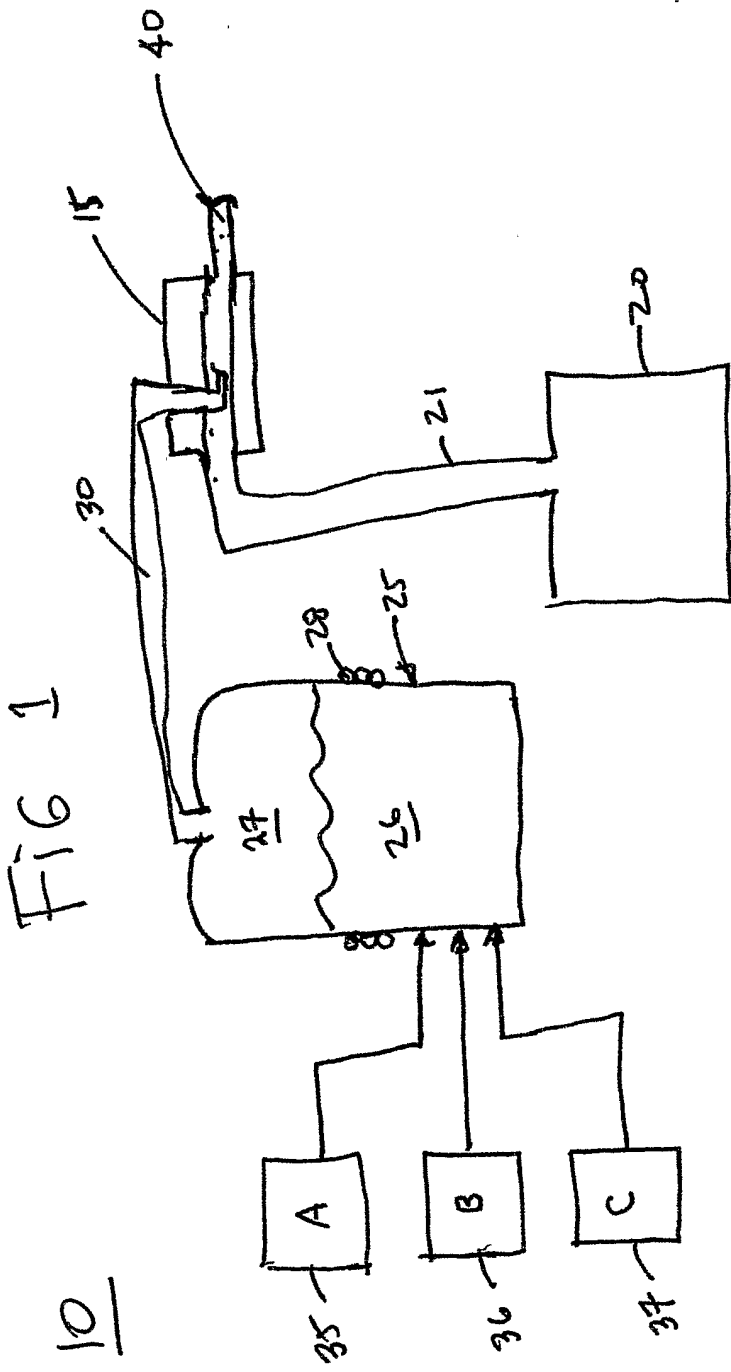
27. The method of claim 26, wherein the alloy includes one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

28. The method of claim 17, wherein one or more of the liquid halides is maintained under pressure.

29. A powder produced by the method of claim 17.

30. A solid produced from the powder of claim 29.

31. An apparatus for producing an alloy or ceramic by the subsurface reduction of a mixed halide vapor of the alloy or ceramic constituents with liquid alkali metal or alkaline earth metal or mixtures thereof, a container for storing each of the constituents in liquid form, a storage container for liquid alkali metal or alkaline earth metal or mixtures thereof, a boiler in communication with each of said containers for storing each of the constituents in liquid form, heating mechanism in heat exchange relationship with said boiler, a reactor in communication with said boiler and said storage container for the liquid metal, pumping mechanism for transferring a predetermined atomic ratio of each liquid constituent to said boiler, and pumping mechanism for transferring liquid metal from said storage container thereto to said reactor, whereby equilibrium vapor from said boiler infected subsurface of the liquid metal in said reactor produces an alloy or ceramic powder of the constituents in the predetermined atomic ratios.



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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/27390

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/12 B22F9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 032 176 A (KAMETANI HIROSHI ET AL) 16 July 1991 (1991-07-16) abstract; figure 1 column 13, line 61 - column 14, line 9 -----	1-13, 15-27, 29-31
X	US 5 958 106 A (ANDERSON RICHARD PAUL ET AL) 28 September 1999 (1999-09-28) cited in the application abstract column 3, line 28 - line 55 -----	1-13, 15-27, 29-31
X	US 2002/005090 A1 (ANDERSON RICHARD PAUL ET AL) 17 January 2002 (2002-01-17) abstract paragraph '0019! -----	1-13, 15-27, 29-31

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

17 December 2003

Date of mailing of the international search report

15/01/2004

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/27390

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5032176	A	16-07-1991	JP 2024506 C	26-02-1996
			JP 2311316 A	26-12-1990
			JP 7047787 B	24-05-1995
			DE 4016502 A1	29-11-1990
			GB 2231883 A , B	28-11-1990
<hr/>				
US 5958106	A	28-09-1999	US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2002005090 A1	17-01-2002
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A , B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
RU 2152449 C1	10-07-2000			
WO 9604407 A1	15-02-1996			
<hr/>				
US 2002005090	A1	17-01-2002	US 5958106 A	28-09-1999
			US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A , B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
RU 2152449 C1	10-07-2000			
WO 9604407 A1	15-02-1996			