(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 056 110
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 81109865.6

(22) Date of filing: 25.11.81

(51) Int. Cl.³: B 22 D 11/06

(30) Priority: 29.12.80 US 220887

(43) Date of publication of application: 21.07.82
Bulletin 82/29

(84) Designated Contracting States: DE FR GB SE

(71) Applicant: ALLIED CORPORATION, Columbia Road and Park Avenue P.O. Box 2245R (Law Dept.), Morristown New Jersey 07960 (US)

(72) Inventor: Curran, Patrick Michael, 16 N. Hillside Avenue, Chatham New Jersey 07928 (US)

(74) Representative: Weber, Dieter, Dr. et al, Weber & Seiffert Postfach 61 45 Gustav-Freytag-Strasse 25, D-6200 Wiesbaden 1 (DE)

(54) **Method for eliminating crystallinity in glassy metal strips.**

(57) The invention describes a method of casting glassy metal strips, which eliminates the occurrence of undesirable crystalline particles. Elimination of the occurrence of crystalline particles is achieved by controlling the chill substrate temperature to maintain the surface at temperatures greater than 115 °C.

EP 0 056 110 A1

DESCRIPTION

METHOD FOR ELIMINATING CRYSTALLINITY IN GLASSY METAL STRIPS

Field of the Invention

This invention relates to a method for casting glassy or amorphous metal strips. In particular, the invention describes a method of casting which eliminates the occurrence of undesirable crystalline particles.

Background of the Invention

It is well established that ribbons of substantial length and varying cross section can be cast into the glassy state by various rapid solidification methods. U.S. Patent 3,856,513 discloses broad compositions of materials which are suitable for casting as glassy ribbons. These ribbons are usually cast on a moving chill surface as described, for example, in U.S. Patent 4,142,571. It has been the practice when casting ribbon alloys on moving metal substrate, to cool the substrate in order to maintain as low a substrate temperature as possible. It has been found that when amorphous ribbons are cast using the techniques described in the prior art, that the substantially glassy metal ribbons often contain some crystalline particles, which for example in iron base alloys are typically alpha (body centered cubic) iron. These crystal particles are normally located near the ribbon surface which contacted the chill substrate during casting. These particles can reduce the corrosion resistance of the ribbons since they represent a chemical inhomogeneity and introduce grain boundaries which are preferential corrosion sites. Crystalline particles may also reduce the thermal stability of the amorphous phase by providing preferred nucleation sites.

The presence of the crystalline particles is evident from the X-ray diffraction pattern of the ribbon surface. A broad diffraction band is characteristic of a glassy structure. The X-ray diffraction pattern of a ribbon surface containing crystalline particles shows a sharp peak which is superimposed over the broad diffraction band. The height of the crystalline peak is generally proportional to the amount of crystalline material. The X-ray diffraction patterns represent surface measurements since the penetration depth of the radiation is generally only about 0.0003 in.

Summary of the Invention

It is an object of this invention to provide a method for casting rapidly quenched metallic glass ribbons which are free from crystalline particles.

It is another object of this invention, to provide a method for casting glassy ribbons with improved thermal stability.

Still another object of this invention is to provide a method for producing glassy metal ribbons with superior corrosion resistance.

These and other objects of the invention will be readily apparent from the following description and claims.

The present invention is an improved method for casting rapidly quenched metallic glass ribbons. The improvement applies to all rapid solidification techniques where metallic stream impinges upon a moving chill surface. The improvement comprises maintaining the temperature of the moving chill surface above about 115°C.

It is preferred to maintain the relative velocity between the quench surface and the metallic stream between about 100 m/sec. and 2000 m/sec.

BEST MODE OF CARRYING THE INVENTION INTO PRACTICE

When a metallic stream impinges on a water-cooled wheel, the wheel is heated by the liquid metal stream and cooled by the flow of a suitable coolant such as water. By adjusting the coolant flow rate and temperature, it is possible to control the temperature of the surface of the wheel. While it is not possible to monitor the instantaneous temperature of the chill surface, it is possible to measure the average temperature at a distance slightly below the surface. This temperature approximates the average temperature of the chill surface. It has been found that the presence of crystalline particles in the glassy ribbon can be substantially reduced or eliminated when this monitored temperature is maintained at about 115°C, preferably above 120°C. Substrate temperatures up to 250°C have been tested and found to effectively eliminate crystallinity. However since as the temperature of wheel surface increases the wear of the surface increases, it is preferred to keep the wheel temperature as low as possible consistant with forming crystalline free ribbon. The following example illustrates the practice of this invention.

Examples 1, 2 and 3

An alloy having the composition: 82 atom percent iron, 12 atom percent boron and 6 atom percent silicon was cast on a 380 mm diameter water cooled copper wheel rotating at 764 rpm. The temperature of the cooling water was 22°C and the flow rate through the wheel was 60 l/m. The metal impinging on the cooled wheel was ejected through a rectangular orifice 0.5 mm wide by 5 mm long. The ejection pressure was 14 Kpa.

The initial wheel surface temperature measured by a thermalcouple located 2.5 mm below the surface was 22°C. The surface temperature increased to 66°C after about 20 seconds of casting and thereafter remained constant. Three samples were taken from the resulting ribbon: 1) near the beginning of the ribbon, after 6 seconds of casting; 2) after 42 seconds of casting; and 3) near the end of the ribbon after about 4 minutes of casting. Each sample was examined to determine the presence of crystallinity on the ribbon surface which had contacted the wheel. The relative amount of crystallinity was gauged by measuring the height of the crystalline peak above the amorphous diffraction band. The results of these tests which are the average of two casting runs are shown in Table I. Note that all samples show appreciable surface crystallinity.

Examples 4, 5 and 6

The conditions for these examples were identical with the conditions for examples 1, 2 and 3 except that the wheel surface temperature was increased. This was achieved by increasing cooling water temperature to 60°C and reducing the cooling water flow rate to about 6.6 l/m. These changes resulted in an initial wheel surface temperature of 60°C, and 116°C being established as the steady state surface temperature after about 20 seconds of casting. Samples were selected and tested as in the previous examples. The test results which are also summarized in Table 1 show appreciable surface crystallinity for the ribbon cast when the wheel temperature was about 60°C, example 4. No surface crystallinity is evident in the ribbon produced after the wheel surface temperature reached 116°C, examples 5 and 6.

Examples 7, 8 and 9

The conditions for examples 7, 8 and 9 are the same as for previous examples, 1-6 except that the water temperature was 55°C and the flow rate was 3.3 l/m. These conditions resulted in a steady state wheel surface temperature of 132°C after about 20 seconds of casting. The test results summarized in Table I again demonstrate the absence of surface crystallinity for the higher, 132°C, wheel surface temperature.

Examples 10-19

Using the same nozzle configuration described in Example 1, a second type of casting experiment was conducted to show the effect wheel temperature on ribbon structure. This experimental procedure permitted a wider range of quenched surface temperatures to be tested. Casting was initiated with no cooling water flow so that the casting surface temperature gradually increased from 22°C to about 230°C. This occurred over a time period of about 120 seconds. Cooling water was then gradually applied to reduce surface temperature to 60°C. The total time of the experiment was about 6 minutes. Samples were taken at time intervals throughout the experiment to represent the various quench surface temperatures. Table II illustrates the results of this test. Crystallinity was observed on the surface of the ribbon cast initially. The relative amount of crystallinity gradually decreased and finally disappeared as the surface temperature of the wheel increased. Decreasing the surface temperature by applying cooling water resulted in the reappearance of crystallinity.

From examination of Tables I and II, it can be seen that the crystallinity in the ribbon disappears when the chill substrate temperature is between about 98°C and 116°C.

TABLE I

CRYSTALLINITY FOR "WARM-WHEEL" AND "COOL WHEEL" TESTS

Examples	Location (feet)	Wheel Temp. (°C)	Crystallinity average (Relative)
1	0- 500	22	585
2	2,000- 2,500	66	560
3	8,100-13,000	66	450
4	0- 500	60	690
5	2,000- 2,500	116	0
6	13,500-14,000	116	0
7	0- 500	55	710
8	2,000- 2,500	132	0
9	13,500-14,000	132	0

TABLE II

SURFACE TEMPERATURE AND CRYSTALLINITY

Example	Location (Feet from Beginning)	Wheel Temp. (°C)	Downside Crystallinity (Relative Units)
10	0- 500	22- 95	440
11	500- 750	95-105	180
12	2,500- 2,500	149-155	0
13	4,500- 4,750	196-200	0
14	6,000- 6,500	220-227	0
15	7,250- 7,500	150-145	0
16	9,250- 9,500	102- 98	90
17	12,250-12,500	71- 70	260
18	15,250-15,500	62- 62	370
19	18,250,18,750	61- 59	410

It is Claimed:

1. In a method for rapidly quenching metallic glass ribbon where an impinging metallic stream contacts a moving chill substrate, the improvement comprising the step of maintaining the surface temperature of the chill substrate above about 115°C.

2. In the method of claim 1, wherein said temperature is maintained above about 120°C.

3. The method of claim 2 wherein said temperature is between 120°C and 250°C.

4. In the method of claim 3 wherein the chill substrate employed is a wheel.

5. In the method of Claim 3 wherein the chill substrate employed is a continuous belt.

European Patent Office

EUROPEAN SEARCH REPORT

0056110

Application number

EP 81 10 9865

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DERWENT JAPANESE PATENT REPORT, vol.4, no.29,(M-2),(511), march 14th 1980	
	* Summary and figure *	1,2,4
	& JP - A - 55 5111 (HITACHI SEISAKUSHO K.K.)	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

B 22 D 11/06

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

B 22 D 11/06
B 22 D 11/00
C 22 C 1/00

CATEGORY OF CITED DOCUMENTS

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
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	19-04-1982	LIPPENS

EPO Form 1503.1 06.78