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Oxidation behavior of bulk amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coatings between 473 and 973 K in air

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Abstract

Amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating was sprayed onto a mild steel substrate using a kinetic spraying method, and the oxidation behavior of the coating was examined at temperatures ranging from 473 to 973 K in air. The coating was oxidized primarily to NiO, TiO_2 and tetragonal-ZrO_2. The coating did not offer adequate oxidation resistance, and its oxidation progressed primarily by the inward diffusion of oxygen, becoming more severe with increasing oxidation time and temperature. During oxidation, the amorphous coating crystallized to orthorhombic $Ni_{10}(Zr,Ti)_7$ and γ-Ni. At 973 K, the coating had completely transformed to a crystalline phase, and the surface oxidized substantially to form an oxidized region.

Keywords: Bulk amorphous alloy; Kinetic spraying; Oxidation; Nickel

1. Introduction

Amorphous materials are attracting considerable attention in industry on account of their useful engineering properties, including high strength, lack of grain-boundary weakness, and superior corrosion and wear resistance compared with traditional crystalline materials [1,2]. In addition, they can be used as a precursor for the production of nanostructured materials. In this study, the kinetic spraying process was used to deposit a bulk amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ feedstock. During kinetic spraying, solid particles were injected into a supersonic gas stream and accelerated above a certain critical velocity. The particles deformed severely upon collision with the substrate and bonded to the substrate as well as to each other to form a coating [3]. Kinetic spraying is basically a solid-state deposition process, which is unlike the thermal spraying process that utilizes the thermal energy of the impact particles [4]. The $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ feedstock is a new Ni-base bulk amorphous system with a high glass forming ability (GFA) and a large undercooling region (ΔT_x) [5,6]. However, the application of $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ as a coating at elevated temperatures to protect the substrate from chemical and mechanical attack is limited due to a transformation from a non-equilibrium amorphous phase to a crystalline phase by thermal activation. In addition, in oxidizing environments, the formation of oxide scale can limit the use of $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$. Therefore, the oxidation characteristics at elevated temperatures are important factors to consider for the widespread, successful utilization of an amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating.

The aim of this study was to examine the oxidation properties of a bulk amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating sprayed onto a mild steel substrate using a kinetic spraying process. The crystallization of the prepared coating, the oxidation products, and the oxidation mechanism were investigated at temperatures ranging from 473 and 973 K in air.

2. Experimental

A $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ bulk amorphous feedstock (57 wt.%Ni–18 wt.%Ti–20 wt.%Zr–3 wt.%Si–2 wt.%Sn) was produced by inert gas atomization [6]. The gas-atomized particles had a mean particle size of 37 μm. A diffuse halo peak, which is typical for an amorphous phase, was observed in the X-ray diffraction (XRD) patterns. The particles were examined by differential scanning calorimetry (DSC) at a heating rate of 0.167 K/s in an inert gas environment. An endothermic peak from the glass transition was observed at 819 K (T_g; glass transition temperature) and a double-step exothermic peak from the crystallization was observed beginning at 870 K (T_x; onset of

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Table 1
Kinetic spraying process parameters for bulk amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating

Process gas type	Helium
Process gas pressure	29 bar
Process gas temperature	823 K
Spraying distance	30 mm
Substrate	Mild steel
Powder feeding rate	4 rpm (36 g/min)
Gun travel speed	100 mm/s

crystallization). The oxygen content of the particles was 0.3 wt.%, as measured using a Leco N/O analyzer.

The gas atomized $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ particles were sprayed onto a mild steel substrate to a thickness of 370–430 μm using a kinetic spraying process. Table 1 lists the kinetic process parameters. The sprayed specimens were cut into approximately 10 mm × 10 mm rectangular plates using a low-speed diamond saw, cleaned with acetone, and oxidized at temperatures ranging from 473 and 973 K in air. After oxidation, the specimens were examined by scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS), electron probe microanalysis (EPMA), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and XRD.

3. Results and discussion

Fig. 1 shows the SEM/EDS/XRD results of the prepared bulk amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating. The top view shown in Fig. 1(a) indicates that the surface layer of the amorphous coating is rough, and slightly loose. Besides the well-flattened splats, some splats have retained their spherical shape due to insufficient impact energy. Generally, during kinetic spraying, the particles are plastically deformed once they impact the substrate. The coating is constructed from deformed particles to produce a continuous coating. The cross-sectional image shown in Fig. 1(b) indicates that rather a dense coating was produced along the depth direction as a result of the additional densification caused by the impact of subsequently deposited particles [4]. The dark, small spots in the coating are pores or oxides. The EDS line profiles shown in Fig. 1(c) suggest that all the coating elements are uniformly distributed. The oxygen content of the sprayed coating was 0.42 wt.%. For oxygen analysis, the substrate was removed, and the coating was crushed to a powder prior to analysis. Fig. 1(d) shows only a broad XRD diffraction pattern in the 2θ range of 36–49°, which is characteristic of an amorphous phase. When the $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ feedstock was sprayed using a high velocity oxy-fuel (HVOF) process, oxygen entrapment from the atmosphere resulted in the formation of Ti and/or Zr oxide phases [7]. In this case, a crystalline γ-Ni solid solution phase was detected due to the resultant depletion of Ti and/or Zr around the oxides. However, in the present kinetic sprayed coating, there was a comparatively lower amount of oxides present and no crystalline γ-Ni phase was detected.

Fig. 2 shows the Ellingham diagram of the oxides that formed on the $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating. The oxide stability increases in the order of NiO, SnO_2, SiO_2, TiO, and ZrO_2. Zr is the most active, and oxidizes to ZrO_2 in three distinct crystalline forms, i.e., cubic (stable between 2643 and 2953 K), tetragonal (stable between 1513 and 2643 K), and monoclinic (stable below 1513 K). These three polymorphs are non-metal deficit, n-type semiconductors, ZrO_{2-x}. The oxidation of pure Zr is controlled mainly by the inward diffusion of oxygen because oxygen anions can migrate easily by exchange with an anion vacancy [8]. Titanium is slightly less active than zirconium. Its transient oxides are TiO, Ti_2O_3, and Magneli phases, with the general formula, Ti_xO_{2x-1}. These phases oxidize rapidly to TiO_2 [9]. Depending on the defect concentrations, pure TiO_2 grows by either the out-

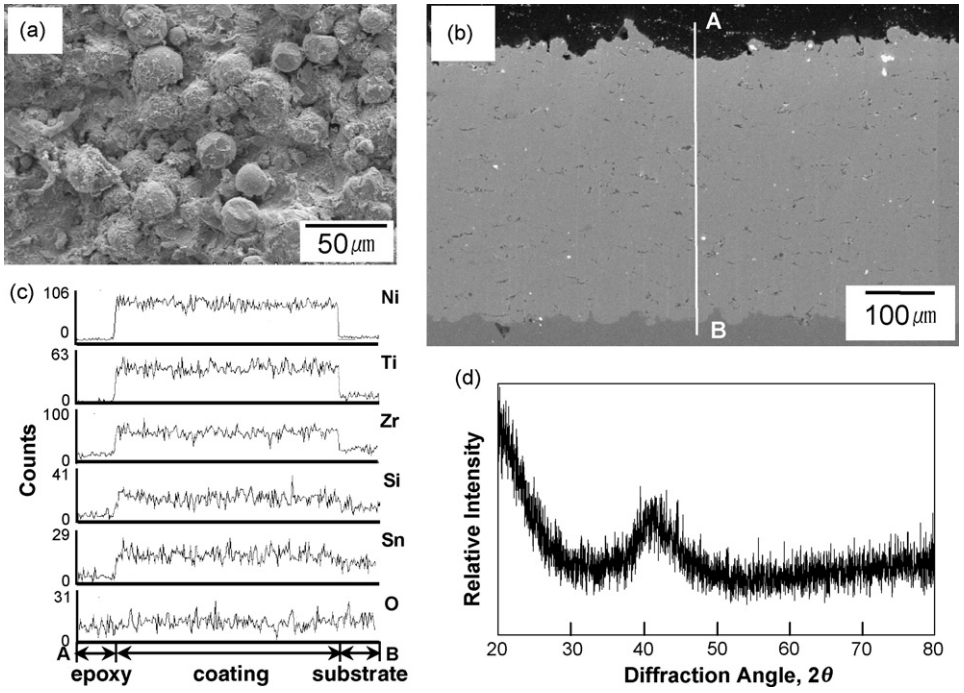

Fig. 1. Bulk amorphous $Ni_{57}Ti_{18}Zr_{20}Si_3Sn_2$ coating. (a) SEM top view, (b) SEM cross-sectional image, (c) EDS line profiles and (d) XRD pattern.