Journal of Alloys and Compounds xxx (2017) 1–7

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Surface vitrification of alloys by pulsed electrical discharge treatment

Lei Zuo, Shujie Pang*, Shanfang Zou, Haifei Li, Tao Zhang**

Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, China

ARTICLE INFO

Article history:
Received 30 July 2016
Received in revised form
1 December 2016
Accepted 23 December 2016
Available online xxx

Keywords:
Amorphisation
Composite materials
Metallic glasses
Microstructure
Mechanical properties
Corrosion

ABSTRACT

Pulsed electrical discharge (PED) treatment was applied as a novel method to synthesize amorphous or amorphous/crystalline composite layers on the surfaces of Zr-, Fe-, Ti- and Al-based crystalline alloys. The formation of amorphous or amorphous/crystalline composite layers was investigated in terms of the significant disparity in glass-forming ability of the alloys. The influences of PED processing parameters on the surface glass formation of $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy were further discussed and the PED-treated alloy exhibited a gradient structure: amorphous surface, amorphous/crystalline composite region and crystalline substrate from surface to inside. Besides, effects of processing parameters on the microhardness and corrosion behavior of the treated $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy were investigated and the results revealed that the PED treatment could improve the microhardness and corrosion resistance of the crystalline substrate alloy. This PED treatment is a promising method to synthesize amorphous or amorphous/crystalline composite layers for novel mechanical, physical or chemical applications.

1. Introduction

Metallic glasses are considered to be suitable candidates for wear- and corrosion-resistant coatings for crystalline metallic components, due to their high hardness and corrosion resistance resulting from their unique structural uniformity [1–8]. With a high cooling rate, laser surface treatment technique has been employed to prepare metallic glass surfaces/coatings [9–11]. In view of high cooling rate, pulsed electrical discharge (PED) treatment may also be a feasible method for preparing glassy metallic surfaces/coatings. During the PED treatment, alloy surfaces can be melted by electrical discharge and subsequently solidified under the cooling effect of alloy substrates during pulse intervals. Additionally, dielectric fluid can be introduced during the treatment, which may also contribute to the cooling effect. Electrical discharge machining has been used for machining workpieces for decades, based on the principle of the conversion of electrical energy into thermal energy by generating a succession of controlled electrical discharges between the electrode and the workpiece immersed in a dielectric fluid [12,13]. Thus, surface vitrification of alloys by PED treatment may be fulfilled by the electrical discharge machining.

Attempts have been made to investigate the surface modifications of metallic materials by PED in the form of electrical discharge machining [14–18]. It has been reported that white layers were generated on a steel workpiece by PED treatment, leading to an increased resistance to corrosion and abrasion [14]. Besides, a crack-less layer of titanium carbide has also been formed by PED treatment to improve the surface properties [15]. Syntheses of coatings on alloy surfaces by PED treatment using powder metallurgy tool electrodes has also been reported [16–18]. However, PED treatment has not yet been used to synthesize amorphous or amorphous/crystalline composite layers on crystalline alloys. Different from laser surface treatment which is one-dimensional spot-scanning process, PED treatment is a two-dimensional process by applying the wire tool electrode to scan the alloy surface (Fig. 1). Thus, compared with laser surface treatment, PED treatment may be more efficiency to fabricate glassy metallic surfaces/coatings.

In the present study, surface treatments by PED using the wire electrical discharge machine were conducted on the Zr-, Ti-, Fe- and Al-based crystalline alloys with significant disparities in glass-forming ability (GFA) as well as thermal properties (Table 1) [19–23]. The influences of GFA as well as melting temperatures and microstructural heterogeneity of the alloys on the surface glass formation were investigated. The effects of processing parameters of the PED treatment, including pulse duration (t_{on}), pulse interval

* Corresponding author.
** Corresponding author.
E-mail addresses: pangshujie@buaa.edu.cn (S. Pang), zhangtao@buaa.edu.cn (T. Zhang).

http://dx.doi.org/10.1016/j.jallcom.2016.12.312
0925-8388/

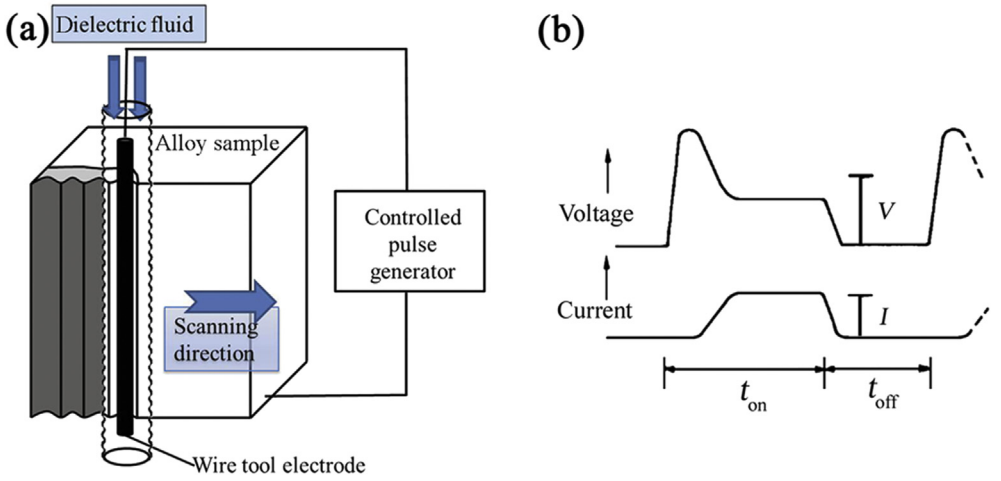

Fig. 1. (a) Schematic diagram of pulsed electrical discharge treatment on alloy surface, and (b) actual profile of a single PED pulse [13].

Table 1
Glass transition temperature (T_g), onset temperature of crystallization (T_x), solidus temperature (T_m), liquidus temperature (T_l) and critical diameters (D_c) of the Zr-, Ti-, Fe-, and Al-based metallic glasses.

Alloy (at.%)	T_g (K)	T_x (K)	T_m (K)	T_l (K)	D_c (mm)	Ref.
$Zr_{55}Al_{10}Ni_5Cu_{30}$	685	774	1090	1156	10	[19]
$(Zr_{0.55}Al_{0.10}Ni_{0.05}Cu_{0.30})_{98}Y_2$	673	763	–	–	12	[19]
$Ti_{45.5}Zr_{6.5}Cu_{39.9}Ni_{5.1}Sn_2Si_1$	670	711	1120	1205	4	[20]
$Ti_{50}Ni_{15}Cu_{25}Sn_5Zr_5$	680	765	–	–	5	[21]
$[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.2}]_{96}Nb_4$	820	870	–	1390	5	[22]
$Al_{86}Si_{0.5}Ni_{4.06}Co_{2.94}Y_6Sc_{0.5}$	–	497	903	1055	~1	[23]

(t_{off}), working voltage (V) and working current (I), on the surface structure and properties of the treated $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy with high glass-forming ability were further studied.

2. Experimental

Alloy ingots with nominal compositions of $Zr_{55}Al_{10}Ni_5Cu_{30}$, $(Zr_{0.55}Al_{0.10}Ni_{0.05}Cu_{0.30})_{98}Y_2$, $Ti_{45.5}Zr_{6.5}Cu_{39.9}Ni_{5.1}Sn_2Si_1$, $Ti_{50}Ni_{15}Cu_{25}Sn_5Zr_5$, $[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.2}]_{96}Nb_4$ and $Al_{86}Si_{0.5}Ni_{4.06}Co_{2.94}Y_6Sc_{0.5}$ (at.%) were prepared by arc-melting the mixture of the pure elements as well as an industry-grade FeB alloy in a Ti-gettered argon atmosphere. To guarantee the compositional homogeneity, the ingots were re-melted at least 5 times. The ingots were first cut into rectangular plates of 4 × 8 × 8 mm by a DK7716 type wire electrical discharge machine. Then, the square faces were polished with #2000 sand papers to eliminate the influences of the cutting. Finally, the polished surfaces of the rectangular plates were treated by PED using the wire electrical discharge machine with different processing parameters, and the schematic diagram and the actual profile of a single PED pulse [13] are shown in Fig. 1. The wire tool electrode is molybdenum wire. The central axis of the wire electrode (~120 μm in diameter) is 60 μm away from the alloy surface during the PED treatment.

Structures of the treated alloys were examined by X-ray diffraction (XRD, Bruker D8-advance) with Cu-Kα radiation, scanning electron microscopy (SEM, JEOL JSM-7500F) coupled with an energy-dispersive spectrometer (EDS) and high-resolution transmission electron microscopy (HRTEM, JEOL-2100F). For the TEM observation, the PED-treated surfaces of the samples were bonded together, and then the cross section was mechanically ground to ~50 μm in thickness and finally electro-polished to perforation at the bonded region with a 25% HNO_3-methanol solution at about 243 K. Thermal properties of the treated alloy surface layer were investigated by differential scanning calorimetry (DSC) at a heating rate of 0.33 K/s. The procedure to prepare DSC samples was as follows: a small piece was cut from the PED-treated alloy surface by diamond cutting machine, and then the small piece surface adjacent to the substrate was polished by sand papers to obtain a sample of several micrometers thick in order to reduce the impact of the substrate. Considering the wave surface of the recast layer, the DSC sample included both crests and troughs of the wave surface. Microhardness of the treated alloy surfaces was measured by Vickers hardness tester (450-SVD) under a load of 50 g for 15 s. Corrosion behavior of the treated surfaces in 3 mass% NaCl aqueous solution was characterized by electrochemical measurements conducted in a three-electrode cell using a PED-treated sample as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. After the specimens were immersed in the solution at room temperature for 1 h to achieve a stable open-circuit potential, potentiodynamic polarization curves were measured at a scan rate of 0.833 mV/s.

3. Results

The main parameters involved in the PED treatment includes pulse duration (t_{on}), pulse interval (t_{off}), working voltage (V) and working current (I). The surfaces of the Zr-, Ti-, Fe- and Al-based alloys were treated by PED at various pulse durations with fixed pulse intervals of 4 μs, working voltage of 82.5 V and working current of 1.2 A, and the optimum pulse durations for surface vitrification of each alloy (Table 2) were preliminarily determined according to the peak intensity and number in the XRD patterns. Fig. 2 shows the XRD patterns of the surfaces of the Zr-, Ti-, Fe- and Al-based alloys treated under their respective optimum t_{on}. A broad

Table 2
Optimum pulse durations for surface vitrification of the Zr-, Ti-, Fe- and Al-based alloys by PED treatment at fixed pulse interval of 4 μs, working voltage of 82.5 V and working current of 1.2 A.

Alloy (at.%)	t_{on} (μs)
$Zr_{55}Al_{10}Ni_5Cu_{30}$	64
$(Zr_{0.55}Al_{0.10}Ni_{0.05}Cu_{0.30})_{98}Y_2$	64
$Ti_{45.5}Zr_{6.5}Cu_{39.9}Ni_{5.1}Sn_2Si_1$	72
$Ti_{50}Ni_{15}Cu_{25}Sn_5Zr_5$	72
$[(Fe_{0.5}Co_{0.5})_{0.75}Si_{0.05}B_{0.2}]_{96}Nb_4$	80
$Al_{86}Si_{0.5}Ni_{4.06}Co_{2.94}Y_6Sc_{0.5}$	32

Please cite this article in press as: L. Zuo, et al., Surface vitrification of alloys by pulsed electrical discharge treatment, Journal of Alloys and Compounds (2017), http://dx.doi.org/10.1016/j.jallcom.2016.12.312