Thermokinetic Simulation of Precipitation in NiTi Shape Memory Alloys

C D Cirstea1, E Karadeniz-Povoden, E Kozeschnik, M Lungu, P Lang, A Balagurov and V Cirstea

1National Institute for Research and Development in Electrical Engineering ICPE-CA, 313 Splaiul Unirii, 030138, Bucharest, Romania

E-mail: 1diana_cirstea@yahoo.com, diana.cirstea@icpe-ca.ro

Abstract. Considering classical nucleation theory and evolution equations for the growth and composition change of precipitates, we simulate the evolution of the precipitates structure in the classical stages of nucleation, growth and coarsening using the solid-state transformation Matcalc software. The formation of Ni3Ti, Ni4Ti3 or Ni3Ti2 precipitate is the key to hardening phenomenon of the alloys, which depends on the nickel solubility in the bulk alloys. The microstructural evolution of metastable Ni4Ti3 and Ni3Ti2 precipitates in Ni-rich TiNi alloys is simulated by computational thermokinetics, based on thermodynamic and diffusion databases. The simulated precipitate phase fractions are compared with experimental data.

1. Introduction

During the last years thermokinetic simulation have the best techniques to predict the evolution of the precipitates, allowing us to obtain materials with desired properties. NiTi shape memory materials show a reversible and diffusion less martensitic transformation between the austenite cubic phase with B2 structure and martensite monoclinic or orthorhombic phases with B19’ or B19 structure [1-3]. In NiTi near-equiatomic alloys trained for practical (or industrial) applications, the properties like shape memory and superelasticity are controlled by the presence of the precipitates. These precipitates can be induced in the B2 matrix of NiTi materials by thermo-mechanical treatment or by aging/annealing supersaturated Ni-rich from the matrix composition. Thus, by balancing the number and size of the precipitates with the aging/annealing time and temperature, the precipitates disturb the simple B2-B19’ transformation to B2-R-B19’ multi-stage transformation due to intermediate R-phase, in the case of Ni4Ti3 [4,5]. These transformations are extremely important, providing a Ni-depletion in the matrix and strain field induced in the surrounding Ni3Ti3 precipitates [1,6-8] with direct influence on martensitic transformation, opposite to Ni1Ti2, Ni3Ti or NiTi2 precipitates that don’t have any influence on martensitic transformation. Ageing or annealing of the Ni-rich NiTi alloys can lead to four types of precipitates and among them Ni4Ti3 and Ni3Ti2 are metastable phases, while Ni1Ti and NiTi2 are stable phases [1,2,5,6].

In order to design NiTi advanced materials we must understand the thermodynamics and kinetics processing design which often starts with a parametric design for chemical composition. For this reason it was shown in literature [1,2,5,9-11] that the change of composition (until 0.1 wt% Ni in composition), temperature (between 325-650°C for aging/annealing), pressure (protective or not protective atmosphere in the processed of those materials) and external force field (cold or hot
working of these materials for training) or every small adjustment lead to significantly different evolution of microstructure driven by the thermodynamics and kinetics of the NiTi system. It is known that thermodynamics is the core of the precipitation simulation and generally it is used the Calphad (calculation of phase diagram) method. The Calphad method is correlated with predictive models for kinetic process of particle size evolution (by modeling techniques quantitatively) [12]. The most kinetic models used for coarsening is represented by the Lifshitz-Slyozov-Wagner (LSW) theory [13-17]. Due to the relations between processes-structure-property of materials, were developed some kinetic models for particle size, or coarsening rate (Morral-Purdy model), or concomitant nucleation, growth and coarsening of precipitates (Kampmann and Wagner numerical (KWN) model) extended to multicomponent alloys systems [15,16,18]. Another design model from Calphad thermodynamic and kinetic to predict phase transformation kinetic is the Kolmogorov-Johnson-Mehl-Avrami (KJMA) model, which is used to study precipitation processes and to generate Precipitation- Temperature – Time (PTT) diagrams [12]. At present, there are a lot of commercial software package available on the Calphad technique like Thermo-Calc, Pandat, MTDATA, FactSage. A commercial precipitation-kinetics software package, MatCalc, that has been developed based on thermodynamic extremum principles [19-20] will be used in this paper to correlate the process-structure modeling of solid-state transformation with practical applications for NiTi materials obtained by spark plasma sintering (SPS) and aging at 400°C.

2. Experimental data

The thermokinetic simulations were performed with the MatCalc software, version 6.00 release 0.100, and the thermodynamic database mc_sma_v1.000, using optimized Gibbs energy functions of metastable phases from Povoden-Karadeniz et al. [21] and kinetic database mc_ni_v2.001.dub [22]. The selected phases for simulations were B2, Ni5Ti3, Ni3Ti1 and Ni2Ti, considering the kinetic behavior from literature [2,5,9] and corresponding to the SPS, AG treatments and to different conditions presented above.

For all simulations, the interfacial energy was set to $\gamma = 0.12 \text{ Jm}^{-2}$ for incoherent Ni5Ti phase. For Ni5Ti3 and Ni3Ti2 phases we used two correction files. The nucleation model used in the simulations was classical nucleation theory (CNT) and the growth model was Svoboda–Fischer–Fratzl–Kozeschnik (SFKK) [19,20].

For the present simulation, the nucleation site for each type of precipitate phase was defined according to experimental observations presented in papers [1-5,10,11,23]: nucleation was allowed in the bulk for Ni5Ti3, on dislocations for Ni3Ti2 and respectively, on grain boundary for Ni2Ti phases. All elements were kept in supersaturated solid solution at time $t = 0$. The results of coherent precipitation of Ni5Ti3 were compared with data observed experimentally for the sintering treatment that was made by spark plasma sintering (SPS) by applying a stress of 50MPa for 5 minute, heating at 900°C and 850°C for 2 minute and followed by aging (AG) at 400°C and water quenched. The aging treatment was carried out at 400°C, for 3 h, in a tubular furnace under argon atmosphere. The entire heat treatments take about 5 hours.

In order to test the applicability of the thermokinetic simulations, the NiTi materials must be characterized from the microstructural point of view by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, it must be done some nanoindentation tests for two compositions, respectively 50.8% Ni-Ti and 51.5% Ni-Ti. By the thermokinetic simulations we test the capability to reproduce the experimental microstructures of NiTi samples obtained by spark plasma sintering (SPS) for two different temperatures (900°C and 850°C) and aging (AG) at 400°C in the oven in argon atmosphere. All samples were embedded, grinded, polished and afterwards etched. The conditions of XRD and SEM and nanoindentation measurements are described in the papers [24]. In order to estimate the phase fraction of each crystalline phase, the XRD experimental spectrum was simulated using Rietveld method by Maud software, where the values of reliability factors were below 5%. The chemical compositions of precipitates were determined by EDS.
The NiTi samples with 51.5 at% Ni-Ti composition, obtained in SPS, were coded E1 for 900°C, respectively E2 for 850°C. Similarly, the NiTi samples with 50.8 at% Ni-Ti composition, were coded E3 for 900°C, respectively E4 for 850°C. The same code is used for thermokinetic simulation.

3. Results and discussions
In this section are presented the results of thermokinetic precipitation simulations in the Ni-Ti system for two different compositions and two different technological fluxes. Only for SPS we have different temperatures, namely 900°C and 850°C, while the conditions for aging (AG) applied on NiTi materials are the same (400°C). The SPS and AG treatment results from simulations conducted for NiTi materials with the atomic composition of Ni50.8Ti and Ni51.5Ti are presented in the figure 1.

![Figure 1. Simulations results for Ni50.8Ti and Ni51.5Ti obtained by SPS at 900°C or 850°C and AG at 400°C (MatCalc software).](image)

In the first step, the precipitation kinetic was simulated for Ni51.5Ti composition taking into account the different SPS temperatures and AG. The results of this simulation are summarized in figure 2 and figure 3. The phase fractions of Ni3Ti and Ni4Ti3 precipitates starts to increase for both heat treatments temperatures, being higher in E1 and E2 (more Ni in composition) than E3 and E4. Moreover, it was found that, during AG treatment, in E2 there is a tendency to decrease the Ni3Ti phase fraction, suggesting a coarsening process which is in accordance with table 1. The calculated precipitate radius at this point (at 400°C) is about 100 nm for E1 and 80 nm for E2, whereas the number density is in the range of 3·10^7 m^-3 (E1) or 1·10^18 m^-3 (E2). The values of precipitate radius calculated for E1 are higher than E2, while the number precipitate of E1 is smaller than E2. In addition, the Ni3Ti phase fraction decrease during AG in E2 and increase slowly in E1, while the Ni4Ti3 phase fraction decrease very slow in E2. The calculated mean radius for Ni3Ti precipitate is about 5-10 nm in E1 case and is much higher than in E2. The number density for Ni3Ti precipitate is high and this can be correlated with the values of the material hardness presented in table 2.

In the second step (Ni50.8Ti), the phase fraction of Ni3Ti and Ni4Ti3 precipitates start to grow for both E3 and E4, but the maximum values are lower than the E1 and E2. Similar to the results from the first step, it was found that during AG treatment, in E4 there is a tendency to decrease the Ni3Ti phase fraction, while in the E3 is growing. The calculated mean radius is about 140 nm for E3 and 60-80 nm for E4. In case of Ni4Ti3 precipitate, the mean radius decreases after AG. The number density for
$\text{Ni}_4\text{Ti}_3$ precipitate is very low according to simulations. The results obtained from simulations for the three parameters under consideration are comparable to [10,11,23,25] for a composition of 50.7%atNi.

Results of thermokinetic simulations of precipitate evolution for $\text{Ni}_4\text{Ti}_3$, $\text{Ni}_3\text{Ti}_2$ and $\text{Ni}_3\text{Ti}$ precipitates, particle size versus number density and the histograms of $\text{Ni}_4\text{Ti}_3$ and $\text{Ni}_3\text{Ti}_2$ precipitates are shown in figures 4 and 5 and are in accordance with table 1.

![Graphs showing phase fraction and mean precipitation radius](image1)

**Figure 2.** Results of the thermokinetic simulation of the precipitate evolution (phase fraction [%] and mean precipitation radius [m]) for E1 and E2 of $\text{Ni}_{51.5}\text{Ti}$.

![Histograms for Ni$_3$Ti and Ni$_4$Ti$_3$ precipitates](image2)

**Figure 3.** Histogram plot for $\text{Ni}_3\text{Ti}$ and $\text{Ni}_4\text{Ti}_3$ precipitates related to figure 2.

Since no thermal events were identified for $\text{Ni}_3\text{Ti}_2$ precipitates during the heat treatments, they were considered zero and, therefore, has not been taken into account.

The results obtained from XRD, SEM and nanoindentation characterizations performed on the manufactured materials can be correlated with the results calculated by simulations. Thus, the phase fraction calculated by the Rietveld method approaches the values obtained by simulation. Also these results usually occurs in NiTi alloys with concentrations of Ni between 50.8 and 51 at. % [2].

The experimental results obtained by XRD shown the existence of a structure corresponding to B2, B19’, $\text{Ni}_4\text{Ti}_3$, and $\text{Ni}_3\text{Ti}$ precipitates with B19’ major phase.
Figure 4. Results of the thermokinetic simulation of the precipitate evolution (phase fraction [%] and mean precipitation radius [m]) for E3 and E4 of Ni$_{50.8}$Ti.

Figure 5. Histogram plot for Ni$_3$Ti and Ni$_4$Ti$_3$ precipitates related to figure 4.

This suggests that the materials obtained by SPS are martensite type, fact confirmed by Young's module values ranging from 42 to 62 GPa according to [26,27]. Also, SEM micrographs (figure 7) show a fully recrystallized microstructure containing few dispersed precipitates at grains and twins boundaries.

| Sample code | Phase [wt%] of B19' | Phase [wt %] of B2 | Phase [wt %] of Ni$_3$Ti | Phase [wt %] of Ni$_4$Ti$_3$ |
|-------------|---------------------|-------------------|--------------------------|-----------------------------|
| E1          | 81.75±4.85          | 9.18±0.52         | 6.49±0.81                 | 2.56±0.31                   |
| E2          | 81.49±4.79          | 10.43±0.67        | 5.33±0.95                 | 2.76±0.36                   |
| E3          | 95.42±4.17          | 2.17±0.91         | 1.18±0.32                 | 1.21±0.21                   |
| E5          | 94.19±0.0           | 2.29±0.29         | 1.63±0.4                  | 1.86±0.42                   |
Figure 6. Simulated XRD results of NiTi sample processed by SPS and AG.

In figure 7 are presented several SEM microstructures representative of different scales.

Figure 7. SEM Microscopy for E1(a), E2(b), E3(c) and E4(d).

Table 2. Results of nanoindentation measurements.

|       | E1       | E2       | E3         | E4        |
|-------|----------|----------|------------|-----------|
| HV (MPa) | 478±39  | 393±38.34 | 336±7      | 285±38.66 |
| E (GPa)| 64.59±2.59 | 44.59±1.06 | 46±8.99    | 42±5.5    |

4. Conclusions

We demonstrated that thermodynamics and mobility databases, combined with nucleation theory and the SFFK growth model for the precipitate evolution are successfully used to evaluate experimental microstructures in SMA related to stable Ni<sub>3</sub>Ti and metastable Ni<sub>4</sub>Ti<sub>3</sub> precipitates. The simulations deliver a prediction of precipitation trends as a function of aging time and temperature, which is important information for the realization of optimized NiTi materials.

The heat treatments applied to shape memory alloys lead to significant structural changes like variations of Young's modulus values characteristic to the martensite phase, depending on time of
mechanical alloying and on the applied thermal cycles. Due to structural changes that appear during the heat treatment processes, the mechanical characteristics also change.

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