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Kinetic modelling of thermophysical properties of shape memory alloys during phase transformation

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HIGHLIGHTS

- Kinetic modelling of the phase transformation of shape memory alloys was conducted.
- The kinetic model can describe the heating rate effect on the phase transformation.
- A Linearity method was developed for estimating the kinetic parameters.
- The Linearity method gives more accurate results of the kinetic parameters.
- A new specific heat capacity model was also developed.

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ABSTRACT

Properties of shape memory alloys during phase transformation are strongly affected by the heating rate based on the kinetics of phase transformation. A new mathematical approach, named Linearity method, was developed for estimating the kinetic parameters and degree of phase transformation at different heating rates. This method was found to be more appropriate in estimating these properties than the existing Kissinger method. A specific heat capacity model considering the heating rate effect was also developed and validated against the experimental results. These estimated properties can be used for determining the behaviour of the materials applied upon heating at varying rates.

1. Introduction

Shape memory alloys (SMAs) are well known as active materials and have been widely applied in civil structural applications to achieve efficient structural performance. The properties of the materials used for enhancing the performance of various structures are the superelasticity and shape memory effect. The superelasticity and shape memory effect are associated with the thermoelastic phase transformation between a low-temperature martensite and a high-temperature austenite phase [1,2]. Upon cooling, the phase transformation of SMAs from austenite phase to martensite phase occurs at martensite start temperature (M_s) and is completed at martensite finish temperature (M_f). Upon heating, the phase transformation of SMAs from martensite phase to austenite phase occurs at austenite start temperature (A_s) and is completed at austenite finish temperature (A_f). At temperatures above A_f, the SMAs demonstrate superelasticity which allows the materials to achieve a large strain induced by loading and to recover the strain completely in a hysteresis loop through subsequent unloading [3,4]. The materials possess shape memory effect in which the residual strains in the alloys can be recovered and the alloys without shape constraint regain the original shape upon heating. During heating, the materials transform from martensite to austenite phase [5,6]. The strain recovery of the temperature-increasing alloys derived from the propagation of phase transformation has been used to control the structural behaviours in order to enhance the performance of many civil structures. Therefore, these properties are needed for accurate prediction of the phase transformation process in order to obtain a robust design for the civil structural applications of SMAs.

SMAs have been used as reinforcements for concrete structures [7–10]. The ability to recover large residual strains based on the shape memory effect has been taken advantage of to achieve

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rehabilitation, prestressing and strengthening of concrete structures. SMAs with residual strains are embedded in concrete structures and constrained. By electrically heating the SMAs, the materials tend to recover the residual strains and generate large recovery stress due to the constraining of strain recovery [11]. The recovery stress is used for prestressing concrete structures [7] or for closing the cracks of concrete structures for rehabilitation [8,9]. The SMAs with residual strains can also be embedded eccentrically in the concrete beam. The recovery stress generated from heating the SMAs leads to a bending action on the concrete beam which counteracts the bending moment imposed due to external loading. In this way, the concrete beam is strengthened [10]. In these applications, the SMAs are subject to heating at varying rates ranging from 0.43 °C/min to 51.4 °C/min. However, no studies have been performed to assess the effect of heating rate on the behaviour of the structures with SMAs when heated.

SMAs have also been used as active fire protection for steel structures [12]. SMAs with prestrains are installed underneath the steel beam and constrained. During heating at high temperatures, the recovery stress generated in SMAs induces a bending moment in the beam counteracting the bending action of the steel beam due to the applied load. Consequently, the bending moment in the steel beam is reduced and the fire endurance period of the steel beam can be improved. Under fire condition such as the ISO standard fire curve [13], the heating rate of the fire temperature varies with time. However, the prediction of the behaviours, such as the phase transformation process and thermal properties, of the materials applied upon heating at varying rates has never been conducted before.

In order to obtain robust design of structures with SMAs which may be subject to heating at varying rates, the heating rate effect on the material properties of SMAs needed for estimating the behaviour of the structures was determined in the current study. The propagation of phase transformation from martensite to austenite needs to be understood for the applications of SMAs when taking advantage of the shape memory effect. In particular, the determination of the specific heat capacity is necessary for estimating the temperatures of SMAs as well as the time required to reach the phase transformation temperatures. An experimental investigation into the effect of heating rate on these properties has been conducted [14]. In this study, the phase transformation temperatures and the specific heat capacity were measured at discrete heating rates. It was found that both the phase transformation temperatures and the specific heat capacity during phase transformation were significantly influenced by the heating rate. Ignoring the heating rate effect on these properties leads to inaccurate estimation of the properties of the materials. However, these experimental measurements were performed at a limited number of heating rates. Since the SMAs may be subject to heating at any given heating rate for their potential usage, there is a need to develop methods for determining these properties for general civil structural applications of SMAs.

In the present study, the kinetics of phase transformation was considered and subsequently adopted to model the degree of phase transformation of SMAs with increasing temperature when different heating rates were applied. A Linearity method was developed for estimating the kinetic parameters in the Arrhenius equation for kinetics so that an accurate model for the degree of phase transformation at any given heating rate can be obtained. From the results of solving the kinetics problem, a specific heat capacity model was also developed to describe the variation of the specific heat capacity during phase transformation under varying heating rates. The properties estimated using this method can then be used to predict the temperature distribution and the strain recovery of the materials. The Linearity method and the specific heat capacity model are validated through comparisons with the experimental results. The current study was performed based on NiTi SMAs since they have been widely applied to civil structures by researchers [7–10,12] due to their favourable properties including high recovery stresses and large recovery strains [11].

2. Kinetics for phase transformation

2.1. Degree of phase transformation

The Arrhenius equation for solving kinetic problems was adopted in this study for modelling the degree of phase transformation of shape memory alloys. It was chosen because it has been a powerful tool in physical science to describe the temperature dependence of material reaction rate at molecular level. It is ideal for the present study to describe the phase transformation process through which the SMA materials absorb the activation energy (E_A) for the development of phase transformation from martensite to austenite during heating [15]. Besides, the fraction of molecules remaining in martensite phase also affects the reaction rate of phase transformation [14,16,17] and this effect can also be determined using the reaction kinetics. Therefore, the rate of phase transformation at any given temperature, T, can be generally described as:

$$\frac{d\alpha}{dt} = A * exp\left(\frac{-E_A}{RT}\right)(1-\alpha)^n \tag{1}$$

where α is the degree of phase transformation taken as the volume fraction of transformed material [15]. The value of α is zero before the start of phase transformation and reaches one when the phase transformation is completed. In this case, the value of α gives the fraction of austenite transformed from martensite phase in the materials with starting and finishing temperatures which vary according to heat treatment temperatures and modelling methods. The rate of phase transformation, $\frac{d\alpha}{dt}$ at time t is a function of R the universal gas constant (8.314 J/mol K), n the reaction order, E_A the activation energy, T the temperature and A the pre-exponential factor.

If the materials are subject to heating at any given heating rate, β, the following equation is obtained.

$$dt = \frac{dT}{\beta} \tag{2}$$

Combining Eqs. (1) and (2) gives

$$\frac{d\alpha}{dT} = \frac{A}{\beta} exp\left(\frac{-E_A}{RT}\right)(1-\alpha)^n \tag{3}$$

The degree of phase transformation can be determined using Eq. (3) at different temperatures if the values of the kinetic parameters as β, A, E_A and n are known.

In order to evaluate the kinetic parameters, differential scanning calorimetry (DSC) tests characterising the propagation of phase transformation from martensite to austenite at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min were conducted for NiTi shape memory alloys heat treated at both 350 °C and 450 °C. These heating rates were used to investigate the heating rate effect on the behaviour of shape memory alloys and they are within the range of the heating rate applied to shape memory alloys which have been used as the reinforcements of concrete structures and the fire protection of steel structures as a result of the temperature rise according to specified fire curves such as the ISO standard fire curve. The results were presented in the previous study through the experimental investigation [14] and were used for determining the kinetic parameters for the current study. The theoretical values calculated from Eq. (3) using the