Magneto-Thermo-Gravimetric technique to investigate the structural and magnetic properties of Fe-B-Nb-Y Bulk Metallic Glass

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Abstract. Magneto-thermo-gravimetric (MTG) technique is highly informative about the changes in the magnetic state, as well as structural changes in a system, which cannot be often noticed in calorimetric measurements. We demonstrate the versatility of this technique in determining the magnetic transition temperature, and the subsequent crystallization process in a (Fe0.72B0.24Nb0.04)95.5Y4.5 Bulk Metallic Glass (BMG). MTG and DSC analyses were carried out at the heating rate of 0.67 K/s from RT ~ 1170 K. As a result of the repeated MTG measurements, a magnetic 2nd amorphous phase was observed in the BMG sample, which could be the first measurement for the Magnetic Short Range Ordering (MSRO). Consequently, the MTG measurement is proved as the most convenient method for determining the various structural and magnetic transitions in a glassy material.

1. Introduction

For most metallic alloys, it has been reported that amorphization by rapid solidification is usually achieved in the case of high cooling rates exceeding 10⁴ K/s [1]. The necessity of the high cooling rates causes a limitation on the sample size resulting in limited industrial application. Besides, low plastic deformations of the BMGs are retarding their engineering application, even though their superior mechanical properties and corrosion resistance [2-4]. Monolithic amorphous phase shows, in general, the catastrophic fracture behavior in the almost amorphous materials [5]. Thus, heterogeneous amorphous structure, such as phase separation and nanocrystallization have been attracted due to their benefits for the plastic deformation phenomenon [6-8], which are usually observed using Transmission Electron Microscopy (TEM). However, quantitative analyses are required to determine the effect of the phase separation or nanocrystallization in the amorphous matrixes on the mechanical properties, such as plastic deformation behavior, which could not be achieved from the TEM profiles, because it deals with the extremely narrow 2 dimensional region of the sample. Furthermore, chemical short range ordering (CSRO), sometimes expected to closely related to the microscopic characteristics of the amorphous sample, such as physical, magnetic, and electrical properties, could not be measured using the TEM technique. In the previous research [9], a unique exothermic nature due to the positive mixing enthalpy between Nb and Y elements was investigated using TEM observation, but any
apparent evidences were not appeared in the high resolution TEM (HRTEM) images. Interestingly, subnano-scale reordering in the ferrous materials could, in principle, affect on a magnetization, thus the CSRO could be investigated using magnetic analyses, such as Vibration Sample Measurement (VSM), magnetic balance (for example, MTG) etc. In the present paper, a new terminology of Magnetic Short Range Ordering (MSRO), similar concept with the CSRO, was introduced first in order to investigate the subnano-scale reordering of the atoms due to the positive mixing enthalpy in the ferrous (Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5} glassy alloy. Glassy ribbon and BMG samples were prepared to investigate magnetic heterogeneity of the structural homogenous amorphous sample, due to their different critical cooling rates.

![Sample Heater Pt pan Magnet Thermocouple](image)

**Figure 1.** Schematic diagram for the MTG measurement.

2. Experimental

Glassy ribbon and BMG samples were prepared by melt spinning and Cu-mold casting methods, respectively. The more detailed experimental methods and magnetic results have been reported in the previous papers [9]. For MTG measurement, the schematic image and the principle were illustrated in the Fig. 1. Ferrous sample having magnetization, $M$ and located in the middle axis of furnace is forced by applied gradient magnetic field, $H$. The force to the sample can be explained by $F_z \approx v M z (\partial H y/\partial x + \partial H x/\partial y + \partial H z/\partial z)$ [10]. Here, the sample volume, $v$ and applied magnetic field gradient $\partial H z/\partial z$ are not reliable on temperature, thus simple proportional relationship, $F_z \propto M z$ is approximately achieved. According to the MTG analyzer principle, sample is forced to be located at the same position by balance control during measurement and the value of force is recorded and plotted as a relative magnetic force curve as a function of temperature. Applied magnetic field on the sample was measured using a Hall sensor and the value was about 8000 A/m in the middle of the sample.

3. Results and Discussions

Figure 2 shows (a) DSC curve of the glassy ribbon sample, MTG curves trace of the ferrous (Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5} (b) glassy ribbon sample, and (c) BMG sample as a function of temperature from RT to 1170 K at a heating rate of 0.67 K/s. From the result of the DSC, the $T_g$ and the $T_x$ were observed as seen in the Fig. 2 (a). However, a $T_c$ was not appeared in the DSC profile, compared with the other ferrous materials. In general, an apparent endothermic peak was observed at the $T_c$ of the ferrous amorphous sample in the DSC measurements. As depicted in Fig. 2 (b) and (c), apparent drops were observed at the $T_c$ in the MTG curves. Moreover, the higher sensitivity enables us to distinguish any structural changes, such as relaxation phenomenon of the amorphous samples, as described in the mark A of the Fig. 2 (b). The amorphous ribbon sample was heated and cooled down up to 823 K ($T_g - 50 K$) on the 1st run, and then reheated repeatedly at the temperature range from RT to 1170 K on the 2nd ~5th runs. The MTG curves show the relative magnetic force (%) as a function of temperature. It should be noted that the $T_c$ was decreased by the structural relaxation resulted from 1st run, which means the internal stress caused by quenching process can influence on the magnetic properties. On the 1st run against the amorphous ribbon sample, a relative magnetic force increased gradually at
around 950 K, and then decreased at around 1075 K. On the 2nd~5th runs, it decreased discontinuously at around 850 K, and then dropped drastically at around 1075 K. It could be expected that any structural and/or magnetic transitions occurred at around 850, 950, and 1075 K, respectively. From the DSC measurement, the $T_g$ and the $T_x$ were measured at 873 and 984 K, respectively. Comparing the DSC result with MTG profiles, one might mistake to regard a $T_c$ as a $T_g$ at 860 K on the MTG curve. The appearance of the $T_c$ is probably caused by magnetic phase transition or MSRO. The MSRO could be one of the magnetic phase transitions and affect magnetic properties. At around 950 K, one can say that a new interaction was created by the rearrangement of the atoms like crystallization reaction. It means that the true onset point of the crystallization is earlier than the $T_x$, determined from the DSC curves, hence the onset point of the crystallization in the DSC curve could be well consistent with the $T_x$ from the MTG result. For 1st~5th runs, it was decreased abruptly in common at around 1075 K, which was considered as the Curie point of the crystalline phase. The reason why the relative magnetic force did not decrease up to 0 % after 1075 K could be probably explained by the creation of new crystalline phase having a higher $T_c$ according to the heat treatments. The increase of the value remained after 1075 K can support the assumption above. In this paper, we named each Curie points of the 1st, 2nd amorphous and crystalline phases for convenience as $T_c1$, $T_c2$, and $T_c3$, respectively. 

![Figure 2](image)

Figure 2. (a) A DSC curve and MTG traces of the ferrous (Fe$_{0.72}$B$_{0.24}$Nb$_{0.04}$)$_{95.5}$Y$_{4.5}$ (b) glassy ribbon and (c) BMG as a function of temperature from RT to 1170 K.

As seen in the Fig. 2 (c), The $T_c1$, $T_c2$, $T_c3$, and $T_x$ of the BMG sample were almost the same as ones of the amorphous ribbon sample. On the other hands, The shape of MTG curve, mark B, and C were different from the result of ribbon sample. First, the different shape of the MTG curve between ribbon and BMG samples was interpreted to the sample shape and the applied magnetic field. Under the applied magnetic field of approximately 8000 A/m, the ribbon shaped sample could be magnetically saturated due to their thin layered shape against to the magnetic field direction, on the other hands, BMG sample was unsaturated. Second, the unique pop-up phenomenon at the mark B could be also explained by the same reason mentioned above, which was typically observed in the unsaturated magnetic condition and called Hopkinson effect [11]. In brief, Hopkinson effect says that susceptibility could be enhanced suddenly and then disappeared at around $T_c$, which is explained by the different decreasing rates of between a spontaneous magnetization and a magnetic anisotropy on heating. Third, the mark C could be the most important issue in this research, because it will enable us to recognize the MSRO evidently first. Compared to the amorphous ribbon sample, the relative
magnetic force did not decrease up to 0% at the $T_{c, 1}$ in the BMG sample. What it means, another amorphous phase can exist after the 1st Curie point of $T_{c, 1}$. A lower cooling rate of the Cu-mold cast than melt spinning method could be the strongest reason for the heterogeneous amorphous state of the BMG sample. Results from the repeated MTG measurements suggest that the magnetic 2nd amorphous phase formed on as-cast state could be the same as the magnetic 2nd amorphous phase formed by heat treatment after the 2nd run, which could be supported by the same $T_{c, 2}$ of the 1st run as ones of the 2nd ~ 5th runs at around 840 K. This result reveals that the magnetic 2nd amorphous phase was created in the 1st amorphous phase matrix, and the preliminary crystalline phase could be created from the 1st amorphous phase, because the $T_{c, 2}$ of the 2nd amorphous phase was remained after the repeated heating. On the other hands, the $T_{c, 1}$ of the 1st amorphous phase was disappeared after the 1st run. In other words, a driving force for the crystallization could be reduced by the creation of the magnetic 2nd phase, and furthermore, the GFA and thermal stability at the supercooled liquid region will be enhanced as the same reason. Here, the magnetic 2nd amorphous phase could be regarded as the MSRO, because it was magnetically rearranged within the subnano-scale, or by changing directions of the atoms. Consequently, the magnetic 2nd amorphous phase observed in the BMG sample reveals that the MSRO could be occurred in the samples of positive mixing enthalpy and can enhance the GFA and thermal stability due to reducing the driving force to the crystallization. Finally, the MTG measurement is the most effective and convenient method for determining magnetic transitions like $T_c$ as well as MSRO of the amorphous samples.

4. Summary
The MTG of ferrous (Fe$_{0.72}$B$_{0.24}$Nb$_{0.04}$)$_{95.5}$Y$_{4.5}$ glassy ribbon and BMG samples have been studied in detail and the results are compared with the data from DSC measurement. In this study, thermal behaviors, including the $T_c$, $T_g$ and $T_x$ of the ferrous (Fe$_{0.72}$B$_{0.24}$Nb$_{0.04}$)$_{95.5}$Y$_{4.5}$ glassy ribbon and BMG were investigated by the MTG analyses sequentially to 1170 K. The results can be summarized as follows.

- The $T_c$ was decreased by the structural relaxation of the glassy ribbon sample, which means the internal stress caused by quenching process can influence on the magnetic property.
- The magnetic 2nd amorphous phase was observed in as-cast BMG sample, which was the same as the phase formed by the heat treatments, because of the same $T_{c, 2}$ between as-cast and as-annealed samples determined by MTG measurements.
- Results of which reveals that the MSRO could be occurred in the samples of positive mixing enthalpy and can enhance the GFA and thermal stability due to reducing the driving force to the crystallization.
- Finally, the MTG measurement is the most effective and convenient method for determining structural and magnetic transition as well as the MSRO of the amorphous materials.

5. References
[1] H.S. Chen 1980 *Rep. Prog. Phys.* 43 353
[2] A. Inoue, T. Zhang, N. Nishiyama 1993 *Mater. Trans.* 34 1234
[3] A. Inoue, T. Zhang, N. Nishiyama 1991 *Mater. Trans.* 34 1005
[4] A. Peker, W.L. Johnson 1993 *Appl. Phys. Lett.* 63 2342
[5] A. Inoue 2000 *Acta Mater.* 48 279
[6] A. Inoue, T. Zhang and T. Masumoto 1990 *Mater. Trans.* 31 177
[7] T. Zhang, A. Inoue, S. Chen and T. Masumoto 1992 *Mater. Trans.* 33 143
[8] H.S. Chen 1980 *Rept. Progr. Phys.* 43 353
[9] S. Lee, H. Kato, T. Tubota, K. Yubuta, A. Makino, A. Inoue 2008 *Mater. Trans.* 49 506
[10] K. Masui, S. Maruno 1981 *Bulletin of Nagoya Institute of Technology* 33 111
[11] M. Kersten, Z. Angew 1956 *Phys.* 7 31