Intermetallics 52 (2014) 57–63

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Shape memory deformation mechanisms of Ru–Nb and Ru–Ta shape memory alloys with transformation temperatures

Anna M. Manzoni [a,*], Anne Denquin [a,1], Philippe Vermaut [b,c,2], Inés Puente Orench [d,4], Frédéric Prima [b,3], Richard A. Portier [b,5]

[a] ONERA, DMSM, 29 Avenue de la Division Leclerc, B.P. 72, 92322 Châtillon, France
[b] Groupe de Métallurgie Structurale LPCS UMR-CNRS 7045, Chimie Paristech, 11 rue P et M Curie, 75231 Paris, France
[c] Université Pierre et Marie Curie, 4 Place Jussieu, 75231 Paris, France
[d] D20 Institut Laue Langevin, 6 rue Jules Horowitz, Grenoble 38042, France

ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form
23 February 2014
Accepted 16 March 2014
Available online 15 April 2014

Keywords:
A. Intermetallics, miscellaneous
B. Shape-memory effects
B. Phase transformation
D. Martensitic structure
F. Diffraction

ABSTRACT

Ru-based high temperature shape memory alloys show different structures at different temperatures and composition. Equiatomic Ru–Ta and Ru–Nb show two subsequent phase transformations, but their individual influence is still unclear because of the difficulty of comparing the high temperature cubic phase, the intermediate tetragonal phase and the low temperature monoclinic phase. It is important to find a way to compare these structures in order to better understand the microstructure of these alloys and their shape memory behaviour. In order to get the necessary information the alloys have been investigated with neutron diffraction technique during in-situ heating up to about 1100 °C.

This study shows the evolution of the lattice parameters and the shape of the unit cells at different temperatures for the three phases these materials exhibit. It proposes a way to compare the different structures and it gives a mathematical expression of the phase transformations. The ultimate goal of this work is to enable a better understanding of the deformation mechanisms in the unit cell and a possible anticipation of the existence of a shape memory effect in these systems.

1. Introduction

Because of martensite transformation temperatures above 800 °C and shape memory properties [1–3], Ru–Nb and Ru–Ta have been found to be a very promising option for high temperature shape memory alloys [4]. Ru-based high temperature shape memory alloys have been object of various studies since the discovery of their shape memory effect in 1998 [1]. A special interest has been accorded to the equiatomic alloys, mostly due to their better shape memory properties [5-13]. Former works have shown that the total shape recovery of the equiatomic alloys is about 3% compared to less than 0.3% in alloys with 43 and 45 at.% Ru [12,14]. Furthermore, the equiatomic alloys are characterized by two successive martensitic transformations, one at high temperature (~1050 °C for RuTa, ~900 °C for RuNb [8,11,12]) from cubic β austenite to tetragonal β' martensite, and one at lower temperature (~785 °C for RuTa, ~750 °C for RuNb [8,11,12]) from the tetragonal martensite β' to monoclinic β'' martensite. Alloys with 45 and 43 at.% Ru show only the high temperature transformation [10,12–14]. The hysteresis of the alloys has been found to be very narrow, namely around 12 °C for both transformations in the equiatomic alloys and between 3 and 7 °C in the alloys with less Ru [8,10,12,13,15].

The shape memory effect in these thermoelastic alloys depends on the mobility of interfaces and the twinning shear amplitude, the latter being a numeric expression of the deformation which takes place during the austenite → martensite transformation [16]. Previous studies show the difficulty of comparing the different structures that occur during the transformations in these types of alloys [12,15]. The main problem of a valuable comparison has been the necessity of obtaining results at the transformation temperatures and the transformation of the unit cell from a tetragonal cell to the six times bigger monoclinic cell.

* Corresponding author. Tel.: +33 8062 42326; fax: +33 8062 42098.
E-mail addresses: anna_manzoni@gmx.net (A.M. Manzoni), anne.denquin@onera.fr (A. Denquin), philippe-vermaut@chimie-paristech.fr (P. Vermaut), puenteorench@ill.fr (I. Puente Orench), frederic-prima@chimie-paristech.fr (F. Prima), richard-portier@chimie-paristech.fr (R.A. Portier).
[1] Tel.: +33 146734492; fax: +33 180386132.
[2] Tel.: +33 143548702; fax: +33 146340753.
[3] Tel.: +33 144276704; fax: +33 146340753.
[4] Tel.: +33 476207477; fax: +33 476207226.
[5] Tel.: +33 143548703; fax: +33 146340753.

http://dx.doi.org/10.1016/j.intermet.2014.03.008
0966-9795/

The aim of this study is to propose a method to compare the structures of equiatomic Ru–Ta and Ru–Nb alloys at room temperature and when heated up to the austenitic phase. The observation of the c/a ratio of the tetragonal cell, which has been introduced in former works [9,12,13] has been expanded by the concept of a supercell in the cubic and the tetragonal phase in order to facilitate the comparison with the monoclinic cell. The evolution of the lattice parameters and the different structures are being discussed in terms of their influence on the deformation, the microstructure and the shape memory effect.

2. Experimental

Both studied alloys $Ru_{50}Nb_{50}$ and $Ru_{50}Ta_{50}$ have been prepared from elements of commercial purity by vacuum arc melting technique. The alloys have been re-melted several times and annealed in a vacuum furnace at 1600 °C for 168 h to ensure homogeneity. Final compositions were determined by atomic absorption spectrometry within an experimental precision of 0.5 at.% and proved to be very close to the intended compositions.

All specimens were cut by electro-discharge machining. Transformation temperatures have been determined on homogenised specimens by differential scanning calorimetry (DSC) from RT to 700 °C on a Mettler Toledo DSC 822e and from RT to 1200 °C on a Netzsch DSC404 apparatus with a heating/cooling rate of 10 K/min.

X-ray diffraction has been performed in a Philips PW 1380 with a Bragg–Brentano geometry and a source which provides Cu Kα radiation.

High temperature in-situ neutron diffraction has been performed at D20 at the ILL Grenoble, using a 4 m × 15 cm position sensitive detector. The wavelength was 1.3 Å and the flux 9.8×10^7 n° cm^{-2} s^{-1}. The recorded spectra cover a range of $2\theta = 153°$. Before the measurements a data calibration has been performed using a Si sample for the correct determination of the wavelengths and NAC for the instrumental resolution function.

In-situ heating has been achieved in a vacuum furnace. The temperature observations cover a range from room temperature up to about 1100 °C. Every 2.5 or 5 °C a spectrum has been recorded for both alloys. The acquisition time for the each spectrum was ~5 min.

The subsequent calculations have been achieved with the help of two software programs, namely Fullprof [17] for the determination of the lattice parameters and Scilab [18] for the calculations of the transformation matrices.

3. Results and discussion

Fig. 1(a) shows the unit cell of both $Ru_{50}Nb_{50}$ and $Ru_{50}Ta_{50}$ alloys at room temperature. Their structure has been determined by XRD measurements and TEM observations (not shown here) and it has been found to be monoclinic (P2/m). The former embodied tetragonal cell is shown in red dashed lines.

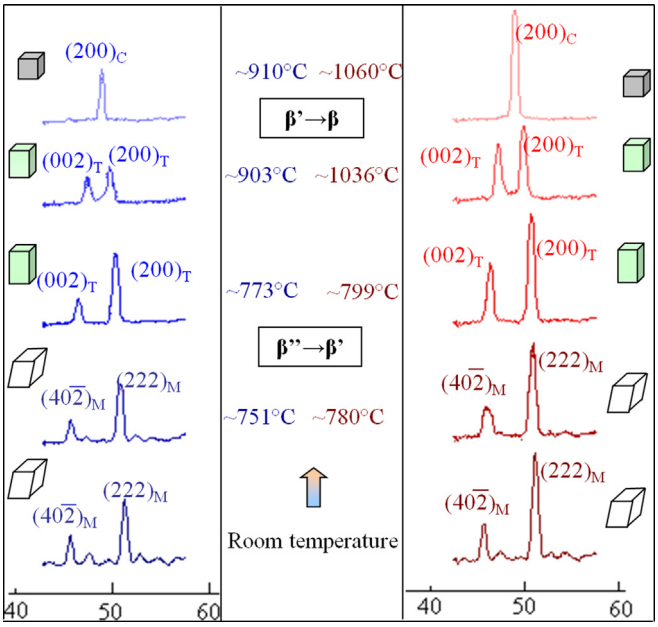

Fig. 2. Evolution of the neutron diffraction spectra ($\sim 43° \leq 2\theta \leq \sim 57°$) of the Ru–Nb alloy (left) and the Ru–Ta alloy (right) as a function of the temperature. (a) Room temperature, (b) just before the martensitic $\beta'' \rightarrow \beta'$ transformation, (c) just after the martensitic $\beta'' \rightarrow \beta'$ transformation, (d) just before the martensitic $\beta' \rightarrow \beta$ transformation, (e) just after the martensitic $\beta' \rightarrow \beta$ transformation. M stands for the monoclinic phase at low temperature, T for the tetragonal phase at medium temperature and C for the cubic phase at high temperature.

Both alloys have been observed by SEM (see Fig. 1(b)) and TEM in order to obtain information on the microstructure. They show a very similar microstructure, which is why only $Ru_{50}Ta_{50}$ is shown in Fig. 1(b). DSC results from former works [11–13] have shown that both alloys exhibit a cubic-to-tetragonal martensitic transformation from austenite to β' martensite, followed by a second transformation from this β'-tetragonal martensite phase to the β''-monoclinic martensite phase [8–13].

In order to follow the changes on the structure of both alloys while rising the temperature from RT up to 1200 °C, neutron diffraction experiments have been accomplished. The results obtained for the observed transformations are discussed from here onwards.

In the following, M stands for the monoclinic β'' phase at low temperature, T for the tetragonal β' phase at medium temperature and C for the cubic β phase at high temperature.

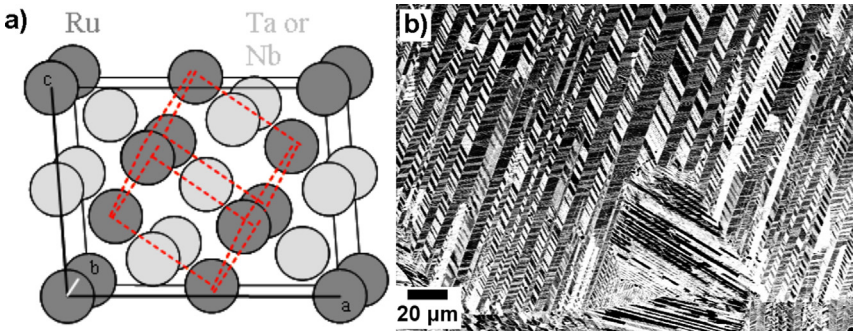

Fig. 1. (a) The monoclinic unit cell with the embodied former tetragonal cell, symbolized with a red dashed line and (b) an overview over the microstructure of $Ru_{50}Ta_{50}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)