



## Microarticle

## Glassy NiTi produced with different cooling times: Structural investigation using molecular dynamics simulations

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## ARTICLE INFO

## Keywords:

Molecular dynamics  
Structure  
Glassy NiTi  
Cooling time  
Local atomic packing

## ABSTRACT

In this research we investigate the structure of glassy NiTi using molecular dynamics simulations. The final configurations are obtained by decreasing the temperature of liquid NiTi rapidly from 2500 K to 300 K, with various cooling times from 0.1 ns to 2.0 ns. We found that the height of the peak values for structural factors slightly increases with an increase in cooling time. From the analysis of local atomic packing using the bond-angle method, we also find that the count of hexagonal close packed (HCP)-like structure drops at the longer cooling time, a finding which is contrary to the trend for body-centered cubic (BCC)-like and icosahedral short-range order (ISRO) structures. It is also observed that face-centered cubic (FCC)-like structure is insensitive to change in cooling time.

## Introduction

As a result of its functionality in many industrial domains, NiTi alloy has attracted the attention of researchers in recent decades [1,2]. This material has some distinctive properties, such as shape memory effect (SME), biocompatibility, superelasticity, damping, and impact absorbance. The SME characteristic allows NiTi alloy to regain its original shape from a deformed position via a thermal process. Properties of the material are very sensitive to the percentage of its atomic composition and contamination by oxygen, nitrogen, and carbon from the environment during fabrication [1,2], and these complications of the fabrication and manufacturing processes hamper the widespread application of NiTi alloy [1,2]. Recently, experimental work has been devoted to developing new additive manufacturing methods to fabricate a highly controlled composition of NiTi alloy; however, this method is considered expensive for commercialization [3,4].

In addition, a theoretical study is indispensable to provide a complete view of the fabrication process of NiTi alloy. A realistic theoretical model at the atomic level can be produced via molecular dynamics (MD) simulations. However, to the best of our knowledge, most MD studies to date have focused on the structural transformation of the B2 to B19' phase and vice versa [5,6], while the initial investigation of the fabrication process of NiTi alloy has only been reported previously by

our group in terms of the melting behavior of NiTi alloy [7] and the pressure effect on liquid NiTi structure [8]. The other MD study has been performed using modified embedded atom method (MEAM) potential to investigate the mechanical properties of single-crystalline metal (Ni and Cu) nanowires [9]. Another critical factor affecting the structure of solid NiTi alloy is the cooling time of the solidification process. In this paper, the detailed analysis of some local structures of glassy NiTi, drawn from our MD simulations at different rapid cooling times, are presented. These results are important to clarify the pattern of the structural change of the crystalline growth process of NiTi alloy at different cooling times.

## Computational details

We utilized the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [10] to carry out all MD simulations. Embedded atom method (EAM) potential is employed to describe the interactions between TiTi, NiNi, and NiTi atoms [11]. Using this potential, it has been shown in our previous simulations that the experimental melting point of eutectoid NiTi alloy has been reproduced accurately up to 94.76% [7]. In this simulation, the initial configuration, which can be seen in Fig. 1, was prepared by heating the B2 crystal structure of NiTi alloy to 2500 K. This temperature was chosen since it

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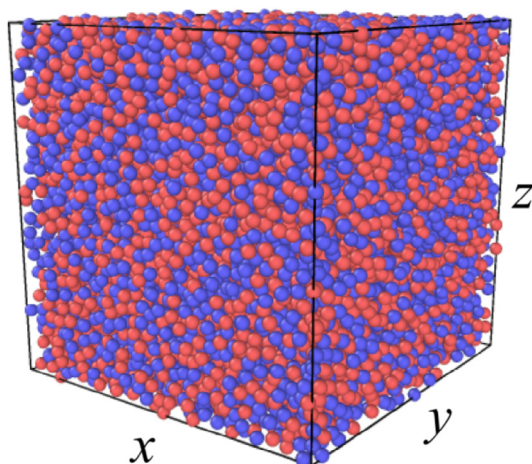
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<https://doi.org/10.1016/j.rinp.2019.102545>

Received 30 June 2019; Received in revised form 29 July 2019; Accepted 29 July 2019

Available online 03 August 2019

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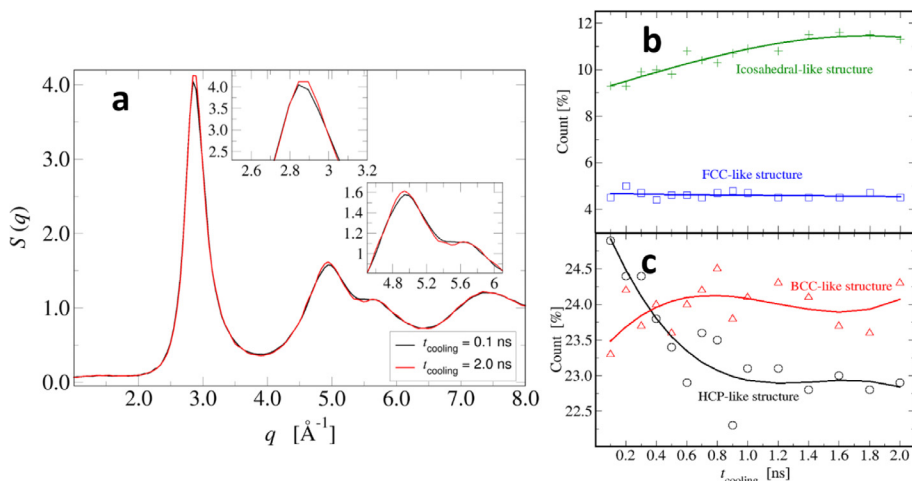


**Fig. 1.** Liquid NiTi configuration at 2500 K. The system contains 8000 atoms for each of Ni and Ti. The red and blue spheres correspond to the Ni and Ti atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is considerably higher than the melting temperature of NiTi alloy to ensure that the effect of B2 crystal structure has disappeared. We applied periodic boundary conditions in the cubic supercell with the same length of  $x$ -,  $y$ -, and  $z$ -directions of  $64.874 \text{ \AA}$ . We used the timestep of  $\Delta t = 1 \text{ fs}$  to solve the equation of motions using the Verlet algorithm. At the beginning of simulation process, we decreased the temperature of the systems from 2500 K to 300 K during  $t_{\text{cooling}} = 0.1 \text{ ns}$  to  $2.0 \text{ ns}$  in the NPT Nosé-Hoover ensemble [12,13] at 0 GPa. The system was then equilibrated for 0.1 ns using the same ensemble. Finally, the data were extracted from the extra MD simulation in the NVT ensemble for 0.03 ns (30,000 MD steps), in which the convergences were already achieved. We carried out the analysis using Ovito [14] and Rings package [15] for the image rendering and structural analysis.

## Results and conclusions

All the results are extracted from the NiTi system at 300 K, which is in a glassy state. Structures of the glassy NiTi obtained from different quench rates are evaluated in terms of structure factor  $S(q)$ . We can see from Fig. 2(a) that only a small difference between the  $S(q)$  of the system at total cooling times ( $t_{\text{cooling}}$ ) of 0.1 ns and of 2.0 ns can be observed. The height of the first and the second peaks of the  $S(q)$  of the system from  $t_{\text{cooling}} = 2.0 \text{ ns}$  are slightly higher, by 0.08 and 0.09, respectively, than for the shorter cooling time. These results are averaged from the atomic configurations of thousands MD step that has



**Fig. 2.** Structural analysis of glassy NiTi alloy at different cooling times: (a) structure factor  $S(q)$  from the system obtained from cooling time  $t_{\text{cooling}} = 0.1 \text{ ns}$  and  $2.0 \text{ ns}$ . The magnification of the first and the second peaks are shown in the upper and lower insets, respectively. Count of local atomic packing obtained by the bond-angle method as a function of  $t_{\text{cooling}}$  for (b) ISRO- and FCC-like, and (c) HCP- and BCC-like structure. The symbols and solid lines correspond to the simulation results and their regressions models (3rd order polynomial), respectively.

converged. From Fig. 2(a) it can be seen that the shoulder of the second peak in the glassy NiTi, obtained from  $t_{\text{cooling}} = 0.1 \text{ ns}$ , clearly exhibits at  $q = 5.69 \text{ \AA}^{-1}$ . This indicates the presence of ISRO local atomic packing, as found in our previous simulation of liquid NiTi under high pressure [8]. In the  $S(q)$  of the system from  $t_{\text{cooling}} = 2.0 \text{ ns}$ , we can see that the shoulder is lower and its location shifts to the left at  $q = 5.34 \text{ \AA}^{-1}$ , and a new smaller peak grows from the shoulder of the second peak of the system from  $t_{\text{cooling}} = 0.1 \text{ ns}$  (see lower inset of Fig. 2(a)). According to the previous report [16], the splitting of the second peak directly corresponds to the existence of the face sharing regular tetrahedra in the short-range order structure.

In order to investigate the local structure of glassy NiTi, we employed the bond-angle method developed by Ackland and Jones [17]. This method evaluates the angular distribution of local neighboring atoms and appoints a structure type, such as FCC, HCP, BCC, or icosahedral, to each atom. We performed this analysis for all atoms without differentiating Ni and Ti species, since the bond-angle method has been designed only for systems containing a single type of atom. From Fig. 2(b), it can be clearly seen that the trend in ISRO local atomic packing increases when the total cooling time is longer, while the tendency for FCC local atomic packing remains constant. Fig. 2(c) shows that at very rapid cooling rates ( $t_{\text{cooling}} = 0.1 \text{ ns}$ – $0.3 \text{ ns}$ ), the HCP local atomic packing count is higher than for BCC structure, with the tendency to decrease and to increase, respectively. For the system at  $t_{\text{cooling}} = 0.4 \text{ ns}$  and higher, the count for BCC local atomic packing overtakes that of the HCP local environment. Thus, we can say that HCP dominates the local structure of glassy NiTi at 300 K for very rapid cooling times, while the most frequent local atomic packing in the system obtained from longer cooling time is BCC type. The further analysis is needed in the future investigations to show whether the BCC local atomic packing is related to the B2 local structure or not.

It can be concluded from our results that the height of the peaks of the structure factors of glassy NiTi slightly increases with the decrease in quench rate. The splitting of the second peak, which is a sign of the presence of face-sharing regular tetrahedra in the short-range order structure, is also found in the glassy NiTi from our longest cooling time of  $t_{\text{cooling}} = 2.0 \text{ ns}$ . From the analysis of local atomic packing using the bond-angle method, we can notice that the count of HCP-like structure decreases at higher quench period, which is contrary to the trend for BCC-like and ISRO structure. BCC local atomic packing is more frequent than the other local structures of glassy NiTi obtained from the  $t_{\text{cooling}} = 0.4 \text{ ns}$  and higher at 300 K. It is also observed in our result that FCC-like structure is insensitive to the change in cooling time.

## Acknowledgment

This work was supported by a Penelitian Dasar Unggulan Perguruan

Tinggi (PDUPT) research grant from the Direktorat Riset dan Pengabdian Masyarakat, Direktorat Jenderal Penguatan Riset dan Pengembangan, Ministry of Research, Technology and Higher Education of the Republic Indonesia (second period) in the fiscal year 2019, under contract No. 035/SP2H/LT/MONO/L7/2019. We thank Dr. Taufiq Widjanarko for his constructive suggestion in this manuscript. We also thank Prof. Benny Tjahjono (Coventry University) for his expert advice and comments on the manuscript.

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