Designing and Microstructure Optimization of Ductile Metal/Shape-memory-alloy Reinforced Bulk Metallic Glass Matrix Composites

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論 文 内 容 要 旨

[Chapter 1 Introduction]

Bulk metallic glasses (BMGs) possess very good properties: good mechanical properties such as high yielding strength, large elastic strain limit, mainly perfect elasticity before yielding, mainly perfect plasticity after yielding, no work hardening, high fatigue resistance and high abrasive resistance; good processability; good corrosion resistance, etc. These superior properties are considered to result from their unique amorphous microstructures or long-range disordered microstructures, which is totally different from conventional crystalline materials. However, the room-temperature brittleness is one main disadvantage for the potential applications of BMGs. The reasons for this brittleness are considered to be very local plastic deformation. In BMGs, the dislocations do not exist because of the long-range disordered microstructures, but the fundamental unit must be a local rearrangement of atoms accommodating the shear strain, called shear transformation zones (STZs). The STZs is activated firstly from many potential sites, and the continued propagation of the applied shear strain occurs when one STZ creates a localized distortion of the surrounding material, which triggers the formation of large planar bands of STZs along maximum shear stress plane, or so-called shear bands. The plastic strain is concentrated in localized shear bands and the propagation of shear bands can be very fast, generating catastrophically fracture. To overcome this limited ductility of BMGs, introducing a heterogeneous microstructure (glassy matrix + secondary phase) or fabricating BMG matrix composites (BMGMCs) can be effective because the secondary phase hinders the rapid propagation of single shear bands, making it branched, stopped or multiplied, to accommodate the improved plasticity. Normally, there are two ways to fabricate the BMGMCs: *in situ* way and *ex situ* way. For *ex situ* BMGMCs, the secondary phases (particle or fiber) are directly added during the fabrication process, thus, the process is simple, and it is easy to induce various reinforcing secondary phase to various glassy matrix. However, the wetting ability, reactivity between the matrix and secondary phase should be considered and the bonding strength of the interfaces between them is always low. For *in situ* BMGMCs, the secondary phases are intrinsically precipitated from the

liquid to generate well bonded interfaces and better mechanical properties than *ex situ* BMGMCs. However, the composition optimization as well as the fabrication process should be well designed.

Recently, Mg-based BMGs attract a lot of interests because of their low density, high specific strength and low cost. However, the room-temperature brittleness also limits the wide-spread utility potentials of Mg-based BMGs. Therefore, Mg-based BMGMCs have been developed, but the researched are focused on *ex situ* ways because of the difficulty to design the proper *in situ* fabrication process. On the other hand, the shape memory phase reinforced BMGMCs have opened a new way to fabricate highly ductile BMGMCs because of the stress-induced martensitic transformation during the deformation of the shape memory phase. However, this kind of BMGMCs is focused on Zr- or Cu-based BMGMCs, no reported in Mg-based BMGMCs. Therefore, the objectives of this thesis are:

- Fabrication of *ex situ* shape-memory-alloy reinforced Mg-based BMGMCs, investigating the microstructures and mechanical properties, as well as comparison with *ex situ* conventional metal-reinforced Mg-based BMGMCs (Chapter 3)
- Designing a novel process and fabrication of *in situ* shape-memory-alloy reinforced Mg-based BMGMCs, investigating the microstructures and mechanical properties, as well as comparison with *in situ* conventional metal-reinforced Mg-based BMGMCs (Chapter 4)
- Microstructure optimization of *in situ* shape memory alloy reinforced Mg-based BMGMCs by optimizing the matrix (Chapter 5) and dispersoid characteristics (average size, volume fraction) to obtain better mechanical properties, as well as establishing relations between dispersoid characteristics and the mechanical properties of the composites (Chapter 6)

[Chapter 2 Experimental methods]

The sample in this thesis is mainly prepared by the following methods:

- Arc-melting: the starting materials of high purity metals are melted under a Ti-gettered Ar atmosphere in a water-cooled copper hearth. The alloys are remelted at least four times to ensure the chemical homogeneity.
- Tilt-casting: the alloys are melted by arc-melting in a tilt casting furnace and then cast into the copper mold by tilting the copper hearth. The alloy liquids flow into the cavity of the mold by gravity of them.
- Gas-atomization: the alloy is inductively melted in a quartz nozzle with a hole at the bottom, when the sample is melted into liquid, high pressure gas-flow is used during the liquid filing by pressures from above. The high pressure gas-flow serves to create turbulence as the entrained gas expands (due to heating) and exists into a large collection volume exterior to the orifice. The liquid droplets are smashed into many small droplets or powders and cooled therein.
- Induction-melting: the alloy is inductively melted in a carbon crucible in a helium atmosphere at 1273 K for 3 min with the nominal desired composition.
- Injection-casting: the BMGs and BMGMCs are fabricated by injection copper mold casting. A small hole of 1~2 mm size is made in the tip of nozzle. The alloys in nozzle are melted by high frequency induction. When the master alloy is fully melted, the nozzle will be pushed down to that certain location and the alloy melt will be injected into the copper mold by Ar gas flow.

The microstructure, thermal and mechanical property investigations are operated by the following methods:

- X-ray diffraction (XRD): the phase present in the specimens prepared in this work are characterized with X-ray diffraction with Cu Kα radiation.
- Scanning electron microscopy (SEM): the microstructures of the specimens are observed using scanning electron microscopy with attached energy-dispersive X-ray spectrometry (SEM-EDX). The acceleration voltage is 15 kV. The test specimens are cut from the bulk specimens and polished to mirror surfaces.
- Transmission electron microscopy (TEM): the local microstructures of the specimens are also observed. The samples are firstly polished to make the thickness less than 30 μm, followed by a dimple process and ion-milling process.
- Differential scanning calorimetry (DSC): differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The heating or cooling rate from start temperature to end temperature are 0.33 K/s.
- Compression test: the strain rate of 5×10^{-4} s^{-1}. The compression samples with the height of 4 mm and diameter of 2 mm were cut in parallel and carefully polished to ensure the end flatness.
- Four-point bending test (4 PB): the upper and lower spans are 10 and 30 mm, respectively, and the strain rate is 5×10^{-4} s^{-1}.

[Chapter 3 *Ex situ* porous NiTi shape-memory-alloy particle reinforced Mg-based BMGMCs]

The reasons to select porous particles instead of dense ones are that the BMGMCs containing porous particles possess two different kinds of average particle size and inter-particle spacing: large-scale compartment divided by the particles and micro-scale compartment within one porous particle. The more complicated microstructures are considered to favor their ductility as well as strength because the small partition regions can further limit the propensity of forming matured shear bands. In fact, each compartment, if standing alone, can deform a lot with high failure resistance. The porous NiTi shape-memory-alloy particles are fabricated by etching Ni-Ti-Gd multiphase precursor particles (B2-NiTi + NiGd) in nitric acid solutions. The NiGd phase is selectively leached out to form pores while the NiTi phase is stable. The size and inter-particle spacing between NiTi among one porous particle are ~0.2 μm. The *ex situ* porous NiTi shape-memory-alloy particle reinforced Mg-Cu-Gd-Ag BMGMCs have been successfully fabricated. These Mg-based BMGMCs shows improved plasticity and fracture strength, better than the conventional dense or porous metal particle reinforced Mg-based BMGMCs. The best plasticity obtained is ~11% with 20 vol.% porous NiTi particle addition. The stress-induced martensitic transformation of the NiTi particles have been confirmed, which is considered to further improve the plasticity as well as work-hardening behavior. Furthermore, the porous structure of the NiTi secondary particles generates very fine-scale local microstructures, the local average size and inter-particle spacing of NiTi is very fine and close to the processing zone size of the matrix, which can further stabilize the shear bands against developing into cracks, thus to obtain better mechanical properties.

[Chapter 4 Designing, fabrication and characterization of *in situ* dendritic NiTi shape-memory-phase reinforced Mg-based BMGMCs]

In the previous part, the Ni-Ti-Gd multiphase containing alloy (B2-NiTi + NiGd) have been fabricated if the composition is well adjusted. Thus, by immersing this kind of alloy in Mg-Cu-Ag melt, the NiGd phase is considered to dissolve into the melt while the B2-NiTi phase is remained. Finally, Mg-Cu-Gd-Ag glassy matrix with *in situ* B2-NiTi dispersoids can be fabricated. Based on this novel fabrication process, the *in situ* dendritic B2-NiTi reinforced Mg-Cu-Gd-Ag BMGMCs have been successfully fabricated. The average size and volume fraction of B2-NiTi phase are ~10 μm and 12%, respectively. The nature of B2-NiTi phase is confirmed by XRD, DSC and TEM investigation. No crystalline phase can be found at the interface between B2-NiTi and glassy matrix, indicating well bonding strength of the interface. The residual thermal stress at the interface is calculated to be ~40 MPa, compressive stress at B2-NiTi, which may facilitate the phase transformation of B2-NiTi during deformation. During compression, the *in situ* BMGMCs show very high plasticity and strength, as well as work-hardening, better than the conventional *in situ* Ti reinforced counterparts with similar size and volume fraction of secondary phase. The stress-induced phase transformation during deformation is considered to induce the volume change and compressive stress field around the NiTi dispersoids to further release the stress concentration and hinder the initiation and propagation of cracks.

[Chapter 5 Microstructure optimization of the matrix of *in situ* B2-NiTi reinforced BMGMCs]

The matrix of *in situ* B2-NiTi reinforced Mg-Cu-Gd-Ag BMGMCs have been optimized by changing the matrix to Mg-Ni-Gd-Ag to eliminate the effects of Ni in the matrix, which degrades the glass-forming ability. The fabricated *in situ* B2-NiTi reinforced Mg-Ni-Gd-Ag BMGMC (A-SC) shows improved fracture strength, ~906 MPa, and high plastic strain, ~6.7%, compared with its monolithic counterpart. The stress-induced martensitic transformation of B2-NiTi phase is confirmed and considered to contribute to the mechanical properties, similar to Mg-Cu-Gd-Ag matrix counterparts. However, the size and inter-particle spacing of NiTi dispersoids are much larger than the processing zone size of the matrix, which should be further optimized to obtain better mechanical properties.

[Chapter 6 Microstructure optimization of B2-NiTi dispersoids of *in situ* B2-NiTi reinforced BMGMCs]

As discussed before, the NiTi dispersoids are precipitated from crystalline Ni-Ti-Gd alloys, the size of NiTi dispersoids can be decreased by increasing the cooling rate of the Ni-Ti-Gd alloys. Therefore, various sizes of Ni-Ti-Gd rods are prepared by tilt casting technique (A-RC). Then similar to A-SC samples, the A-RC BMGMCs are fabricated. The size of NiTi dispersoids has been successfully optimized by increasing the cooling rate of Ni-Ti-Gd alloys, from 8 μm to 2 μm, very close to the processing zone size (1.5 μm). With smaller sized B2-NiTi dispersoids, the plasticity, fracture strength, as well as work-hardening rate are increased. A novel model has been developed to analyze the relations between dispersoid conditions (average size, inter-particle spacing) with the plasticity of BMGMCs. Furthermore, the volume fraction of NiTi dispersoids has also been optimized by adjusting the composite composition (B-RC). The optimized average size and inter-particle spacing of NiTi dispersoids are ~2 μm, stabilizing the shear bands to develop into cracks and improving the interactions between the matrix and the dispersoids. The best plasticity obtained is ~23%, highest among all kinds of *in situ* Mg-based BMGMCs to date.

論文審査結果の要旨

金属ガラスは広い過冷却領域を有するアモルファス合金であり結晶粒界がないことから耐食性が高く、低ヤング率と高弾性限を有する。しかし、金属ガラスは、一般に、単軸変形下において局所不安定すべりによって破壊し、塑性変形や加工硬化を殆ど示さないため、その実用化が大いに制限されている。金属ガラスのこのような欠点を補う方法として、剛性や延性を有する第2相粒子分散による複合材料化が有効であることが知られている。第2相粒子の分散方法には、直接添加法とその場反応法があり、後者は、粒子／母相間に強固な結合が期待できる大きな利点を有する一方で、反応析出の設計が課題となっていた。本論文では、新しいその場反応作製方法を提案し、延性金属／形状記憶合金が分散する金属ガラス複合材料の作製と複合組織の最適化に成功した。

本論文は全7章で構成され、第1章では、本研究の目的、研究背景、および本論文の構成について述べている。第2章では、本研究に利用した合金作製方法、構造観察方法、および、力学測定方法について述べた。第3章では直接添加法により、ポーラスニチノールが分散する金属ガラス複合材料の作製と性質について述べた。ポーラス粒子内部の小さなマトリックス領域の大きさと領域間距離を同定した。更に、変形中のニチノール相の応力誘起変態により、この複合材料が高い塑性変形能、高破断強度および高加工硬化指数を示すことを明らかにした。第4章では、新しいその場反応法を設計し、ニチノール粒子またはチタン粒子が分散する金属ガラス複合材料の作製と性質について述べた。形状記憶合金が分散する金属ガラス複合材料は、変形中に生じるニチノールの応力誘起変態に起因して、通常の金属（チタン）が分散する複合材料よりも、更に優れた力学性質を示すことを明らかにした。第5章では、金属ガラス複合材料のマトリックス組成の最適化について述べた。前章で作製した複合材料では、分散するニチノール中の Ni がマトリックスに溶出することにより、マトリックスのガラス形成能が低下する欠点があった。そこで、Ni を含む高ガラス形成能合金をマトリックスに用いることによって、その欠点を解決した。第6章では、金属ガラス複合材料のニチノール分散粒子の大きさ、および、体積分率の最適化について述べた。前章で作製した複合材料の分散相の大きさ、および、粒子間距離は、理想的な金属ガラスの塑性加工域（plastic processing zone）サイズより大きいという欠点があった。前駆合金の組成を調整するとともに、冷却速度を制御することによって、この欠点を解決した。ニチノールの分散組織を最適化した複合材料は23%の高い塑性変形量が示し、これまでその場反応法によって作製したマグネシウム金属ガラス複合材料の中において、最も優れた力学性質を示すことを明らかにした。第7章では、本研究で得られた成果を総括した。

以上のように本論文は、延性金属／形状記憶合金が分散する金属ガラス複合材料を作製し、その高塑性変形および加工硬化を明らかにしたもので、延性金属／形状記憶合金強化金属ガラス複合材料の塑性変形に関して、新規性および独創性があり、高い学術的価値を有するものと評価できる。

学位審査委員会は、郭　威氏の研究結果が金属ガラス複合材料の分野において極めて有益な成果を得るとともに、複合材料科学の進歩発展に貢献するところが大であると判断した。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。