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Review

Production methods and properties of engineering glassy alloys and composites

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ABSTRACT

Since the first synthesis of glassy alloys in 1960, a great large number of studies have been carried out in basic science and technological aspects. At present, glassy alloys and composites have been used as functional and structural materials. The production method for their practical materials was limited to a quenching type technique for many years before around 1990, but the finding of bulk glassy alloys caused a drastic change in production method of glassy alloys to a copper mold casting type technique which has enabled the production of glassy alloys in a three dimensional bulk form. Furthermore, glass alloy composites produced by semi-solid progressive solidification have been successfully developed recently, even using impure charge materials. The drastic changes in the production method and material form have also resulted in significant extension of application fields of glassy alloys. This paper aims to review the production methods and properties of glassy alloys and composites with useful critical sizes above 100 μm or below 4 μm in thickness for glassy powder in conjunction with the present situation of applications for their glassy alloys and composites which do not belong to materials with an ordinary thickness size range of 10–50 μm.

1. Introduction

Since the first synthesis of amorphous alloy in Au–Si system by rapid quenching [1], a large number of amorphous alloys have been developed in conjunction with various quenching techniques from melt [2–9]. Amorphous alloys in ribbon, wire and powder forms have been produced and used as commercialized materials. The ordinary critical sizes of these amorphous alloys are about 20–30 μm in thickness for ribbon, about 100–200 μm in diameter for wire and less than 25 μm in thickness for powder, respectively. Such size limitations were drastically reduced by the findings of BMG alloy compositions in Mg-, La- and Zr-based multicomponent alloy systems [10–13]. Their findings have also caused a drastic change in the production method from melt quenching type to copper mold casting type and bulk glassy alloys with centimeter size in diameter have been developed in various alloy kinds of alloy systems [5,14]. It is therefore important to get general information on the relation between production methods and properties for glassy alloys which have been used as practical materials. This paper aims to review the production methods and properties of engineering glassy alloys in wire, sheet, powder, rod and net shape forms with critical dimension above 0.1 mm, the processing techniques of surface coating, rolling, micro-forming and welding for bulk glassy alloys and the properties of their processed materials.

2. Glassy alloy wires with diameters up to 1.5 mm

The first synthesis of glassy alloy wire was made by using the in-rotating-water spinning technique in 1981 [15]. The glassy alloy wire with a circular cross section can be produced by injecting the molten alloy through a quartz nozzle into a rotating water layer which was formed in the rotating drum by centrifugal force. The amorphous wire diameter is in the range from about 50 μm to 250 μm and the wire diameter is roughly equal to the hole diameter of the quartz nozzle. The glassy alloy wires with a diameter of about 100 μm were produced for various alloy systems such as Pd–Cu–Si [15], Pd–Ni–P [16], Pt–Ni–P [17], Fe–Si–B [18], Co–Si–B [19], Co–Fe–Si–B [19], Fe–P–C [20], Ni–Si–B [21] and Cu–Zr systems [22] for several years from 1981 to 1985. Later, Al-based glassy alloy compositions were found in 1987 [23] and Al-based amorphous

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wires with a diameter of 70 μm was also produced by applying a melt extraction method to the new alloy composition [24].

All these glassy alloy wires exhibit good bending ductility which can be shown through a 180 degrees bending without fracture and can be cold-drawn to more than 70% reduction in cross sectional area at room temperature without intermediate annealing treatment. The cold drawn wires show significant increase in tensile strength as well as tensile elongation. For instance, the $Fe_{75}Si_{10}B_{15}$ glassy alloy wire shows high tensile strength of about 3700 MPa and distinct plastic elongation of about 2% in the cold drawn state [25]. Tensile fracture of the wires occurs along the maximum shear stress plane and its fracture surface consists of smooth and vein patterns.

In addition, Fe- and Co-based glassy alloy wires have been reported to exhibit unique magnetic properties. For instance, the $Fe_{75}Si_{10}B_{15}$ glassy wire exhibits rather large ΔE effect ($\Delta E = (E_s - E_0)/E_0$, E stands for Young's modulus, while E_s and E_0 stand for Young's moduli measured at saturation and zero field, respectively.) of about 6% for the wire diameter of 100 μm and the ΔE effect value tends to decrease with increasing wire diameter due to the formation of more relaxed glassy structure [25]. The cold drawing causes a distinct increase of AC coercive force to about 30 Oe, resulting in the generation of good magnetic square hysteresis loop due to Barkuhauzen flux jumping effect. In the systematic study on the change in tensile strength, Young's modulus and AC coercive force with cold drawn reduction ratio for of $Fe_{75}Si_{10}B_{15}$ and $Co_{73.5}Si_{12.5}B_{15}$ glassy alloy wires, we can recognize general tendencies, namely, a maximum value of tensile strength around 40% reduction ratio, continuous decrease in Young's modulus with increasing reduction ratio and a maximum AC coercive force around 40% reduction ratio for both the wires. Fig. 1 shows the AC hysteresis loops of the cold-drawn Fe- and Co-based glassy alloy wires subjected to cold drawing as well as the change in the AC coercive force of the Fe- and Co-based wires in as-spun and cold drawn states with applied field [25]. These wires show nearly constant AC coercive force in the cold-drawn state, in contrast to the linear increase in AC coercive force of the as-spun wires with applied field.

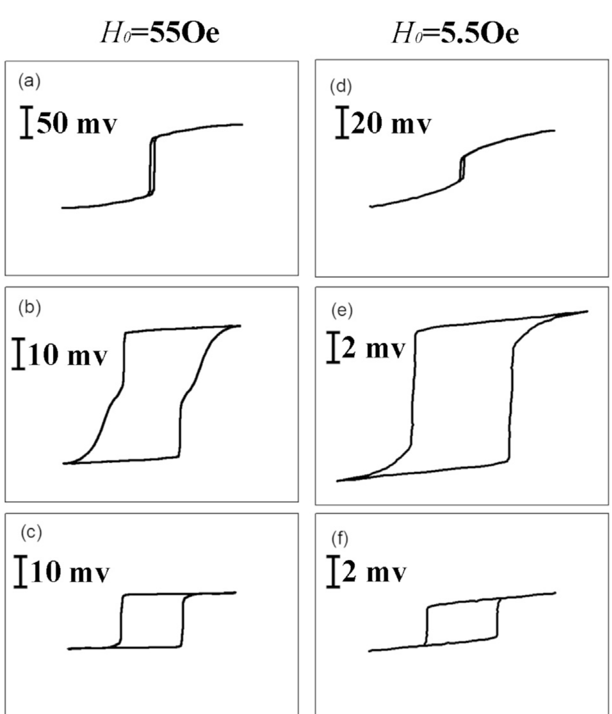

Fig. 1. BH loops of $Fe_{75}B_{15}Si_{10}$ (a, b, c) and $Co_{72.5}B_{15}Si_{12.5}$ (d, e, f) glassy wires with $d_0 = 125$ μm. (a) and (d): as quenched; (b) and (e): $R = 20\%$; (c) and (f): $R = 80\%$ [25].

Owing to the unique magnetic properties of the cold drawn wires, we tested dynamic magnetic properties of the wires in a picked coil having 500 turns [25] and reported that exposure to a switching field of about 200 Oe produced a sharp voltage pulse associated with flux jump. The voltage pulse per cross-sectional area-turn of coil reached as high as 6 V/cm^2 per turn. Thus, flux reversal occurs at high speed and hence the wires can be used to generate sharp voltage pulses. As possible applications, we know uses in devices such as switches, flowmeters, tachometers, proximity sensors, credit cards, and robotic sensors.

Based on the above-described interesting basic achievements, Unitika Corporation has developed a mass-production type in-rotating-water spinning equipment. Fig. 2 shows a schematic illustration of the mass-production type in-rotating water spinning equipment equipped with a winder [26]. It is noticed that this process can produce continuously a glassy alloy wire which is accumulated in the rotating water layer and wind simultaneously. The drawing technique has also been developed in a continuous mode at room temperature and elevated temperatures. It has been reported that the warm drawing is useful to produce fine wires with diameters below 30 μm by few drawing processes [27]. The warm-drawn wires possess a higher stability against structural relaxation, a higher Young's modulus, a higher proportional limit and higher tensile fracture strength compared with the cold-drawn wires [27]. Unitika Corporation has also developed a conveyer belt spinning technique, though the injection way of the ejection molten alloy beam into rapidly flowing water layer is the same as that for the in-rotating-water spinning method [28]. The conveyer method has some advantages of achieving more mass production and higher cooling rate. However, the equipment is on a large scale and hence its production cost is considerably higher.

Around 1980, the production of glassy alloy wires was also tried by the injection method of melt in a confluent fluid (Kavesh method) as well as by the glass-coated melt spinning method (Taylor method) [29]. However, we recognized that the melt must be injected in a confluent cooling fluid with viscosity nearly equal to that of the molten metal and solidified before the changing into droplets for the former method. It was therefore rather difficult to get a continuous glassy alloy wire with smooth outer surface. Similarly, the latter method has a disadvantage that the melting temperature of metallic alloys processed is nearly equal to the softening temperature of the

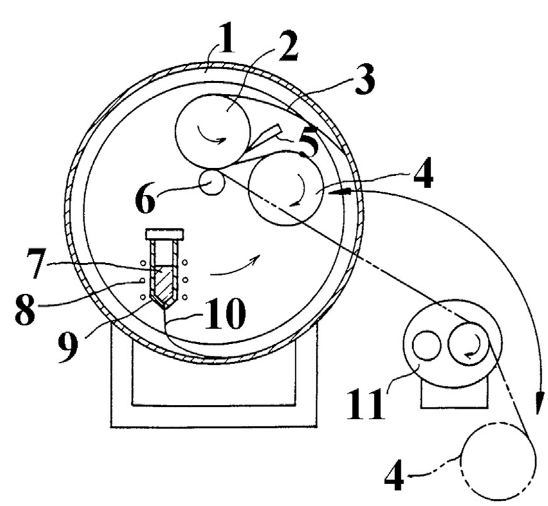

Fig. 2. Schematic illustration of the in-rotating-water spinning apparatus combined with a winder. 1. Rotating drum; 2. First magnet roller; 3. Wire specimen; 4. Second magnet roller; 5. Scraper; 6. Nip roller; 7. Molten alloy; 8. High frequency coil; 9. Melting crucible; 10. Ejected alloy; 11. Winder [26].