INVESTIGATION OF THE RELAXATION PROCESS OF EARLY METASTABLE STATES OF THE $Fe_{40}Ni_{40}Si_{14}B_6$ SYSTEM

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Dedicated to Professor Mladen Paić on the occasion of his 90th birthday

An investigation of the low–temperature relaxation process has been performed in which the structure of the frozen liquid metal is transformed into the structure which the sample acquires at the room temperature. The samples were obtained by quenching on a Cu single roll and then conserved at low temperature as soon as formed. It was noted that the activation of the relaxation process occurs in a temperature interval of 10–125 K. That is somewhat unexpected, because of the nature of the usual relaxation process in amorphous systems. The activation energy of the so-called early metastable states in $Fe_{40}Ni_{40}Si_{14}B_6$ amorphous system was found to be 1.5 kJ/mole.

1. Introduction

Amorphous systems obtained by ultra–rapid quenching are, as is known, metastable systems when compared to the amorphous structures containing the equilibrium concentration of the free volume and when compared to the crystalline state. The fact that the as-quenched amorphous systems tend to transform into more stable amorphous states can be viewed as a consequence of a relaxation process

which starts at the very beginning of the system formation. It has been experimentally verified [1,2] that the amorphous system is a frozen liquid with a very unstable structure at the moment of its creation, which tends toward greater stability via the mentioned relaxation. As observed earlier [1,2], a very intensive relaxation process takes place in which the structure of the as–quenched ribbon is transformed into the structure which the ribbon acquires when the room temperature is reached. Investigation of this relaxation process enables us to obtain information about the transformation of the liquid-metal into the amorphous system and about the interaction of atomic components during the process of cluster formation. In this work, the results of the described relaxation process in $Fe_{40}Ni_{40}Si_{14}B_6$ system are presented as well as the characteristic parameters involved in the process. It was found suitable to introduce the term "early metastable states" for the states which are present in the sample at the moment of solidification of ultra–rapidly quenched molten metal [2]. These early states appear as a result of high concentration of excess free volume being uniformly distributed throughout the amorphous matrix. Such concentration of free volume is explained by assuming that the as-formed sample is in fact a frozen liquid.

2. Experimental procedure

In order to investigate the early metastable states it is necessary to obtain a ribbon with its initial structure conserved immediately after the liquid alloy is solidified. For this purpose, immediately after quenching on a Cu single roll quencher, the obtained metal-glass ribbon is cooled and retained in liquid nitrogen (see Ref. 1). The experimental procedure that follows is very specific and has to be performed completely at the temperature of liquid nitrogen. The relaxation process is followed by observing the changes of electrical resistance of the samples. The resistance measuring apparatus was specially constructed to operate at the temperature of liquid nitrogen [3]. A sectional view of the apparatus for the electrical resistance measurements is shown in Figs. 1 and 2. The apparatus consists of a Dewar vessel (d) with four pairs of electrodes sunk in liquid nitrogen (e). (In Fig. 1 only one pair of electrodes is shown because of the sectional view). The electrical contacts of electrodes (f) to the ends of the sample (a) were made using springs (c). The samples, still kept in liquid nitrogen, were subsequently transferred, together with the liquid nitrogen, into the apparatus for electrical resistance measurements. There they were clasped by special (cooled) grips and then each sample was connected to four electrodes. When doing measurements on a sample, (after the test showed that all the contacts are good) the sample was brought to thermal contact with one of four bodies of different mass (designated by (a) in Fig. 2). Since the whole procedure is performed in liquid nitrogen, the body was also at the temperature of liquid nitrogen. A good thermal contact between the body and the sample insured that the two keep the same temperature. A thermal insulator (b) placed under the samples minimizes heat losses. The sample temperature was measured by a thermocouple (c). The measurement of the electrical resistance started after liquid nitrogen was removed from the Dewar vessel. Due to different masses of the bodies, the samples

were heated to room temperature at different rates. In this way it was possible to obtain the electrical resistance values at different heating rates. The electrical part of the apparatus comprised a Hewlett-Packard HP-3852A system which included an integral voltmeter, two multiplexers and a general–purpose switch. The apparatus was controlled by a computer. The computer–control program enabled the repetition of electrical resistance measurements after a definite time interval and an evaluation of the heating rates. The samples used were of 70 mm length, with the average width of 1.3 mm and the thickness of 0.032 mm. X-ray diffraction was used for testing the amorphous state of the samples after the measurements were completed.
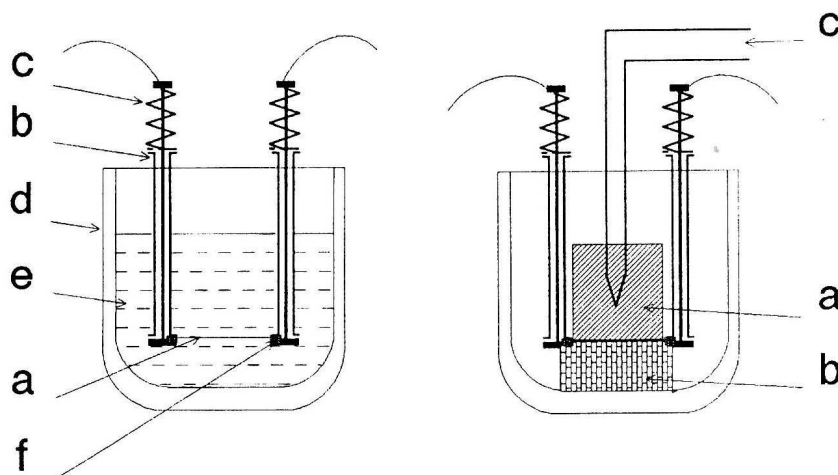

Fig. 1. The sheme of the electrical resistance measurements apparatus immediately after placing the sample. (a) the sample; (b) electrodes; (c) strong spring; (d) Dewar vessel (e) liquid nitrogen; (f) the connections of the electrode to the sample.

Fig. 2. The apparatus for electrical resistance measurements with the additional elements for the sample relaxation measurements. (a) the mass which influences the sample heating; (b) thermal insulator; (c) thermocouple (right).

3. Results

The activation energy can be evaluated if a characteristic parameter of the relaxation process is measured at different heating rates of the sample [4]. A great number of measurements pertaining to the relative change of electrical resistivity were, therefore, performed at different heating rates of the samples. The temperature dependence of the relative change of electrical resistance at constant heating rates was measured and the results for a few different samples are shown in Fig. 3. As can be seen, there is a narrow temperature interval where the relative change of electrical resistance tends to decrease rapidly for each sample. For higher heating

rates, this temperature interval is shifted towards lower values. The temperature intervals in which the values of relative changes in electrical resistance fall as well as the heating rates for individual samples are given in Table 1. The theory of Kissinger [4] establishes the following linear dependence:

$$\ln(T^2/a) = E/kT + \text{const.} \qquad (1)$$

where E is the activation energy, T is the temperature of the activation process, a the heating rate and k the Boltzmann constant. Using the Eq. (1) and the data in Table 1, we obtained the functional dependence shown in Fig. 4. The experimental values obtained for relative change of electrical resistance are linear functions of the temperature. The activation energy can be calculated from the slope of the linear function shown in Fig. 4. The activation energy for the low-temperature process was evaluated to be 1.5 kJ/mole. This is therefore the energy which the very unstable early metastable states of $Fe_{40}Ni_{40}Si_{14}B_6$ system contains immediately upon solidification.

<center>

TABLE 1.

Data from Fig. 3 that were used for the determination of the activation energy of $Fe_{40}Ni_{40}Si_{14}B_6$ alloy.

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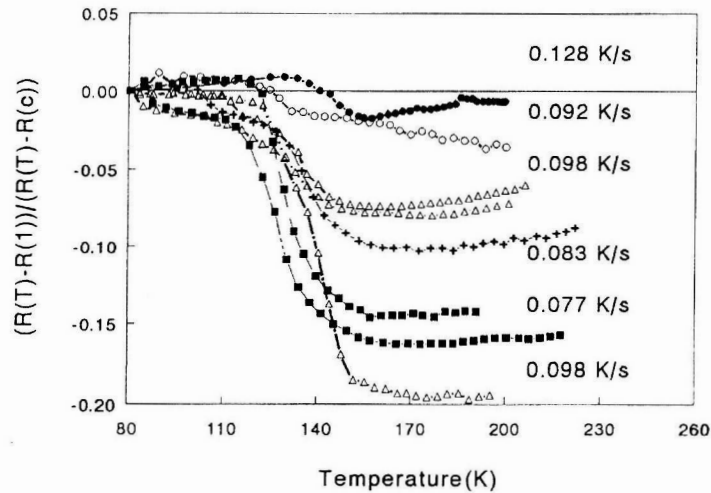| a [K/s]	T [K]	$\ln(T^2/a)$	$10^3/T$ [K^{-1}]
0.128	132.5	11.829	7.55
0.098	122.5	11.939	8.16
0.092	120	11.961	8.33
0.083	117	12.013	8.55
0.077	114.5	12.045	8.73

Fig. 3. The results of measurements of the electrical resistance as the temperature gradually increased for unrelaxed samples and different heating rates.
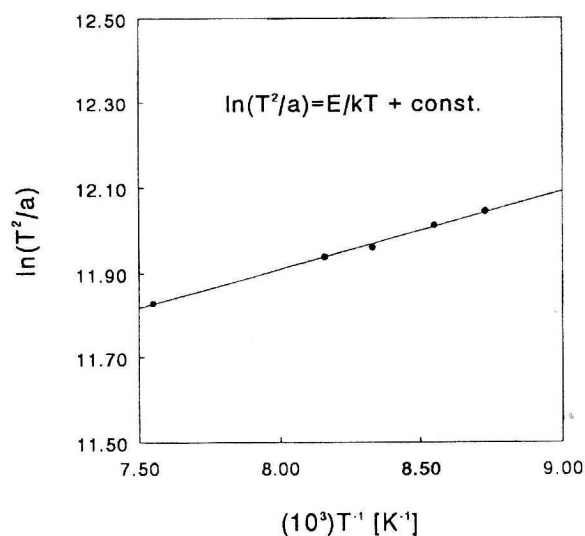
Fig. 4. The Kissinger straight line obtained from the data given in Table 1 and from data in Fig. 3.

4. Conclusion

An investigation has been performed of the low-temperature relaxation process in which the structure of a freshly formed amorphous ribbon is transformed into the structure which the ribbon attains after reaching the room temperature. The activation energy of this relaxation process, computed by the use of Kissinger method, is 1.5 kJ/mole. The result obtained shows a drastic change of the electrical resistance during the relaxation process, occurring in a narrow temperature interval, which can be interpreted as a transformation of the early amorphous structure. In order to explain the results, the following assumptions have to be accepted:

i) there is a great loss of the excess free volume during the process in the amorphous structure and

ii) the free volume is clustered, this process having approximately the same activation energy.

The first assumption explains the great decrease of the electrical resistance. The fact that this fall occurs in a narrow temperature range can be explained by the second assumption. Both assumptions imply that the structure of the as–formed sample can be approximated by the structure of a frozen liquid i.e. with the molten master alloy. The structure of the as-formed sample is very close to the structure of a liquid and the average free volume per atom is expected to be considerable and statistically uniformly distributed over the whole structure. Finally, the investigation of the early metastable states can provide information pertaining to the initial amorphous structure and its ordering, which results in the structure of the

amorphous sample observed at room temperature. The investigation is of interest from the fundamental point of view and because of possible applications in the control of the final amorphous sample structure.

Acknowledgement

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ISTRAŽIVANJE PROCESA RELAKSACIJE RANIH METASTABILNIH STANJA SISTEMA $Fe_{40}Ni_{40}Si_{14}B_6$

U radu je opisano istraživanje niskotemperaturnog relaksacijskog procesa kojim se struktura zamrznutog tekućeg metala, dobijenog kaljenjem na jednom valjku, transformira u strukturu koju traka ima kada dostigne sobnu temperaturu. Uočeno je da se proces relaksacije počinje aktivirati pri određenoj energiji, što nije bilo za očekivati s obzirom da se radi o relaksacijskom procesu u amorfnom sistemu. Za aktivacijsku energiju kojom se relaksiraju rana metastabilna stanja u sistemu $Fe_{40}Ni_{40}Si_{14}B_6$ dobivena je vrijednost 1.5 kJ/mol.