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Alloying effect on *K*-shell fluorescence parameters of porous NiTi shape memory alloys

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ABSTRACT

The $K_{\alpha,\beta}$ shell production cross-sections and K_β/K_α intensity ratios of porous Ni –49 at% Ti shape memory alloys were determined using energy dispersive X-ray fluorescence (EDXRF) technique. Also, the alloying effect on the *K* shell fluorescence parameters was investigated. The samples were excited by 59.5 keV γ-rays from an ^{241}Am annular radioactive source. The K X-rays emitted by the samples were counted by an Ultra-LEGe detector with a resolution of 150 eV at 5.9 keV. The structure analyses of the samples were also made using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The deviations between the present results and theoretical values, calculated for pure Ti and Ni, were attributed to charge transfer phenomena and/or rearrangement of valance shell electrons and porosity.

1. Introduction

NiTi shape memory alloys (SMAs), also known as "Nitinol" alloys, have been widely used in industrial and medical devices due to their good biocompatibility, unique shape memory properties, mechanical properties, superior damping capability, and excellent corrosion and wear resistance [1,2]. The porous NiTi SMAs have been regarded as a promising biomaterial for use an artificial bones and teeth roots. Moreover, these alloys have the adjustable mechanical properties, reduced weight and increased biocompatibility due to their porous structure allowing in-growth of the human tissue, nutrition exchange and medicament transportation within human bodies [3,4]. At low temperatures, the porous NiTi SMAs form "martensite" structure, however heating leads to destruction in the phase and causes phase transformation to a stable structure "austenite" [1]. NiTi alloys exhibit a one-step martensitic phase transitions from the high temperature B2 to the B19′ (monoclinic) phase or a two-step martensitic phase transitions from B2 to R to the B19′ phase. The R-phase is a rhombohedral distortion of the B2 lattice along the $[1\,1\,1]_A$ direction [5]. One- or two-way shape memory effects are accompanied by reversible thermoelastic transitions and changes of internal stress in the material during cooling and heating. The phase transition properties of the porous NiTi alloys strongly depend on the chemical composition, hot/cold processing, thermal or thermo-mechanical cycles. Besides, the temperature range of transitions, the mechanical and shape memory properties, also strongly depend on the same fabrication process [6].

3d transition metals have a variety of physical properties and have been used in a large number of applications. Because of this, studies to understand the valance-electron configurations of 3d transition metals in various systems have been carried out [7]. EDXRF method and *K* shell fluorescence parameters have been used to provide useful information on the electronic structure of 3d transition metals [8–14]. It is well known that the X-ray fluorescence parameters depend on the physical and chemical environments of the elements in a sample. This dependence can be explained as due to changes of the 3d electron population in the transition metal.

Brunner et al. [15] investigated the chemical influences on the K_β/K_α X-ray intensity ratios in Cr, Mn, Fe and Cu. They thought that this effect arises from the contraction of 3d orbitals, which in turn is due to screening altered by a varying 3d charge delocalization. Polasik [16] carried out multiconfiguration Dirac–Fock calculations for 3d transition metals to explain the dependence of the K_β/K_α X-ray intensity ratios on the changes in configurations of valance electron configurations. He found that the K_β/K_α X-ray intensity ratios increase with atomic number for each type of electronic

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Table 1
The list of the porous NiTi alloys fabricated with different processes.

Samples no.	Sample composition (at%)	Preheating temperature (°C)	Cold compaction pressure (MPa)	Solution heat treatment and time	Porosity (%)
1	Ni-49Ti	100	100		47.31
2	Ni-49Ti	200	100		43.71
3	Ni-49Ti	250	100		42.51
4	Ni-49Ti	300	100		42.10
5	Ni-49Ti	350	100		41.61
6	Ni-49Ti	200	100	1050 °C, 10 min	43.71
7	Ni-49Ti	200	100	1050 °C, 20 min	43.71
8	Ni-49Ti	200	100	1050 °C, 30 min	43.71

configuration, and are quite sensitive to changes in the valance electron configuration. Furthermore, Ni K_α X-ray fluorescence spectra were measured for 32 kinds of materials containing Ni by Konishi et al. [17] using a double-crystal X-ray spectrometer. The chemical shifts and the linewidths of the materials were determined from the measured spectra. Dagistanli et al. [18] calculated 3d occupation numbers of transition elements corresponding to various types of atomic configurations by using the linear muffin–tin orbital method. In addition, studies of *K* shell fluorescence parameters of 3d metals and their complexes and alloys have been performed by our groups using ED-XRF technique [19–23].

In this study, the alloying effect on the $K_{\alpha,\beta}$ X-ray production cross sections and K_β/K_α X-ray intensity ratios in the porous Ni −49 at% Ti shape memory alloys produced by self-propagating high-temperature synthesis at the different preheating temperatures has been investigated.

2. Experimental procedure

2.1. Sample preparation

Ni (99.8 wt-%) and Ti (99.5 wt-%) powders with an average size of −325 mesh (Alfa Aesar) were used. Mixed powders of Ni and Ti with 51 at-% Ni were blended in a rotating container for 24 h to produce a homogenous mixture. The resulting mixture was then pressed into cylindrical compacts, 10 mm in diameter, using a hydraulic press at a cold compaction pressure of 100 MPa. The green samples, after compacting at 100 MPa were preheated up to different temperatures, 100, 200, 250, 300 and 350 °C at a ∼15 °C/min heating rate in a furnace in a high purity argon gas atmosphere. The samples were then subjected an electrical discharge pulse (14 kV and 30 mA) for ∼2–4 s at each preheating temperature. The temperature of the green samples increased briefly as current was applied, ignition started. Once ignited, the combustion wave self-propagated rapidly along the axis of the specimen, and porous NiTi SMA was synthesized. To investigate the effects of solution treatment on microstructures, some of the synthesized samples, which were preheated at 200 °C after compacting at 100 MPa, were separately solution treated at 1050 °C for 10, 20 and 30 min in a furnace in a high purity argon gas atmosphere. The combustion channels followed a parabolic route along the specimen when it was ignited at the upper face. The orientation of channels indicates that combustion propagated perpendicular to the arc axis. The porosity of the fabricated samples was measured by the relative density method [4]. The general porosity consists of open and closed porosity. Ni–Ti alloy samples fabricated by different fabrication process as listed in Table 1.

2.2. ED-XRF measurements

The geometry of the experimental set-up and experimental equipment have been described in a previous study [24]. Samples were cut from the plugs and polished with emery papers to remove macro-level surface roughness and contamination, and cleaned in acetone and ethanol. The samples were excited by a filtered ^{241}Am radioisotope source which essentially emits monochromatic (59.5 keV) gamma rays. Fluorescent K X-rays were detected by a collimated Ultra-LEGe detector. One of the main problems in analyzing the data to determine the fluorescence parameters is spectral deconvolution due to strong peak overlapping in the ED-XRF. Good statistics is not enough for this purpose, and a careful fitting scheme is required in order to obtain accurate values for the peak areas. In the present work, a peak fitting program, developed by Origin Company, was used to determine accurate peak intensity. Fig. 1a and b shows $K_{\alpha,\beta}$ X-ray spectra of Ni and Ti for sample 5.

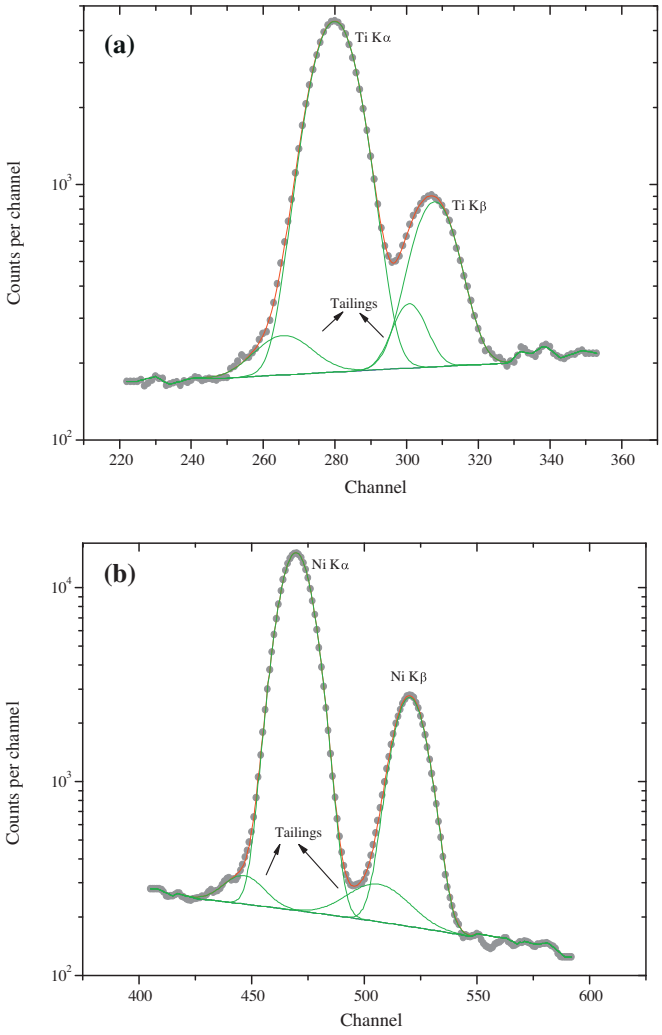

Fig. 1. (a) Ti K X-ray spectra of sample 5. (b) Ni K X-ray spectra of sample 5.