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Fabrication and characterization of Fe-based amorphous coatings prepared by high-velocity arc spraying

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ABSTRACT

Fe-based coatings with a high amorphous content were firstly developed by the traditional twin wires arc spray technology. In consideration of empirical rules, including the multi-component system, an optimal concentration of small atoms, negative heat of mixing and an appropriate atom size mismatch among the main components, the cored wires were designed to contain eight elements, which have an optimized atomic volume strain criterion λ_n, in range of 0.14–0.21, to render the coatings a high glass forming ability. Then the coatings were prepared using the above-designed cored wires through a rapid arc spray melting and solidification process. Crystalline phases could not be identified from the XRD patterns within the XRD resolution limits, suggesting that the as-sprayed coatings were approximately comprised of fully amorphous phases. With a dense structure and a low porosity of only 2%, the amorphous Fe-based coatings exhibited an attractive combination of high hardness (900–1100 $HV_{0.3}$) and superior bonding strength (44.9–54.8 MPa). The coating at $\lambda_n = 0.21$ had the lowest Gibbs free energy difference ΔG, exhibited the largest super-cooled liquid region ΔT_x, Lu's criterion factor γ value and the heat of crystallization (ΔH) values, which indicating the highest GFA.

1. Introduction

With a combination of high mechanical strength, superior corrosion resistance and excellent soft magnetism, the development of bulk metallic glasses (BMGs) has attracted much attention in the recent decades to meet the ever-growing requirements of the industry [1,2]. However, the wide applications of BMGs are still limited due to their inherent drawbacks, such as apparent room-temperature brittleness [2], high fabrication cost and the technical difficulties in fabrication of large-size products.

Thermal spray has been recognized as one of the most promising approaches to reduce the preparation cost, improve the toughness, and thus widen the industrial application field of the Fe-based amorphous materials [3]. Recently, significant efforts have been conducted to develop high performance Fe-based amorphous coatings by high velocity oxy-fuel (HVOF) spray, plasma spray (PS), twin-wire arc spray (TWAS), etc [4,5]. These thermal spray technologies show promising applications in ships in marine environment, containers for the spent nuclear fuel, oil and gas industries and power stations [3].

However, during thermal spray processes, the formation and retention of a non-equilibrium phase, i.e. an amorphous phase, is still a challenging task. It requires not only a high glass forming ability of the powder feed stock, but also a sufficiently rapid cooling rate of the melted droplets in the thermal spray process. The cooling rate of the molten droplets in the PS was reported to be $\sim 10^7$–10^8 K/s [3]. Even that in HVOF process ($\sim 10^4$ K/s [3]) or arc spray process ($\sim 10^5$ K/s [3]) was orders of magnitude lower, it is still high enough to deposit many alloy compositions above the respective critical cooling rate, thereby maintaining a vitreous state. In recent years, HVOF and PS technologies have been considered as the two most attractive approaches for the deposition of amorphous coatings [4]. Otsubo et al. [6] and Kishitake et al. [7] reported that coatings with 100% amorphous phase content were successfully fabricated by HVOF and low-pressure plasma spraying (LPPS). However, in order to get a high amorphous phase content and chemical composition uniformity in amorphous coatings, powder feedstock for the HVOF or PS processes should be generally prepared by gas or water atomization of BMGs, which is quite tedious to increase the cost greatly. In addition, the amorphous phase content and composition homogeneity of the as-obtained powder feedstock cannot be guaranteed since they are extremely sensitive to various atomization approaches and operating parameters.

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In the present study, we firstly reported that Fe-based coatings with a high amorphous content were fabricated by a more simple and efficient coating process, i.e., the traditional twin wires arc spray (AS) technology. Compared to HVOF and PS processes, AS exhibits many unique advantages, such as a high spray rate, a short treating time, a low production cost, and on-site operation ability [8]. By this route, the wide applications of Fe-based amorphous coatings would come into reality to protect industrial components from deterioration in various aggressive environments. Meanwhile the restrictions in the practical application caused by the size limitation of bulk metallic glass would be released.

2. Composition design concept for the cored wires

In order to obtain the high amorphous content coatings, the feedstock used for the thermal spray processes should have a high glass forming ability (GFA). As proposed by Inoue [9] and Johnson [10], alloys with high GFA generally possessed the following compositional features: (I) a multi-component system, (II) significant atomic size ratios above 12%, (III) negative heat of mixing and (IV) deep eutectic rule based on the T_{rg} criterion. Therefore, the following four criteria were adopted for the composition design of the cored wires in the present study.

2.1. Multi-component

Based on the “Confused principle” [11], the GFA of glass formers would be enhanced by a multi-component alloy system, i.e., the more elements involved, the lower the chance to form a viable crystal structure, and the greater the chance of glass formation. In the present study, eight elements (Fe, Cr, Si, B, Nb, Mo, Ni and Al) were selected to form the Fe-based alloy system.

2.2. Topological models

For the bulk metal-metalloid materials, the best composition to form a glass is to contain about 75–85 at.% of the metal component and 25–15 at.% of the metalloid component according to the topological models [12]. In consideration of the burning loss and inevitable oxidation of the metalloid during the arc spray process, the composition in the present study was designed to contain 20 at.%, 25 at.%, and 30 at.% of the metalloid elements (B, C, Si.), respectively.

2.3. Negative heat of mixing

A large negative heat of mixing among the constituent elements is known to strengthen the interaction among the constituent elements and promote the chemical short range ordering in the liquid [13]. In the represent study, the mixing enthalpy calculated by Miedema’s model for the Fe–B, Cr–B, Nb–B, Fe–Si, Nb–Si, Cr–Si, Fe–C, Nb–C, Cr–C, Nb–Cr and Fe–Nb pair is −26, −31, −54, −35, −56, −37, −50, −102, −61, −7, and −16 kJ/mol, respectively [3].

2.4. Atomic volume strain criterion

For a multi-component alloy system, effects on the GFA of atomic volume strain was proposed to be evaluated by an empirical criterion λ_n [2], which in agreement with the experimental data of various alloy systems. The λ_n for the best glass-forming alloys of a multi-component system is calculated to be about 0.18 by Eq. (1).

$$\lambda_n = \sum_{B=1}^{n-1} |\Delta V_{AB}/V_A| \cdot C_B = \sum_{B=1}^{n-1} \left|(R_B/R_A)^3 - 1\right| \cdot C_B \qquad (1)$$

where R_A and R_B are the radii of the solvent and solute atoms, respectively. C_B (In atomic percent) is the solute concentration of element *B*. V_A is the atomic volume of *A*. ΔV_{AB} is the difference in atomic volumes between *A* and *B*. Thus, in order to obtain a high amorphous content, three feedstock materials were designed with special λ_n values of 0.14, 0.18, 0.21, which were labeled as F20, F25, F30 coating, respectively.

3. Experiment procedures

3.1. Cored wires

Fig. 1 shows the process for the preparation of cored wires used for AS. Initially, Chromium (99%), Boron carbide (B 85%, C 8%), Ferrosilicon (72%), Niobite (Nb 55%), ferromolybdenum (Mo 55%) and a trace amount of aluminum (Al 97%) were mixed by ball milling as the core (Fig. 1(a)). The ball milling was carried out at 180 rpm in ethanol using a stainless steel vial and balls with a ball/powder weight ratio of 5:1. The mixed powders were dried in a rotary evaporator at 60 °C for 24 h at a negative air pressure of 5 Pa, and then surrounded by an outer skin of 304L austenitic stainless steel to form cored wires, as shown in Fig. 1(b). The cross-sectional image of the as-prepared cored wire was shown in Fig. 1(c). The composition of the cored wires, as shown in Table 1, was designed according to the analysis in part 2.

3.2. Development of coatings

AISI 1020 steel was used as the substrate in the present investigation. The nominal chemical composition of the AISI 1020 steel is 0.23 wt.% C, 0.24 wt.% Si, 0.016 wt.% S, 0.012 wt.% P, 0.4 wt.% Mn and balance Fe. Prior to the arc spray process, the substrate was cut into a dimension of 30 mm × 10 mm × 8 mm, subsequently polished by SiC papers down to 150-grit, ultrasonically degreased in acetone, and then grit blasted with alumina powders. The prepared

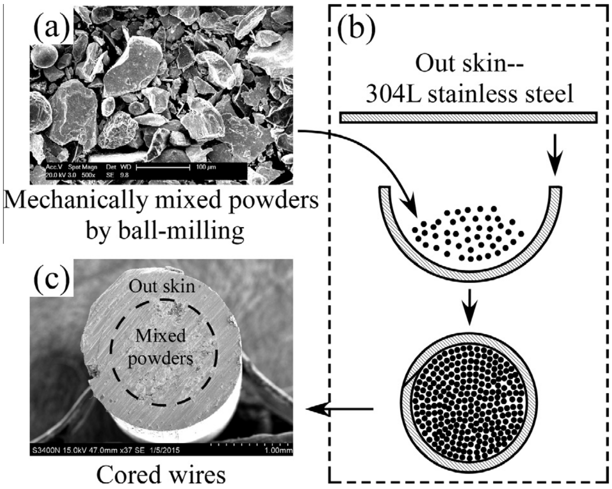

Fig. 1. (a) Morphology of the mixed raw powders, (b) preparation process of the core-wires. (c) Cross-sectional morphology of the as-prepared cored wires.

Table 1
The nominal composition of the prepared cored wires.

	Cr	B	C	Si	Nb	Mo	Ni	Fe
F20	<24.2	<16.5	<1.5	<2.0	<2.5	<1.0	<5.0	Bal.
F25	<21.5	<21.0	<2.0	<2.0	<2.5	<1.0	<5.0	Bal.
F30	<18.8	<25.5	<2.5	<2.0	<2.5	<1.0	<5.0	Bal.