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Thermodynamic properties and crystallization kinetics of the $Co_{90}Sc_{10}$ amorphous alloy

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ABSTRACT

The thermodynamic properties and crystallization kinetics of the $Co_{90}Sc_{10}$ amorphous alloy prepared by rapid quench technique were investigated by X-ray diffractometer (XRD), differential scanning calorimeter (DSC), and simultaneous thermal analyzer (STA). In the isochronal heating process, the activation energy of crystallization is 388 kJ/mol, which was calculated by Kissinger method. The Johnson-Mehl-Avrami (JMA) model was used to describe the isothermal transformation kinetics. The variation of the activation energy of the isothermal process indicated that tiny Co particles precipitate out in the supercooled liquid region and become the nuclei of crystallization that reduce the activation energy at the beginning of crystallization process. Comprehensive results show that a-$Co_{90}Sc_{10}$ is a promising soft magnetic material for various applications.

1. Introduction

Co-based amorphous alloys have both scientific and technological unique properties. They exhibit excellent soft magnetic properties, such as low coercivity, low hysteresis loss, high permeability, and near-zero magnetostrictive effect etc. The Co-based amorphous alloys have wide applications in electronics, magnetic recording heads, magnetic sensors, and transformers [1]. Since 1970s amounts of magnetic Co-based amorphous alloys have been developed, which can be classified in metal-metal alloys such as Co-(Zr, Nb, Mo) [2], and metal-metalloid alloys such as Co-B, Co-P [3,4]. Multicomponent Co-based amorphous alloys fabricated by rapid quenched method were developed to obtain the enhanced magnetic properties, such as Co-Fe-B, Co-Si-B, Co-Fe-Si-B, Co-Fe-Zr-B, Co-Fe-Zr-Si-B, etc [5–7]. Co-based bulk metallic glass with both ultrahigh strength and good soft magnetic properties were also developed, such as Co-Fe-B-Si-Nb and Co-Fe-Ta-B [8,9].

Recently, our group reported a new kind of Co-based amorphous alloy $Co_{90}Sc_{10}$. This amorphous alloy exhibits the highest saturation magnetization (1.3T at 300 K) and Curie temperature (860 K) in comparison to any known Co-based amorphous alloys. Moreover, the $Co_{90}Sc_{10}$ amorphous alloy (a-$Co_{90}Sc_{10}$) shows excellent soft magnetic properties. Based on these findings, a-$Co_{90}Sc_{10}$ appears to be an attractive candidate of soft magnetic materials for applications [10]. Hence, it is interesting and necessary to understand the thermodynamic and kinetic properties of the a-$Co_{90}Sc_{10}$ alloy.

In this paper, the thermodynamic properties and crystallization kinetics of the a-$Co_{90}Sc_{10}$ alloy were systematically investigated by X-ray diffractometer (XRD), differential scanning calorimeter (DSC), and simultaneous thermal analyzer (STA). The activation energy of the crystallization can be obtained from the temperature dependence of the reaction-rate constant, which is known as Kissinger's method [11]. The kinetics of crystallization of amorphous alloys is often described by the phenomenological Johnson-Mehl-Avrami(JMA) equation for isothermal experiments [12]. All the results demonstrate that the a-$Co_{90}Sc_{10}$ material would be a very competitive soft magnetic material for different applications.

2. Experimental methods

Master alloys, with the nominal composition of $Co_{90}Sc_{10}$, were synthesized from a mixture of the elements with purity of 99.9% by arc melting under a Ti-gettered Ar atmosphere. The a-$Co_{90}Sc_{10}$ ribbons were produced using a single roll melt spinner with a copper wheel at a speed of 47 m/s in the Ar atmosphere. The resulting ribbons were typically 20 μm thick by 2 mm wide. In order to remove surface oxidation prior to experiments, the ribbons were carefully polished and finally washed in acetone in an ultrasonic cleaning machine.

An X-ray diffractometer system (Brucker, AXS D8) using Cu Kα-radiation within an angular range of 30° < 2θ < 80° was used to identify the structures of samples prior to all measurements.

The thermodynamic and kinetic properties of the a-$Co_{90}Sc_{10}$ ribbons were investigated in a simultaneous thermal analyzer (STA, NETZSCH STA 449F3) and a differential scanning calorimeter (DSC, TA Q2000). Aluminum and Alumina crucibles were used as sample holders,

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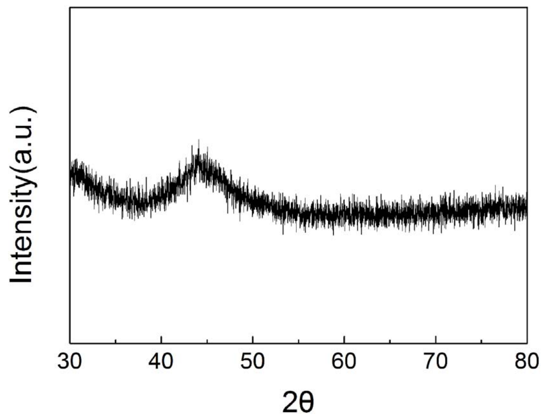

Fig. 1. XRD pattern of the as-prepared a-$Co_{90}Sc_{10}$ ribbon.

respectively. As-prepared samples were heated to 1500 K at a constant heating rate of 10 K/min in STA. The heat treatment of the samples was also performed under the same conditions. The isochronal DSC experiments were carried out at different constant heating rates ranging from 2 K/min to 100 K/min in the DSC instrument. Then isothermal crystallization of samples was tested at different temperatures. The samples were heated up to the annealing temperature at a heating rate of 20 K/min and then hold at this temperature to follow the crystallization until completion. Finally, the samples were cooled down to room temperature.

3. Results and discussions

3.1. XRD analysis

XRD pattern of the as-prepared a-$Co_{90}Sc_{10}$ ribbon presents a broad diffuse hump, which is the typical characteristics of the amorphous structure, as shown in Fig. 1.

3.2. Thermodynamic properties

The DSC curve of the as-prepared a-$Co_{90}Sc_{10}$ samples obtained from STA at the heating rate 10 K/min is shown in Fig. 2. Two exothermal peaks were observed in the DSC curve, which indicates two crystallization event occurred in the temperature range from 750 K to 950 K. The glass transition temperature (T_g) was also detected in the DSC curve. Therefore, the value of $\Delta T_x = T_{x1} - T_g$ is 92 K, which indicates that the a-$Co_{90}Sc_{10}$ materials have a quite good glass forming ability and thermal stability. The thermal parameters of the a-$Co_{90}Sc_{10}$ materials were summarized in Table 1. At the heating rate of 10 K/min, the

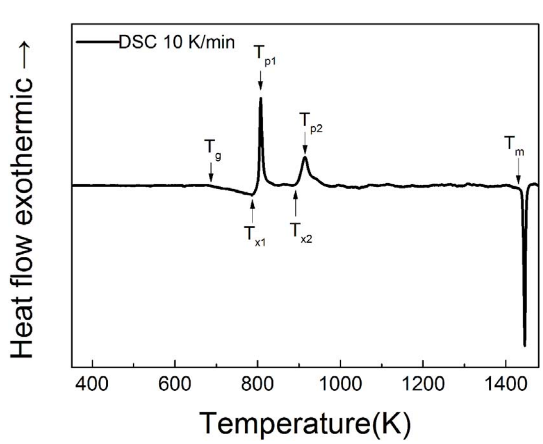

Fig. 2. DSC curve of a-$Co_{90}Sc_{10}$ at the heating rate of 10 K/min.

Table 1
Thermal parameters T_g (glass transition temperature), T_x (onset temperature of crystallization), ΔH_x (transformation enthalpy), T_m (fusion temperature), ΔH_m (fusion enthalpy), ΔT_x (supercooled liquid region) and T_{rg} (reduced glass transition temperature) of the a-$Co_{90}Sc_{10}$ materials.

T_g (K)	T_{x1} (K)	$\lvert\Delta H_{x1}\rvert$ (J/g)	T_{x2} (K)	$\lvert\Delta H_{x2}\rvert$ (J/g)	T_m (K)	$\lvert\Delta H_m\rvert$ (J/g)	ΔT_x (K)	T_{rg}
695	787	74.04	896	27.18	1439	64.68	92	0.48

Table 2
The magnetic and thermal properties comparison of different Co-based amorphous alloys. M_s is the saturation magnetization. T_c means the Curie temperature. T_x represents the onset temperature of crystallization.

	Ms (T) at 300 K	T_c (K)	T_x (K)	State of samples
$Co_{90}Sc_{10}$ [10]	1.3	860	787	ribbon
$Co_{66}Fe_4Ni_1Si_{15}B_{14}$ (Metglas® 2714A) [17]	0.57	498	823	ribbon
$Co_{67}Fe_4Mo_{1.5}Si_{16.5}B_{11}$ (Vitrovac 6025) [18]	0.55	483	813	ribbon

T_g and the onset temperature of the first crystallization, T_{x1}, are 695 K and 787 K, respectively. The second crystallization occurs at 896 K. The crystallization enthalpy ΔH_{x1} = 74.04 J/g and ΔH_{x2} = 27.18 J/g were obtained by integrating the heat flow peaks from the DSC curve. The reduced glass transition temperature T_{rg} of a-$Co_{90}Sc_{10}$ is 0.48 while it is usually between 0.5 and 0.6 for Co-based multicomponent amorphous alloys [13–16]. As shown in Table 2, the crystallization temperature of a-$Co_{90}Sc_{10}$ is approximate with the commercial multicomponent Co-based amorphous ribbons. It should be noticed that this is uncommon for a binary amorphous alloy which contains no high melting point elements having a comparative high crystallization temperature as the multicomponent amorphous alloys. Considering the outstanding magnetic properties and the relatively high crystallization temperature, the a-$Co_{90}Sc_{10}$ demonstrates a strong competitiveness in Co-based soft magnetic materials.

DSC curves of a-$Co_{90}Sc_{10}$ were recorded during continuous heating at different heating rates (2, 5, 10, 20, 40 and 100 K/min) as shown in Fig. 3(a). The position of the first crystallization peak shifts to higher temperatures with the increasing heating rates and the numerical values of the characteristic transformation temperatures and enthalpies are listed in Table 3.where Φ is the heating rate, T_p is the peak temperatures, and C is a constant. The plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$ are shown in Fig. 3(b). The fitted straight line is clearly observed in Fig. 3(b), which is in good accordance with the Kissinger's equation. The value of activation energy in a-$Co_{90}Sc_{10}$ is 388 kJ/mol. As a contrast, the values of different Co-based amorphous alloys in the literature are shown in Table 4. Activation energy of amorphous alloys suggests the resistance to crystallization that is to say the thermal stability of amorphous alloy [19]. Amorphous alloy with a higher activation energy will be more stable. The activation energy varies with the composition of amorphous alloy. The more-component-elements amorphous alloys also have the higher activation energy in the most cases. Therefore it can be revealed that a-$Co_{90}Sc_{10}$, a binary alloy, has the relatively high activation energy among these multi-component Co-based amorphous alloys.

3.3. Isothermal behaviors

In isothermal crystallization process, the crystalline volume fraction x as the function of annealing time is given by Ref. [26]: