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PRODUCTION OF AMORPHOUS RIBBON WITH A NEARLY CONSTANT DEGREE OF AMORPHOUSNESS

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\mathbf{th}}$ birthday

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This paper describes a modified melt spinning method that provides for production of amorphous ribbons with a nearly constant short-range order. The ribbon structure can be controlled by relevant parameters, and if these parameters are constant, the ribbons produced have approximately the same degree of amorphousness. A detailed investigation proved that it was necessary to control accurately the melting temperature and the surface velocity of the drum on which the quenching is made. The system is computer controlled using specially adapted software. The particular phases during the process of amorphous ribbon production are turned on in accordance with the temperature of the melt. We made a comparative measurement of produced ribbons proving that ribbons produced with the same parameters have approximately the same degree of amorphousness.

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1. *Introduction*

During the last 30 years, the methods for successful preparation of amorphous samples have been developed through extremely rapid quenching of molten metal on block surfaces. Paul Duwez first successfully applied that method in 1960 [1]. Then a number of methods were developed to obtain samples of good quality for measuring of different physical properties. In the earlier period, the samples were very porous and small, so the measuring of physical properties was reduced to establishing the fact whether the samples were amorphous or not. In 1970 the so-called method of mill was developed which yielded the ribbon form [2]. Professor Leontić developed the method that made two-side quenching possible in a such way that the molten metal was quenched on rims of two very fast rotating wheels.

Finally, the so called melt-spinning method of quenching molten alloy on a single roller has been developed, which is nowadays widely accepted [3]. This method has made possible the production of ribbons of optional length which could be used for physical measurements, as well as in industry, mainly because of their very good mechanical and magnetic qualities. In accordance with the experience, it has not been possible that the ribbons be produced with the same degree of amorphousness either along their whole lengths or when the same parameters were used for production of the ribbons. It was evident, however, that the ribbons produced were of different structure along their length either on the same ribbon or on ribbons produced by applying different quenching method.

This paper describes an improvement of the device for quenching by the melt-spin method.

2. Description of apparatus

Figure 1 shows a modification of the device for production of reproducible amorphous ribbons which was realized through an upgrade of the standard structure of the widely accepted melt-spin method. In addition to the standard parts, the drum on which the quenching is performed (1), a quartz container (2) in which the alloys melt, and the high frequency generator used for heating the alloys (3), the following elements were added:

- Optical radiation thermometer (4);
- System for the control and programming of the speed of the drum rotation (5) and (6).
- System for discharging liquid nitrogen used for conservation of a newly produced ribbon (7).

It is very important that the quenching applied by this method of producing the ribbons is performed in an atmosphere of highly pure argon of almost 99.99% purity. In order for such a pure atmosphere to be achieved, it is necessary that the device is hermetically sealed in a chamber evacuated twice in order to obtain a vacuum of 10^{-4} mbar. In such an atmosphere, pure argon is discharged. The first discharge of argon is intended for "scrubbing" the atmosphere so that the second discharge can create the atmosphere of desired purity. The chamber is not shown in the Fig. 1.

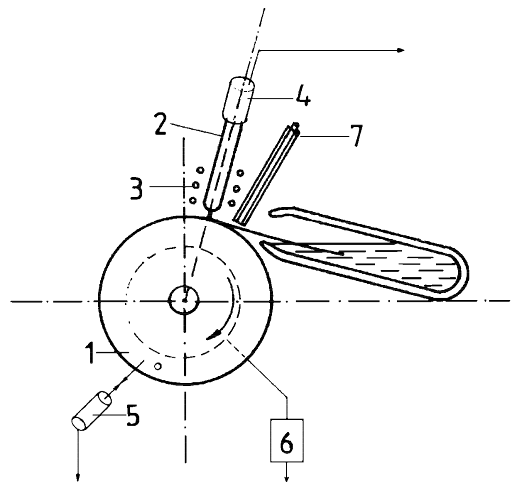

Fig. 1. Device for the production of amorphous ribbon: (1) The drum on which the quenching is done; (2) Quartz container for melting the alloy; (3) High-frequency heating coil, (4) Optical radiation thermometer; (5) and (6) System for the control and programming the speed of rotation of the drum; (7) System for the discharging of liquid nitrogen which is used for the conservation of the produced ribbon.

According to our experience, in order to produce the amorphous ribbons with approximately the same degree of amorphousness, it is necessary that during the process of quenching the roller surface velocity [1], the temperature of the melt and the speed of flowing melt are constant. This means that the above mentioned parameters should be the same for reproducible quality of amorphous ribbons with respect to their structure. Besides the three mentioned parameters, the following ones also affect the degree of amorphousness: geometry of the jet, distance from jet to the drum, pressure of argon inside the chamber, the angle of the melt ejection, force of the jet ejection and the quality of the roller surface. These parameters can to be realized in different productions of amorphous ribbons with significant degree of reproducibility so that they do not affect the degree of amorphousness. In the experiments for production of the ribbons which were investigated, mass the of master alloy was 5 g, distance from the quartz furnace to the drum surface was 1.2 mm, and the furnace was in the shape of a test-tube with circular orifice of 0.6 mm in diameter. In our experiments, pressure of argon was chosen to be equal to the atmospheric, whereas the angle of jet of molten alloy with reference to the roller surface was 7°. Production of the amorphous ribbons by applying the described DOVDE process was attempted manually, that is, after the roller had obtained a predefined speed of rotation and the optical thermometer showed a specific temperature of molten alloy, then the ejection of the molten alloy was carried out. After a few trials it was found that a computer guided program is necessary in order to avoid errors caused by human factor. For the computer-guided production of amorphous ribbons, we installed the IEEE488 acquisition board into the computer. The program for the complete process has been realized through the "Test Point" software which is appropriate for this application, particularly for instruments produced by the company "Keithley".

In order for the computer guided process to be realized, it was necessary to provide communication between the computer and the quenching-device sensors and to resolve the problem of bringing the system to the so called "work point". To bring the system to the work point means to create conditions under which the quenching of the same master alloy will provide amorphous ribbons with approximately the same short-range setting. In other words, based on experience, this means to achieve simultaneously a temperature of the molten metal and a number of drum rotations equal to predefined values.

Communication between the computer and the quenching device was accomplished by the Kethley Multimeter 2000 with installed scan card (200-Scan Card). This combination enabled the communication with sensors to be realized every 2.5 ms in one of 10 channels. In a specific case, only 5 channels are being used so that the control of each point of the system is being done after 12.5 ms.

Bringing the system to the work point was accomplished by using the program which was made as an application of the "Test Point" software. At first, it seemed that the simple process of providing the temperature of the molten metal and the speed of drum rotations with predefined values can hardly be realized. The explanation lies in controlling the temperature of the alloy being quenched and melted by the HF generator. It is known that this temperature will depend on the mass of the master alloy, its shape, and the position of master alloy with respect to the coil. The solution for bringing the system to the "work point" during the process was achieved by monitoring the temperature of master alloy instead of controlling it. In fact, the speed of the drum, which can be changed very precisely, changes depending on the temperature, so that at any one moment, both temperature and speed of the drum obtain the desired values for quenching.

The program, developed as an application of the "Test point" software, consists of three parts. The first part prepares the apparatus for the operation and item presents the check list. Each item is supposed to be checked, followed by the next. The questions refer to review of the most strained elements of the device, as well as to the operations which should be performed for starting the device.

In the second part of the program, the specific values of the parameters needed for the quenching process to be completed, must be supplied. These parameters are the temperature at which the quenching of the master alloy is taking place and the drum rotation speed at the moment of quenching.

The third part of the program actively guides the process of super-fast, controlled quenching and allows visual monitoring of the parameters which define the process.

The process of the production of the amorphous ribbons starts by selecting the right option. The option relative to forming of early metastable states activates the system with liquid nitrogen, so that newly formed amorphous ribbon is conserved by liquid nitrogen. The first step in the process is starting the HF generator, which causes the heating of the master alloy in the quartz container. On the screen one can see how the values of the master alloys instantaneous temperature and the values of the roller surface velocity change. The relation between these two parameters is fixed as follows:

$$V_{\mathrm{roll}} = \frac{V_{\mathrm{quenching}}\, T_{\mathrm{instantaneous}}}{T_{\mathrm{quenching}}}$$

Both parameters, the roller surface velocity and temperature of the molten alloy at the moment of quenching, have predefined values.

It would be very hard to present all details of the program concerning small improvements of the apparatus during the phase of starting the system. However, there are two details in the program which deserve to be pointed out. First, it was found that the molten alloy should be heated a few degrees above the melting point in order to be sufficiently liquid and thus to improve its flow from the quartz container. This correction is entered directly into the program. The second detail relates to the placing of a graphite interface on the lower part of the container where the coil is located. The purpose of this addition is to maintain the temperature of the alloy during the process of the ribbon production and to prevent freezing of the molten alloy at the orifice of the container.

When the temperature of quenching T has been reached, in accordance with the above relation, the roller surface velocity is set to the predefined velocity of the drum on which the quenching is taking place. At this time the molten alloy is discharged onto the drum and the quenching is performed.

3. *Results and conclusion*

The produced ribbons were investigated for low-temperature relaxation features. This technique (shown in Fig. 2) provides for measuring the temperatures of a newly formed ribbon when the heat flow is passing through it. The ribbons were placed in a vacuum chamber between two holders, and one was at the temperature of 0 °C, and the temperature of the other one was increased at a constant rate. The rate of the temperature increase of this holder, consisting of a tungsten foil, is constant and precisely controlled to an accuracy of ±5 °C. If the temperature of the heater (1) is increased, the heat flow passing through the sample is increased, too. The heat flow increase is registered by a temperature increase measured with thermocouples fixed at a certain point of the sample. It is very important that the thermocouples (4) are as thin as possible to minimize any errors caused by loss of heat through the thermocouples. In the present investigation, Cromel-Alumel thermocouples were used. Their wires are 150 μm in diameter, so that their cross-section is much smaller than that of the thinnest ribbon used for investigation. This assures us that the quantity of lost heat through thermocouple will not influence the low-temperature relaxation phenomena. Precise measurement of temperature is performed at one point of the sample. Since the rate of temperature increase of the heater is constant, increase of temperature at the thermocouples (4) is also constant. The rate of the temperature increase of the heater was 0.3 °C/s. It is clear that this constant increase of the temperature of the sample will continue until the low-temperature relaxation occurs. Low-temperature relaxation transforms amorphous structure using a part of energy of heat flow. In this transformation, the atomic short-range order will be changed using a part of the heat-flow energy. As a consequence, decrease of the temperature of the thermocouples (4) will happen. This phenomena has been recorded by measurements with four different samples.

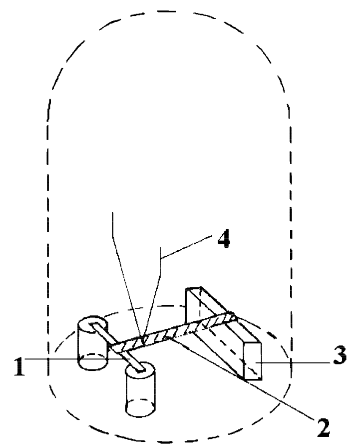

Fig. 2. System for the testing of the ribbons: (1) Heater; (2) Sample; (3) Reference junction (kept at 0 °C); (4) Cromel-Alumel thermocouples.

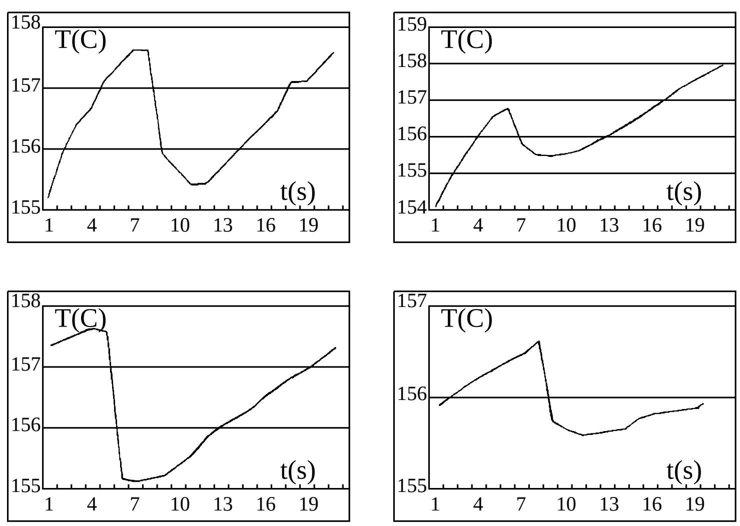

Fig. 3. Low-temperature relaxation of four different amorphous ribbons composed of $Ni_7Fe_{84.7}Zr_3B_{5.3}$.

Figures 3a, b, c and d show that the increase of temperature is evident during the low-temperature relaxation which was applied to four ribbons composed of $Ni_7Fe_{84.7}Zr_3B_{5.3}$. The system was made by melting the components in an argon arc furnace in Lawrence National Laboratory (Berkeley, California, U.S.A.). The ribbons were produced for the research program called "Spring Magnets". The ribbons were randomly selected from a collection of 12 ribbons using the criterion that their dimensions were not significantly different. The last mentioned condition was not difficult to meet since the dimensions of produced ribbons were nearly identical. The ribbons were quenched at a temperature of 1275 °C on the roller of the surface velocity of 3110 rad/s. The length of the studied ribbons was 30 mm.

The diagrams in Fig. 3 show that in all of the four measurements, the low-temperature relaxation takes place almost immediately after the temperature reaches about 157 °C, whereas the shape of the curves is slightly different. It is evident that the temperature variation at which the low temperature relaxation starts is approximately ±0.5 °C. This proves that the produced ribbons have uniform short-range ordering. The answer to the question as to why the shape of the low temperature relaxation curves is not identical, lies most probably in the fact that the cross-sections of the samples differ, and they influence the thermocouple measurement.

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PROIZVODNJA AMORFNIH TRAKA GOTOVO STALNOG STUPNJA AMORFNOSTI

Opisujemo usavršenu metodu taljevine na rotirajućem valjku kojom se proizvode amorfne trake gotovo stalnog kratko-dosežnog uređenja. Struktura traka može se upravljati putem parametara, a ako su ti parametri stalni, proizvedene trake imaju jednake stupnjeve amorfnosti. Pažljiva ispitivanja su pokazala da je potrebno točno podesiti temperaturu taljevine i obodnu brzinu hlađenog valjka kojim se postiže brzo hlađenje. Uređajem upravlja računalo koje rabi posebno preuređen program. Pojedine faze proizvodnje se uključuju ovisno o temperaturi taljevine. Načinili smo usporedbena mjerenja s proizvedenim trakama uz jednake parametre koja pokazuju da postižemo stalne stupnjeve amorfnosti.