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Non-isothermal kinetic analysis on the phase transformations of Fe–Co–V alloy

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ABSTRACT

In this study, occurrence of different phase transformations was investigated in a FeCo-7 wt% V alloy upon heating to 1200 °C by the dilatometry method at different heating rates (5, 10, and 15 °C min^{-1}). It was found that four phase transformations (including B2-type atomic ordering in α phase, first stage of polymorphic transformation ($\alpha \rightarrow \alpha_r + \gamma$), ordering to disordering, and second stage of polymorphic transformation ($\alpha_r \rightarrow \gamma$) occur in this alloy up to 1200 °C. Two isoconversional methods, as Starink and Friedman, were used to determine variation of the activation energy with temperature, $E(T)$. Moreover, the empirical kinetic triplets (E, A, and $g(\alpha)$) were calculated by the invariant kinetic parameters (IKP) method and fitting model.

1. Introduction

FeCo alloys are known as soft magnetic materials with a high saturation magnetization [1,2]. Not only the high saturation magnetic moment, but also Curie temperature, and high permeability properties of Fe–Co alloys make its potential from magnetic recording head to drug delivery applications [3–9]. In FeCo alloys, two types of phase transitions have been established reliably, namely atomic ordering with the formation of a B2-type superstructure, and a polymorphic $\alpha \rightarrow \gamma$ transformation [1]. The ordering temperature is 730 °C; the ordering rate depends on the temperature, and at temperatures close to that commonly used for annealing of vicalloys, this rate is sufficient for the long-range order to be completed in several minutes [1]. However, the binary FeCo alloys are too brittle and difficult to fabricate due to the formation of a B2-type superstructure [1,10]. The ordering transformation is so rapid in the binary equiatomic alloy that it is impossible, under industrial conditions, to retain the disordered structure [11]. Hence, commercially available alloys contain a ternary addition in order to facilitate fabrication at room temperature [11–15]. The most commonly employed additive is vanadium [1,5,11–14]. The main role of vanadium is through its effect on kinetics of the atomic ordering transformation [11], so that, the disordered phase in the vanadium containing FeCo alloys can be retained by quenching [1,7]. In addition to the atomic ordering transformation, the polymorphic $\alpha \rightarrow \gamma$ transformation in α phase occurs in these alloys upon heating [1,16]. Not only ordering transformation, but also polymorphic transformation is one of the most effective phase transformations on the magnetic properties of these alloys [17], because Curie temperature of FeCo alloys coincides with α to γ transition temperature [16]. Temperature of the polymorphic transformation in the FeCo alloy with 50% Co lies above 900 °C [1,16,18]. The alloying with vanadium decreases this temperature [18].

On the other hand, FeCo alloys containing more than 2 wt% V possess semi-hard magnetic properties [1,2,19]. Further addition of vanadium increases the magnetic hardness even more, so that FeCo-(7–13) wt% V alloys can be used in producing active parts of rotors of synchronous hysteresis motors (SHMs) [19]. Depending on the amount of vanadium, the coercive force (H_c) of these alloys varies between 4.0 and 24.0 kA/m, and the residual induction (B_r) is between 0.6 and 1.25 T [19].

In a recent study by the present authors [20], it was shown that FeCo-7 wt% V alloy interestingly exhibits a wide range of magnetic properties, being strongly dependent on annealing conditions It was pointed out that the annealing conditions determine the governing phase transformations (including ordering and allotropic transformations) in this alloy. Therefore, quantification of the relation between annealing conditions (time and temperature) and the kinetics of these transformations is very important to design appropriate processing conditions. Despite its importance, the kinetics of phase transformations in FeCo–V alloys has not

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received enough attention. Accordingly, this paper is mainly aimed at study the non-isothermal kinetic analysis of phase transformations in a FeCo-7 wt% V alloy.

Thermal analysis is recognized as one of the best methods to gain the mechanism and kinetic analysis of various transformations of materials [21–24]. Continuous heating dilatometry (DIL), as one of the thermal analysis methods, is often employed to study the kinetics of solid-state transformation in alloys and steels [25–28], and the length change associated with the phase transformation is measured. For example, in the case of the allotropic transformation, the dilatometer signal is characterized by a pronounced contraction due to the difference in specific volume of α and γ phases. In this study, thermal analysis technique is used to determine the influence of annealing conditions on the occurrence of different phase transformations. Moreover, the obtained results are employed to calculate the true kinetic triplets of the non-isothermal phase transformations in the FeCo-7 wt% V alloy. For this purpose, the isoconversional Starink [29,30] and Friedman (FR) [31] methods in combination with the invariant kinetic parameters (IKP) method [32] and model fitting [24,33–35] were used.

2. Theoretical background

The results of the non-isothermal dilatometry can be used to calculate the kinetic parameters of the investigated process, i.e. the activation energy (E), the pre-exponential factor (A) and kinetic model ($g(\alpha)$) which are called the "kinetic triplet". Kinetic analysis of the solid-state reactions that are ruled by a single process, the reaction rate can be expressed by Eq. (1):

$$\frac{d\alpha}{dt} \cong \beta\frac{d\alpha}{dT} = Aexp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (1)$$

where α is the degree of conversion, β is the linear heating rate (°C min^{-1}), T is the absolute temperature (K), R is the general gas constant (J mol^{-1} K^{-1}), t is the time (min), A the pre-exponential factor (min^{-1}) and E is the activation energy (kJ mol^{-1}).

Integration of Eq. (1) leads to [29,34]:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A\int_0^t \exp\left(\frac{-E}{RT}\right)dt \qquad (2)$$

where $g(\alpha)$ is the integral form of the reaction model (Table 1). It should be noted that most of these models are specific to the solid-state reactions. They have a very limited applicability when interpreting the phase transformations kinetics that do not involve any solid phase [24].For constant heating rate conditions, the integral with respect to time is usually replaced with the integral with respect to temperature:

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp\left(\frac{-E}{RT}\right)dT \qquad (3)$$

This rearrangement introduces the explicit value of the heating rate in Eq. (3), i.e., the application area of the equation is limited to the processes, in which the sample temperature does not deviate significantly from the reference temperature [24].

Since, the integral in Eq. (3) does not have an analytical solution, a number of approximate solutions have been developed. All of these approximations lead to a direct isoconversional method. The isoconversional methods are the most reliable methods for the calculation of activation energies of thermally activated reactions [29,30,36–43]. Model-free kinetics is based on an isoconversional technique that calculates the effective activation energy as a function of α of a chemical reaction [24]. In other words, E values and E vs. α dependence have been calculated by means of isoconversional methods, while they do not give any information about A and $f(\alpha)$. Hence, in this article the kinetic analysis is performed not only by isoconversional methods but also by the invariant kinetic parameters (IKP) method [32] and fitting models [24,33–35].

Table 1
Algebraic expressions for $g(\alpha)$ used to describe the solid state reactions [53,54].

No	Model notation	Reaction model	$g(\alpha)$
1	P2	Power law, $n = 1/2$	$\alpha^{1/2}$
2	P3	Power law, $n = 1/3$	$\alpha^{1/3}$
3	P4	Power law, $n = 1/4$	$\alpha^{1/4}$
4	R1	One-dimensional phase boundary reaction	α
5	R2	Two-dimensional phase boundary reaction	$1-(1-\alpha)^{1/2}$
6	R3	Three-dimensional phase boundary reaction	$1-(1-\alpha)^{1/3}$
7	F1	First-order reaction (Mample)	$-\ln(1-\alpha)$
8	F2	Second-order reaction	$(1-\alpha)^{-1}-1$
9	A3/2	Avarmi-Erofeev, $n = 1.5$	$[-\ln(1-\alpha)]^{2/3}$
10	A2	Avarmi-Erofeev, $n = 2$	$[-\ln(1-\alpha)]^{1/2}$
11	A3	Avarmi-Erofeev, $n = 3$	$[-\ln(1-\alpha)]^{1/3}$
12	A4	Avarmi-Erofeev, $n = 4$	$[-\ln(1-\alpha)]^{1/4}$
13	D1	One-dimensional diffusion	α^2
14	D2	Two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$
15	D3	Three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$