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X-ray and neutron diffraction studies and reverse Monte Carlo simulations of an amorphous Ni₆₀Ti₄₀ alloy produced by mechanical alloying

K D Machado¹, P Jóvári², J C de Lima³, A A M Gasperini³, S M Souza³,
C E Maurmann³, R G Delaplane⁴ and A Wannberg⁴

¹ Departamento de Física, Universidade Federal do Paraná, 81531-990, Curitiba, PR, Brazil

² Hamburger Synchrotronstrahlungslabor HASYLAB am Deutschen Elektronen-Synchrotron DESY, Notkestrasse, 85, D-22603, Hamburg, Germany

³ Departamento de Física, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil

⁴ The Studsvik Neutron Research Laboratory, Uppsala University, S-61182 Uppsala, Sweden

E-mail: kleber@fisica.ufpr.br (K D Machado)

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Abstract

The local atomic order of an amorphous Ni₆₀Ti₄₀ alloy produced by mechanical alloying was studied by x-ray diffraction (XRD) and neutron diffraction techniques (ND). The total structure factors derived from the XRD and ND measurements were simulated by using the reverse Monte Carlo (RMC) method. The simulations were used to compute the partial pair distribution functions $G_{ij}^{\text{RMC}}(r)$ and the partial structure factors $S_{ij}^{\text{RMC}}(K)$. From these functions, coordination numbers and interatomic distances for the first neighbours were calculated. There is a shortening in the heteropolar distance and a preference in forming unlike pairs, indicating a relatively strong chemical short-range order in the alloy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Amorphous Ni–Ti alloys can be formed over a wide compositional range which extends from 20% to about 70% Ni, making this system very suitable for amorphization studies [1]. In a recent article [2], we studied the local atomic order of an amorphous Ni₆₀Ti₄₀ alloy (a-Ni₆₀Ti₄₀) produced by mechanical alloying (MA) [3] using EXAFS, XRD and reverse Monte Carlo (RMC) simulation [4–7]. RMC is a method for structural modelling based directly on experimental data. In order to study the local structure of amorphous alloys, the total structure factor $S(K)$ derived from XRD or ND measurements can be used as input data. There are several papers reporting results about the application of the RMC method to

investigate the structures of amorphous alloys [8–11]. From the simulations, the partial pair distribution functions $G_{ij}^{\text{RMC}}(r)$ and partial structure factors $S_{ij}^{\text{RMC}}(K)$ can be found, and from them, coordination numbers and interatomic distances can be determined. In our previous article, a conventional x-ray source was used to get XRD measurements, and it allowed only a relatively small K_{max} ($K_{\text{max}} = 7.4 \text{ \AA}^{-1}$). In order to find more reliable structural data for this alloy, we made a new XRD measurement at a synchrotron source, obtaining a larger K_{max} ($K_{\text{max}} = 19.4 \text{ \AA}^{-1}$). This XRD $S(K)$ was combined with a ND $S(K)$ to perform a new RMC simulation, supplying more detailed structural information due to the contrast between the two structure factors.

2. Theoretical fundamentals for RMC simulations

2.1. Structure factors

According to Faber and Ziman [12], the x-ray structure factor is obtained from the scattered intensity per atom $I_a(K)$ through the following equations:

$$S(K) = \frac{I_a(K) - \langle f^2(K) \rangle}{\langle f(K) \rangle^2} \quad (1)$$

$$S(K) = \sum_i \sum_j w_{ij}(K) [S_{ij}(K) - 1], \quad (2)$$

where K is the transferred momentum, $S_{ij}(K)$ are the partial structure factors and $w_{ij}(K)$ are given by

$$w_{ij}(K) = \frac{(2 - \delta_{ij})c_i c_j f_i(K) f_j(K)}{\langle f(K) \rangle^2}, \quad (3)$$

and

$$\langle f^2(K) \rangle = \sum_i c_i f_i^2(K), \quad (4)$$

$$\langle f(K) \rangle^2 = \left[\sum_i c_i f_i(K) \right]^2. \quad (5)$$

Here, $f_i(K)$ is the atomic scattering factor and c_i is the concentration of atoms of type i . For neutron diffraction the K -dependent $f_i(K)$ functions should be replaced by the K -independent coherent scattering lengths [13]. Due to the negative scattering length of Ti ($b_{\text{Ti}} = -3.438 \text{ fm}$) the difference between x-ray and neutron weights is quite large: $w_{\text{NiNi}}^{\text{X}}(K = 0) = 0.431$, $w_{\text{NiTi}}^{\text{X}} = 0.451$, $w_{\text{TiTi}}^{\text{X}} = 0.118$, while $w_{\text{NiNi}}^{\text{N}} = 1.654$, $w_{\text{NiTi}}^{\text{N}} = -0.736$, $w_{\text{TiTi}}^{\text{N}} = 0.082$. The partial and total pair distribution functions $G_{ij}(r)$ and $G(r)$ are related to $S_{ij}(K)$ and $S(K)$ factors through

$$G_{ij}(r) = \frac{2}{\pi} \int_0^\infty K [S_{ij}(K) - 1] \sin(Kr) dK. \quad (6)$$

and

$$G(r) = \frac{2}{\pi} \int_0^\infty K [S(K) - 1] \sin(Kr) dK. \quad (7)$$

From the $G_{ij}(r)$ and $G(r)$ functions the partial and total radial distribution functions $\text{RDF}_{ij}(r)$ and $\text{RDF}(r)$ can be calculated from

$$\text{RDF}_{ij}(r) = 4\pi\rho_0 c_j r^2 + r G_{ij}(r), \quad (8)$$

and

$$\text{RDF}(r) = 4\pi\rho_0r^2 + rG(r). \quad (9)$$

where ρ_0 is the density of the alloy (in atoms \AA^{-3}). Interatomic distances are obtained from the maxima of $G_{ij}(r)$, and coordination numbers are calculated by integrating the peaks of $\text{RDF}_{ij}(r)$.

2.2. The RMC method

The basic idea and the algorithm of the standard RMC method are described elsewhere [4–7] and its application to different materials is reported in the literature [8–11]. In the RMC procedure, a three-dimensional arrangement of atoms with the same density and chemical composition of the alloy is placed into a cell (usually cubic) with periodic boundary conditions and the $G_{ij}^{\text{RMC}}(r)$ functions corresponding to it are directly calculated through

$$G_{ij}^{\text{RMC}}(r) = \frac{n_{ij}^{\text{RMC}}(r)}{4\pi\rho_0r^2\Delta r}, \quad (10)$$

where $n_{ij}^{\text{RMC}}(r)$ is the number of atoms at a distance between r and $r + \Delta r$ from the central atom, averaged over all atoms. By allowing the atoms to move (one at a time) inside the cell, the $G_{ij}^{\text{RMC}}(r)$ functions can be changed and, as a consequence, $\mathcal{S}_{ij}^{\text{RMC}}(K)$ and $\mathcal{S}^{\text{RMC}}(K)$ are changed. Thus, $\mathcal{S}^{\text{RMC}}(K)$ is compared to the $\mathcal{S}(K)$ factor in order to minimize the differences between them. The function to be minimized is

$$\psi^2 = \frac{1}{\delta} \sum_{i=1}^m [\mathcal{S}(K_i) - \mathcal{S}^{\text{RMC}}(K_i)]^2, \quad (11)$$

where the sum is over m experimental points and δ is related to the experimental error in $\mathcal{S}(K)$. If the movement decreases ψ^2 , it is always accepted. If it increases ψ^2 , it is accepted with a probability given by $\exp(-\Delta\psi^2/2)$; otherwise it is rejected. As this process is iterated, ψ^2 decreases until it reaches an equilibrium value. Thus, the atomic configuration corresponding to equilibrium should be consistent with the experimental total structure factor within the experimental error. By using the $G_{ij}^{\text{RMC}}(r)$ functions the coordination numbers and interatomic distances can be calculated.

Simulations were carried out with 3000 atoms, $\delta = 0.008$ and a density $\rho_0 = 0.0771$ atoms \AA^{-3} , which was found from the slope of the straight line ($-4\pi\rho_0r$) fitting the initial part (up to the first minimum) of the total $G(r)$ function [14]. For each simulation, the minimum interatomic distances were fixed at $r_{\text{Ni-Ni}} = 2.0$ \AA , $r_{\text{Ni-Ti}} = 2.0$ \AA and $r_{\text{Ti-Ti}} = 2.6$ \AA . Coordination constraints were not used.

3. Experimental procedure

Binary mixtures of high-purity elemental powders of nickel (Merck 99.5%, particle size: <10 μm) and titanium (BDH 99.5%, particle size: <10 μm) with nominal composition Ni₆₀Ti₄₀ were sealed together with several steel balls into a cylindrical steel vial under an argon atmosphere. The ball-to-powder weight ratio was 5:1. A ball mill Spex Mixer/Mill model 8000 was used to perform MA at room temperature. The mixture was continuously milled for 9 h. A ventilation system was used to keep the vial temperature close to room temperature. The composition of the as-milled powder was measured using the energy dispersive spectroscopy (EDS) technique, giving a composition of 39.8 and 60.2 at.% of Ti and Ni, respectively. Impurity traces were not observed.

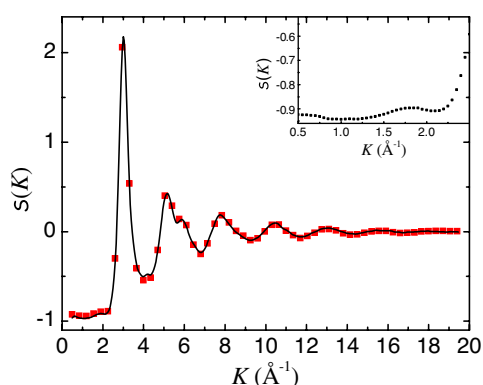


Figure 1. Experimental (squares) and RMC simulated (full curve) total XRD structure factors for a-Ni₆₀Ti₄₀ alloy.

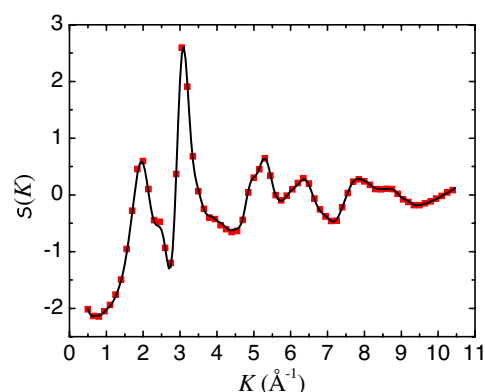


Figure 2. Experimental (squares) and simulated (full curve) total ND structure factors for a-Ni₆₀Ti₄₀ alloy.

The XRD measurement was carried out at the BW5 beamline [15] at HASYLAB. All data were collected at room temperature using a Si(111) monochromator and a Ge solid state detector. The energy of the incident beam was 121.3 keV ($\lambda = 0.102 \text{ \AA}$). The cross section of the beam was $1 \times 4 \text{ mm}^2$ ($h \times v$). A thin-walled ($10 \text{ }\mu\text{m}$) quartz capillary with 2 mm diameter was filled with the powder sample. The energy and average current of the storage ring were 4.4 GeV and 110 mA, respectively. To check for possible instabilities of the beam and the detector electronics, scattered intensities were recorded in ten consecutive scans. The raw intensities were corrected for dead time, background, polarization, detector solid angle and Compton scattering as described in [15]. The total structure factor was computed from the normalized intensity $I_a(K)$ according to Faber and Ziman [12] (see equation (1)).

Neutron diffraction experiments were carried out with the Liquid and Amorphous Materials Diffractometer, SLAD, at NFL, Studsvik [16]. The powdered sample was contained in a thin-walled vanadium container. The incident wavelength of the neutrons was 1.116 \AA . The scattered intensity was measured between 0.4 and 10.4 \AA^{-1} . The static structure factor was obtained from the scattered intensities after applying corrections for absorption, multiple scattering and inelasticity followed by normalizations to a vanadium standard, which were done with the CORRECT program described in [17].

4. Results and discussion

Figures 1 and 2 show the experimental XRD and ND structure factors for a-Ni₆₀Ti₄₀ (squares).

The ND $S(K)$ shows a very high first sharp diffraction peak (FSDP) at about 2 \AA^{-1} , which also appears in the XRD $S(K)$, but with a much lower intensity, as shown in the inset of figure 1.

The results of the simulations are shown in figures 1 and 2 (full curves) and a very good agreement is found. The $G_{ij}^{\text{RMC}}(r)$ functions obtained are seen in figure 3, and the coordination numbers and interatomic distances obtained from them are shown in table 1. The $S_{ij}^{\text{RMC}}(K)$ factors extracted from the simulation are shown in figure 4. If no other *a priori* structural information is available then the separation of the three partial structure factors requires three independent diffraction measurements. The present study is based on the fitting of only two diffraction data sets by using additional information in the form of simulation constraints

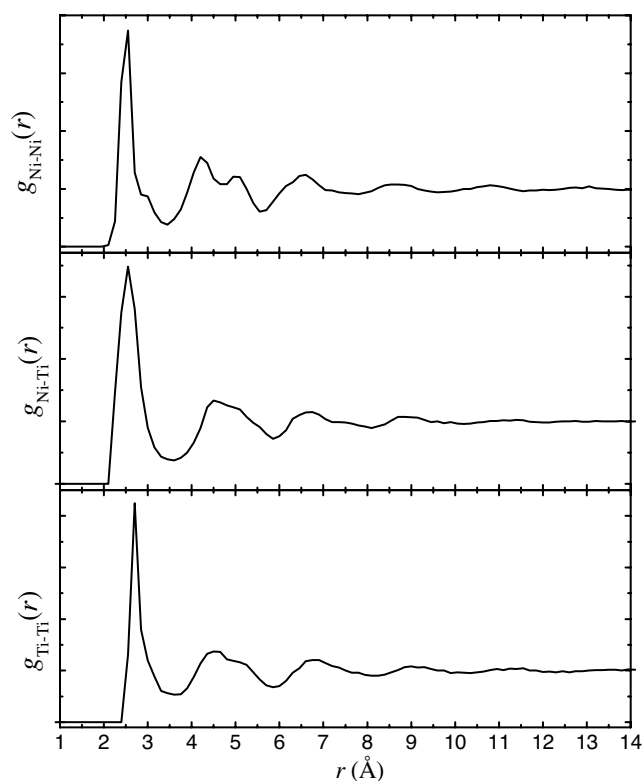


Figure 3. $G_{ij}(r)$ functions derived from the RMC simulations.

Table 1. Structural data for amorphous Ni₆₀Ti₄₀ alloy.

Bond type	Ni–Ni	Ni–Ti	Ti–Ni	Ti–Ti
N	7.0(2)	5.9(2)	8.9(2)	4.5(2)
r (Å)	2.52(2)	2.57(2)	2.57(2)	2.70(2)

(density and minimum interatomic distances); therefore the model dependence of the results should be investigated in detail. For this purpose a series of additional simulations have been carried out by varying the data sets fitted, the K -range of the fit and the minimum interatomic distances. All these runs were started from the same random configuration. The results can be summarized as follows.

- (i) Configurations obtained by fitting neutron data only were significantly more disordered (if peak heights of partial pair correlation functions and angle distributions are considered) than those calculated from the x-ray structure factor.
- (ii) Peak heights practically did not change when the x-ray data were fitted only up to 10.4 \AA^{-1} ; therefore this discrepancy is **not** a consequence of the extended K -range of the x-ray measurement but rather of the different information contents of the two structure factors.
- (iii) Models obtained by the simultaneous fitting of the two data sets are much closer to the x-ray model.
- (iv) Especially in the case of the neutron structure factor, the quality of the fit was quite sensitive to the Ni–Ti peak position which can be shifted slightly to higher r values by

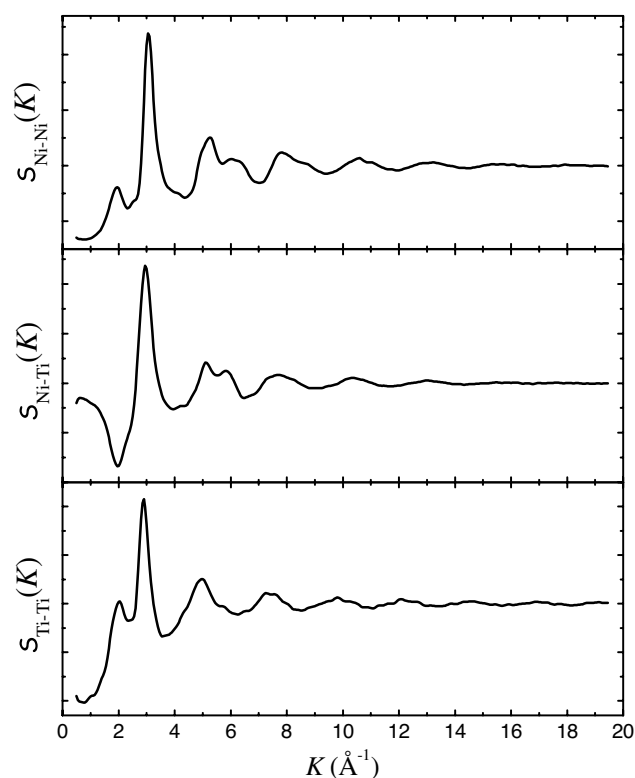


Figure 4. $S_{ij}(K)$ factors derived from the RMC simulations.

increasing the minimum Ni–Ti distance. Good or tolerable fits could be achieved if the minimum distance remained below 2.4 Å. Although the peak shape of $g_{\text{Ni-Ti}}(r)$ was seriously distorted by the high minimum distance, the position of the peak (determined e.g. by a Gaussian fit) did not change. When the minimum Ni–Ti distance was raised from 2.33 to 2.48 Å, ψ^2 increased by more than one order of magnitude (from 28 to about 400 with $\delta = 0.008$; see figure 5). Therefore it can be concluded that the Ni–Ti mean distance (2.55–2.57 Å) is significantly shorter than the sum of atomic radii (2.70 Å).

Gazzillo *et al* [18] reported the $S_{\text{Ni-Ni}}(K)$, $S_{\text{Ni-Ti}}(K)$ and $S_{\text{Ti-Ti}}(K)$ calculated using a non-additive hard sphere model for amorphous $\text{Ni}_x\text{Ti}_{1-x}$ ($x = 0.3, 0.5, 0.7$) alloys. The $S_{ij}^{\text{RMC}}(K)$ factors obtained by us show the same features as those reported (see figure 6 of [18]), in particular the FSDP in $S_{\text{Ni-Ni}}(K)$ located at about $K = 2 \text{ \AA}^{-1}$. In [2] and [18], there was a shoulder in $S_{\text{Ti-Ti}}(K)$ located at about $K = 2 \text{ \AA}^{-1}$. Here this shoulder is resolved and a FSDP can be found at the same place.

It is interesting to note that the heteropolar Ni–Ti distance is shorter than the sum of the Ni and Ti radii, and is similar to the Ni–Ni distance. This shortening in the heteropolar distance was suggested by Hausleitner and Hafner [19]. They investigated several amorphous alloys formed by transition metals using molecular dynamics simulations, and obtained the structure factors, coordination numbers and interatomic distances. According to them, if the components of an alloy have a large difference in number of d electrons, there is a pronounced non-additivity of the pair interactions and a strong interaction between unlike atoms. Since Ni and Ti have two and seven d electrons, respectively, there is a large difference in this alloy,

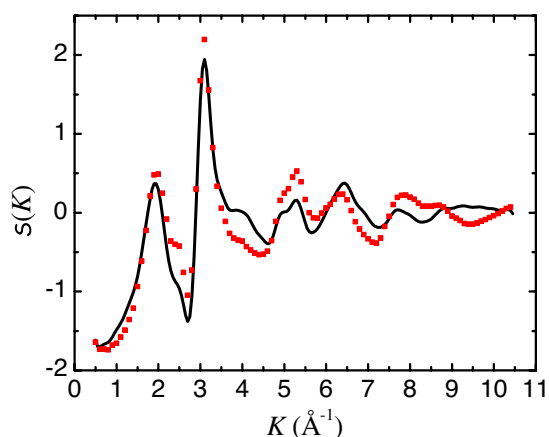


Figure 5. Experimental (squares) and RMC simulated (full curve) total ND structure factors for a-Ni₆₀Ti₄₀ when the minimum distances between Ni and Ti are increased.

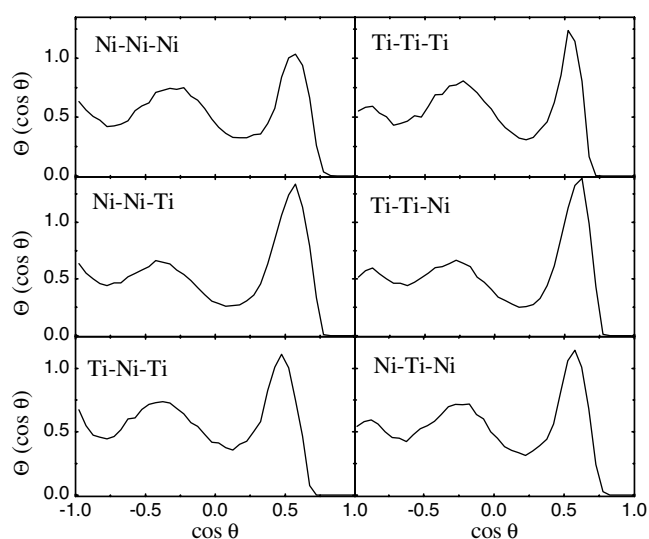


Figure 6. Partial bond angle distribution functions $\Theta_{i-j-k}(\cos \theta)$ for a-Ni₆₀Ti₄₀.

which can explain the shortening effect seen in the Ni–Ti distance, which becomes similar to the Ni–Ni distance. This indicates that the alloy can exhibit a large chemical short-range order (CSRO). The CSRO can be estimated by calculating the Warren chemical short-range order parameter α_W given by [18]

$$\alpha_W = 1 - \frac{N_{12}}{c_2 N_1} = 1 - \frac{N_{21}}{c_1 N_2}, \quad (12)$$

where N_{ij} are the coordination numbers and $N_i = \sum_j N_{ij}$. The α_W parameter is null for a random distribution. If there is a preference for forming unlike pairs in the alloy, it becomes negative; otherwise, it is positive if homopolar pairs are preferred. In our case, using coordination numbers given in table 1, we found $\alpha_W^{\text{RMC}} = -0.143$, indicating a relatively strong CSRO. For a comparison, the compound NiTi has $\alpha_W = -0.143$, suggesting that the local structures of the amorphous alloy and the crystalline compound are similar.

It is interesting to investigate the angular distribution of the bonds between first-neighbour atoms. Figure 6 shows the six partial bond angle distribution functions $\Theta_{i-j-k}(\cos \theta)$ where

j is the atom in the corner. It is interesting to note that the chemical environment around Ni atoms is somewhat different from that around Ti atoms. A similar phenomenon was found in glassy Ni₆₂Nb₃₈ [20]. All $\Theta_{i-Ni-k}(\cos\theta)$ functions ($i, k = \text{Ni or Ti}$) have a peak around 180°, indicating the existence of linear chains $i-Ni-k$. On the other hand, all $\Theta_{i-Ti-k}(\cos\theta)$ functions have a peak around 150°, which is not seen in $\Theta_{i-Ni-k}(\cos\theta)$ functions, and linear chains $i-Ti-k$ are found to a lesser extent. $\Theta_{Ni-Ni-Ni}(\cos\theta)$ also has peaks at 55° and 107°, the latter being close to the tetrahedral angle. $\Theta_{Ni-Ni-Ti}(\cos\theta)$ has peaks around 55°, like $\Theta_{Ni-Ni-Ni}(\cos\theta)$, and 112°, and $\Theta_{i-Ni-Ti}(\cos\theta)$ peaks at 60° and 112°, besides 180°. The peaks of $\Theta_{Ti-Ti-Ti}(\cos\theta)$ are found at 58°, 103° and 150°, and $\Theta_{Ti-Ti-Ni}(\cos\theta)$ has peaks around 52°, 106° and 150°. Finally, $\Theta_{Ni-Ti-Ni}(\cos\theta)$ peaks at 55° and 103°, in addition to 150°. All these angles are found in trigonal prismatic and tetrahedral distorted units, which are also found in the NiTi compound, confirming their similarity.

5. Conclusion

The local structure of a-Ni₆₀Ti₄₀ alloy produced by MA was studied by XRD and ND techniques and also through RMC simulations of the total XRD and ND structure factors. From the RMC simulations we obtained coordination numbers and interatomic distances. There is a shortening in the Ni–Ti distance caused by the large difference in number of d electrons between Ni and Ti, which gives rise to a strong chemical short-range order in the alloy, as determined by the calculated Warren CSRO parameter.

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