氏　　　　　名	リー　サン　ミン 李　　相　　旻
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指　導　教　員	東北大学教授　牧野　彰宏
論文審査委員	主査　東北大学教授　牧野　彰宏　東北大学教授　高梨　弘毅 東北大学教授　今野　豊彦　教授　早乙女　康典

論文内容要旨

During the past two decades, much effort has been made to develop many kinds of ferrous metallic glasses due to their functionality based on the electromagnetic induction effect as well as their superior physical and chemical properties such as a high yield strength of more than 4 GPa and corrosion resistance. However, ferrous metallic glasses such as Fe- and Co-based alloys show poor glass forming ability (GFA) and low thermal stability at the glass transition temperature (T_g), which has hindered commercial applications of these glasses. If it were possible to improve the thermal stability of ferrous metallic glasses, the viscous workability at T_g would open up many kinds of applications utilizing their functionality.

From the viewpoint of functionality of the ferrous metallic glasses, magnetic transition, i.e., soft magnetic property with a glassy state to hard or semi-hard magnetic property with a nanocomposite having soft and hard or semi-hard phases, must be investigated to facilitate industrial applications. Nanocomposites of ferrous materials including rare earth elements (e.g.,Y, Nd, and Sm) and a transition metal (e.g., Fe or Co) can be composed of both a soft magnetic phase of higher B_s and hard magnetic phase of larger H_c, which may interact with each other and produce a larger BH_{max}. It is noteworthy that the interaction between soft and hard phases could occur at a specific distance. The most important factor for the successful fabrication of the nanocomposite would seem to be dispersion of the nano-structured hard phase into the soft phase matrix homogeneously by crystallization of the hard phase through appropriate heat treatment.

In this study, we mainly aimed to obtain both high thermal stability and magnetic transition via crystallization with Fe-based metallic glasses. To achieve a high thermal stability and functionality simultaneously, the precipitation of the $Fe_{23}B_6$ type structure was focused on by exploring an Fe-B-Nb system, and an atomic rearrangement-induced magnetic nanocomposite formation was investigated by additions of rare earth elements (Y, and lanthanoids). Furthermore, to facilitate industrial applications, thermal stability and viscous workability was confirmed by fabrication of glassy powders and their consolidation on spark plasma sintering. In addition, we tried to fabricate of ferrous metallic glass thin films and to carry out imprinting with them in the supercooled liquid region. Detailed objectives of this study was summarized as follows,

(1) To improve GFA and high thermal stability of an Fe-B-Nb-based metallic glass by the addition of Y element through Inoue's empirical rules and precipitation of the $Fe_{23}B_6$ type structure.

(2) To obtain thermal stability and GFA of the initial glassy state of Fe-B-Nb glass former by the addition of lanthanoids elements (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu).

(3) To explore the atomic-scale heterogeneity to examine the possibility of magnetic nanocomposite formation due to the positive mixing enthalpy between Nb and lanthanoids elements (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu).

(4) To explore the possibility of fabricating $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ glassy powders and of consolidating them in the supercooled liquid region on SPS without crystallization.

(5) To investigate shear stress effect on the early viscous flow phenomenon of $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ metallic glassy powder on SPS.

(6) To improve the mechanical strength of $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ metallic glass matrix composite (MGMC) by addition of fine tungsten carbide particulates.

(7) To fabricate ferrous metallic glass thin films (FMGTFs) of Fe-B-Nb-Ln (Lanthanoids) by electron cyclotron resonance sputtering and to analyze magnetic transition by heat-treatment in order to evidence the functionality.

(8) To explore possibility of imprinting of ferrous metallic glass thin films (FMGTFs) of Fe-B-Nb-Nd in supercooled liquid region in order to investigate viscous workability.

The effects of rare earth (RE) addition on the glass forming ability (GFA) and thermal stability of a Fe-B-Nb marginal glass former was investigated and the origin of the highly improved GFA in the multicomponent system was discussed with related to a characteristic exothermic phase transformation, chemical short range ordering (CSRO), in the supercooled liquid region due to the positive mixing enthalpy between Nb and RE elements. The separating tendency between Nb and RE elements is considered to suppress precipitation of metastable $Fe_{23}B_6$ and bcc-Fe crystalline phases, thus to result in highly improving GFA and distinct high thermal stability against heat treatment of the alloy system. In chapters 3 and 4, the RE addition effect on $(Fe_{0.72}B_{0.24}Nb_{0.04})_{100-x}RE_x$ was investigated with a viewpoint of GFA and thermal stability by evaluating thermal properties, activation energy for crystallization and by observing magnetic short range ordering (MSRO). The results of chapters 3 and 4 can be summarized as follows.

(1) Doping Y was confirmed to improve GFA of the $Fe_{72}B_{24}Nb_4$ alloy. The maximum critical glass forming diameter in $(Fe_{0.72}B_{0.24}Nb_{0.04})_{100-x}Y_x$ (x= 0 ~ 6) system was 7 mm (350 times larger than the $Fe_{72}B_{24}Nb_4$ base alloy) of a $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ alloy.

(2) Characteristic exothermic phase transformation within the supercooled liquid region was observed for the alloys with ≥ 3.5 at.% Y element. This is considered to be resulted from a chemical short range ordering associated with the large positive heat of mixing between Nb-Y elements.

(3) $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ alloy was found to maintain glassy phases even after a heat treatment at T_g (= 871 K) for 21.6 ks (= 6 hours). This indicates that this bulk metallic glass has distinct higher-thermal stability with compared to other Fe-/Co- based bulk metallic glasses developed to date.

(4) MTG results 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.

(5) A novel exothermic reaction was seen in all $(Fe_{0.72}B_{0.24}Nb_{0.04})_{100-x}(Ln)_x$ (Ln= La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu, x = 2 - 10 at.%) glass formers by lanthanoid addition of 4-6 at.%, which revealed an atomic-scale heterogeneity of the Fe-B-Nb and Fe-B-Ln phases.

(6) Kissinger analysis revealed that the occurrence of the heterogeneous glassy phases is closely related to the enhanced activation energy of the crystallization, i.e., high thermal stability.

(7) MTG results, appearance of 2nd glassy or amorphous phase of Fe-B-Nb-heavy Ln (Er or Tm, etc.) in the range of 500-600 K after heating to 1173 K, supported the assumption obtained by Kissinger analysis.

(8) An exothermic reaction in supercooled liquid region provided a possibility of an existence of heterogeneous atomic rearrangement, which were evidenced by MTG and TMA, and can be concluded that the atomic-scale rearrangement improved thermal stability, as supported by Kissinger analysis.

In chapter 5, the effect of stress on the viscous densification of $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ gas-atomized glassy powders during the SPS procedure was investigated by the displacement analysis under various applied pressures using cast cylinder and glassy powder samples in the compressive tests and in the SPS process, and $(Fe_{0.72}B_{0.24}Nb_{0.04})_{95.5}Y_{4.5}$ metallic glassy matrix composite (MGMC), containing 10 vol.% fine tungsten carbide (WC) particulates with an average size of 5 μm, was fabricated by the spark plasma sintering (SPS) process to improve mechanical strength by enhancing the complexity of the bonding state. The results can be summarized as follows.

(1) Viscous densification of the glassy powders was found to start at T_f = 663 K under a preset stress of 600 MPa, which is 248 K lower than that measured by TMA under 32 kPa.

(2) A series of SEM images showed the densification behavior of the glassy powder compacts and exhibited direct evidence for the stress-induced viscous flow in the glassy powder compact consolidated at 673 K, which is 200 K lower than T_g (= 873 K) determined by DSC.

(3) The patterned or mirrored surfaces imprinted on the compacts demonstrated the fine (micro or nano) imprintability enhanced by the external stress of less stable metallic glasses, even well below T_g.

(4) The maximum reduction of 256 K was achieved by subjecting glassy powders to an applied stress of 600 MPa. This drastic reduction of T_g can be interpreted to result from the stress concentration effect due to their spherical shapes.

(5) Maximum yielding strengths were achieved at 2045, 1012 and 3020 MPa for samples A (cut horizontal to the consolidation direction), B (cut perpendicular to the consolidation direction) and C (blended with 10 vol.% WC of 5 μm), respectively.

(6) The addition of WC increased the complexity of the bonding state due to strong interlocking and drastically enhanced the compressive strength. The fine hard particles such as WC can play a decisive role in improving mechanical properties by absorbing and dispersing the stress.

In chapter 6, ferrous metallic glass thin film (FMGTF) of $Fe_{71}B_{19}Nb_{3.4}Nd_{6.3}$ was prepared by electron cyclotron resonance sputtering to investigate imprintability using viscous workability and magnetic transition for functionality. Before the study of viscous workability and functionality, the effect of the oxide layer on surface hardness of metallic glass and FMGTF samples was investigated by AES and the instrumented nanoindentation test. The results can be summarized by follows.

(1) The depth of oxide layers and hardness profiles revealed that a thicker oxide layer strongly enhanced surface hardening of the glassy sample.

(2) On surface, high concentrations of oxygen and rare earth were obtained. Fe-B-Nb-Nd and Fe-B-Nb-Sm FMGTF samples showed thicker metallic oxide layer of 10 and 8 nm, respectively.

(3) FMGTF samples obtained by ECR sputtering were harder than the as-cast or the as-SPSed samples both on surface and underlayer. The origin of the enhanced hardness is related to the stress and compositional difference due to the higher cooling rate and oxygen rate.

(4) Ferrous metallic glass thin film (FMGTF) of $Fe_{71}B_{19}Nb_{3.4}Nd_{6.3}$ was prepared by electron cyclotron resonance sputtering, resulting in a high SCLR of 96 K and a semi-hard coercivity of 28.5 kA/m by crystallization.

(5) Furthermore, the FMGTF was imprinted through viscous deformation in the SCLR. The $Fe_{71}B_{19}Nb_{3.4}Nd_{6.3}$ FMGTF sample after imprinting at $T_g + 20$ K for 20 s under 60 MPa was confirmed as retaining its amorphous structure, and a microimage of the imprinted FMGTF sample revealed a clean and precise surface and edges.

This is the first report of successful imprinting with ferrous Fe-based metallic glass and our findings are expected to facilitate commercial applications of MEMS or NEMS. Micro- and nano-scale surgical instruments capable of cutting, griping, drilling, etc., can be realized through the synergy effect of viscous workability and functionality developed in the present paper.

論文審査結果の要旨

電子機器の小型化・精密化が目覚ましい勢いで進む中、MEMS (Micro electro mechanical system)やNEMS (Nano electro mechanical system)技術が注目されている。しかしながら今日までのシリコンをベースにした半導体製造工程による MEMS と NEMS の開発は、機能性の多様化やコスト面で限界がある。他方、金属ガラスは、過冷却液体温度域とその近傍において、金属固体でありながら急激な粘性の低下を示すユニークな合金である。そのため、安価なプロセスであるインプリントを用いた3次元構造物を作製し得る可能性があり、特に磁性金属ガラスは次世代 MEMS や NEMS の可能性を広げるものとして期待される。しかしながら、現在、Fe や Co をベースにした磁性金属ガラスの多くは、低いガラス形成能とガラス遷移温度での低い熱的安定性のため、粘性加工性を利用した3次元加工が殆ど不可能である。また、磁性を利用した機能性の面においても、軟磁気特性しか持たないため、幅広い応用展開を考えた時、大きなメリットは無いのが現状である。

本論文では、近年注目されている MEMS や NEMS 分野において、金属ガラスをマイクロ発電機やナノインプリント磁気媒体などへの応用展開を図るため、その粘性加工性や機能性を同時に向上させることを目的とし、全7章からなる。

第1章では諸言であり、背景と研究目的について述べている。

第2章では実験方法について解説している。

第3章では高ガラス形成能を示す軟磁性 Fe 基バルク金属ガラスの創製に取り組み、従来からガラス相を形成すると知られている Fe-B-Nb 合金に希土類元素を添加することにより、Nb と希土類間の正の混合エンタルピーによる反発力から原子レベルのヘテロガラス構造が形成されることと、その結果、種々の Fe-B-Nb-希土類合金系が著しく高いガラス形成能と熱的安定性を示すことを見出した。

第4章ではこの高いガラス形成能と熱的安定性の発現機構について MTG (Magneto-thermo-gravimetry) と Kissinger plot を用い、その詳細を明らかにした。

第5章ではこの高いガラス形成能と熱的安定性に着目し、ガスアトマイズ法を用いた均質なガラスパウダーの作製と SPS (Spark plasma sintering)を用いた粘性加工によって、緻密な大型バルク材が容易に作製できることを示した。また、熱処理によるガラス相の一部結晶化により、磁気的特性が soft から semi-hard に変化することを見出した。

第6章では Fe-B-Nb-Ln（Ln: ランタノイド）系金属ガラスの粘性加工性について検証を行い、作製した薄膜状金属ガラスが十分なインプリント性を有することを示した。

第7章は総括である。

以上要するに、本研究の主な成果は、ガラス遷移温度での高い熱的安定性と優れた粘性加工性をもつ新しい磁性金属ガラスの創製、熱処理による部分結晶化によって同一材料で発現する軟または半硬磁気特性を利用した金属ガラスの高機能化、および金属ガラスによる次世代の磁性 MEMS や NEMS の新たな展開の可能性を示したことであり、金属ガラス材料学と MENS、NEMS 分野の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。