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Abstract

Porous crystalline nitinol is widely applied in various fields of science and technology due to the unique combination of physical and mechanical properties as well as biocompatibility. Porous amorphous nitinol is characterized by improved mechanical properties compared to its crystalline analogues. Moreover, this material is more promising from the point of view of fundamental study and practical application. The production of porous amorphous nitinol is a difficult task requiring rapid cooling protocol and optimal conditions to form a stable porous structure. In the present work, based on the results of molecular dynamics simulations, we show that porous nitinol with the amorphous matrix can be obtained by injection of argon into a liquid melt followed by rapid cooling of the resulting mixture. We find that the porosity of the system increases exponentially with increasing fraction of injected argon. It has been established that the system should contain about $\sim 18$–$23\%$ argon for obtain an open porous structure, while the system is destroyed by overheated inert gas when the argon fraction is more than $\sim 23\%$. It is shown that the method of argon injection makes it possible to obtain a highly porous system with the porosity $\sim 70\%$ consisting the spongy porous structure similar to aerogels and metallic foams.

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1. Introduction

Porous titanium nickelide alloy Ni$_{50}$Ti$_{50}$ known as nitinol is promising due to unique combination of physical and mechanical properties such as open porosity, biocompatibility, shape memory effect and high strength \[1,2\]. Therefore, porous nitinol is preferable in medicine, aerospace and transport industries for production of construction details, implants and filter elements \[3,4\]. The presence of such properties is largely determined by the crystal structure that supports the austenitic-martensitic (B2$\rightarrow$B19') and martensitic-austenitic (B19'$\rightarrow$B2) transitions under thermal and mechanical influences \[1\]. The main advantage of porous crystalline nitinol is the simplicity of its preparation and the availability of initial powder raw materials for synthesis, for example, by powder metallurgy methods \[5\]. The synthesized porous samples usually have an open porous structure with the average linear size of the pores $\sim 200\mu$m, that is close to the pore size in bone tissues \[6\]. At the same time, porous crystalline nitinol has some limitations, which include increased fragility (with increasing porosity, the fragility also become larger) and the tendency to form cracks \[7,8\].

From point of view of fundamental studies and practical applications, porous amorphous nitinol is of great interest \[9\]. This material is less exposed to crack formation due to the absence of defects, which inevitably occur in the case of the crystalline analogue. It has an increased resistance to external deformations that is confirmed by the results of molecular dynamics simulations. For example, it was shown in Ref. \[10,11\] that the Young’s modulus of porous amorphous nitinol at tensile and compression deformations is more than twice larger then in the case of the crystalline material with the porosity $\phi \in [7.5; 35]\%$. Despite these advantages, it is difficult to synthesize experimentally porous amorphous nitinol. The main reason for this is the need to apply the quench with extremely high rates (more than $1 \times 10^6$ K/s) to obtain a stable amorphous structure \[12\]. Difficulties may also arise at choice an appropriate method for the synthesis of a porous structure. The known methods for preparing porous alloys, such as powder sintering \[13\], additive technologies \[14\], spark plasma sintering \[4\], and self-propagating high-temperature synthesis \[15,16\], can lead to formation of a crystalline structure in the powder contact zones \[17,18\]. The presence of crystalline inclusions can lead to the degradation in the mechanical characteristics of the porous alloy, for example, due to an increase in the probability of the nanosized cracks formation at the interface between crystal and amorphous phases \[19,20\]. Therefore, the method of direct melt foaming by gas injection is the most preferable for obtaining the amorphous structure without crystalline inclusions \[21,22\].
This method is widely used to form the pores in various metal melts by gas injection (most often by argon) under high pressure or gas-evolving foaming agents (for example, calcium oxide CaO, titanium hydride TiH₂) or by means of obtaining oversaturated metal-gas solutions followed by cooling the foamed liquid melt. However, this method is difficult to apply for production of porous amorphous nitinol due to the high melting point of Ni₅₀Ti₅₀ alloy (∼1570 K) and due to the lack of information about the optimal conditions for foaming the corresponding melt. Insufficient understanding of the pore formation mechanisms in the nitinol melt requires detailed studies related to molecular dynamics simulations.

In the present work, the process of liquid nitinol foaming via argon injection is studied by means of molecular dynamics simulations. The simulation conditions are close to the experimental ones implemented, for example, in the method of direct melt foaming by gas injection [21, 22]. We determine the optimal fraction of the injected argon and the thermodynamic parameters of the system to obtain the porous amorphous alloy with the required porosity and the required pore morphology. The possibility of obtaining porous amorphous nitinol with closed pores (porosity up to 35%) and with an open percolating porous structure (with porosity up to 70%) is demonstrated. In Section 2, the melt foaming procedure and the details of the applied hybrid interparticle interaction potential are discussed. Section 3 is devoted to discussion of the obtained results. The conclusion is given in Section 4.

2. Argon injection procedure

Initially, crystalline nitinol consisting 68 750 atoms of Ni and 68 750 atoms of Ti was chosen. Molecular dynamics simulations are performed in the isobaric-isothermal (NPT) ensemble with the time step 1 fs using the LAMMPS simulation package [23]. At all stages of the simulations, the pressure is equal to 1 atm.

The interaction between Ni, Ti and Ar atoms is specified using the hybrid interaction potential. For Ni-Ni, Ti-Ti and Ni-Ti interactions, the 2NN MEAM potential is applied to compute the total energy of the system [24]:

\[ E = \sum_{i=1}^{N} \left[ F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i}^{N} S_{ij} \phi_{ij}(r_{ij}) \right]. \]  

(1)

Here, \( F_i \) is the embedding function for the atom \( i \) within a background electron density \( \rho_i \); the pair potential \( \phi_{ij}(r_{ij}) \) and screening function \( S_{ij} \) are evaluated at the distance \( r_{ij} \) between atoms.
In the 2NN MEAM potential, the pairwise interaction $\phi_{ij}(r_{ij})$ is not assigned a simple functional expression. As a rule, the value of the quantity $\phi_{ij}(r_{ij})$ is estimated by the embedding energy and the energy per atom

$$\phi_{ij}(r_{ij}) = \frac{2}{Z_1} \left\{ E^u_i(r_{ij}) - F_i(\rho_i) \right\}. \quad (2)$$

In Eq. (2), $Z_1$ is the number of nearest-neighbor atoms, $E^u_i(r_{ij})$ is the energy per atom [25]:

$$E^u_i(r_{ij}) = -E_c(1 + a^* + da^*^3)e^{-a^*}, \quad (3)$$

where

$$a^* = \sqrt{\frac{9B\Omega}{E_c}} \left( \frac{r_{ij}}{r_e} - 1 \right). \quad (4)$$

Here, $r_e$ is the equilibrium nearest-neighbor distance; $E_c$ is the cohesive energy; $d$ is an adjustable parameter; $B$ is the bulk modulus; $\Omega$ is the equilibrium atomic volume of the reference structure. The values of these parameters for Ni-Ti system are given in Table IV of Ref. [24]. The cutoff radius of the 2NN MEAM potential is 5.0 Å for considered binary system. For Ni-Ar, Ti-Ar and Ar-Ar interactions, the binary Lennard-Jones potential is applied [26]:

$$E_{LJ}(r_{ij}) = 4\epsilon_{\alpha \beta} \left[ \left( \frac{\sigma_{\alpha \beta}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha \beta}}{r_{ij}} \right)^6 \right], \quad \alpha, \beta = \{\text{Ni, Ti, Ar}\}. \quad (5)$$

The parameters of this potential – the potential well depth $\epsilon_{\alpha \beta}$ and the effective atom diameter $\sigma_{\alpha \beta}$ – are given as follows: $\epsilon_{\text{Ar-Ti}} = 8.7 \times 10^{-2}$ eV and $\sigma_{\text{Ar-Ti}} = 3$ Å for Ar-Ti interaction; $\epsilon_{\text{Ar-Ni}} = 7.9 \times 10^{-2}$ eV and $\sigma_{\text{Ar-Ni}} = 3.04$ Å for Ar-Ni; $\epsilon_{\text{Ar-Ar}} = 1 \times 10^{-2}$ eV and $\sigma_{\text{Ar-Ar}} = 3.41$ Å for Ar-Ar [27]. The applied cutoff radius of the Lennard-Jones potential is $2.5\sigma_{\alpha \beta}$.

The argon injection procedure and the preparation of porous amorphous nitinol are carried out through the following steps:

- The liquid sample is melted at the temperature $T = 1.2T_m$, where the melting temperature is $T_m \simeq 1570$ K, and, then, it is brought to the thermodynamic equilibrium state during the time 0.1 ns.

- The injection of Ar atoms is carried out. This procedure means the random replacement of some Ni and Ti atoms by Ar atoms [see. Figure [1(a)]. Here, the proportion of Ni and Ti atoms in the system always remains the same and corresponds to Ni$_{50}$Ti$_{50}$ alloy. The liquid samples are prepared by injection of argon in the fractions $f = 10, 14, 15, 16, 17, 18, 19,$
20 and 23\% from the total number of atoms in the system. After the injection of argon, the system is again brought to the thermodynamic equilibrium state.

- The liquid nitinol mixed with argon is rapidly cooled to the temperature 300 K at the cooling rate $1 \times 10^{12}$ K/s. The redistribution of the components occurs during the cooling procedure, as a result of which argon is separated from amorphous nitinol [see Fig. Figure 1(b) and 1(c)]. The separation of argon gas and solid nitinol occurs heterogeneously. This leads to the formation of the foamed amorphous samples, where the percolating network of pores filled with argon. Note that the porosity and distribution of pores in the system may be dependent on the cooling rate applied to generate the porous amorphous system [28, 29].

- The foamed samples were held at the temperature 300 K for the time 0.1 ns for stabilization of the amorphous matrix. Then, argon is completely removed from the system. The resulting porous amorphous samples are held again at the temperature 300 K.

The porosity $\phi$ of the obtained samples is determined by the well-known expression [30]:

$$\phi = \left(1 - \frac{\rho}{\rho_0}\right) \cdot 100\%,$$

where $\rho$ is the density of a porous sample, $\rho_0 = 6.21 \text{g/cm}^3$ is the density of nitinol without pores at the temperature $T = 300$ K.
To avoid the artifacts due to the molecular dynamics simulations of a porous system, the following condition must be satisfied: the average linear pore size must be less than the linear size of the simulation box. In this case, there will be no significant artifacts generated by the periodic boundary conditions. In the present study, the linear size of the simulated system is set so that it exceeds the characteristic size of the pores formed in the system. For example, in the case of the porosity 25%, the linear size of the system is $L \approx 14.8$ nm, while the average linear pore size is $l \approx 3$ nm. In the case of the maximum considered porosity 70%, we have $L \approx 26$ nm and $l \approx 20$ nm.

3. Porosity as function of Argon fraction

Figure 2 shows the dependence of the porosity $\phi$ on the injected argon fraction $f$. We find that porous amorphous nitinol contains only closed pores at argon less than $\sim 18\%$. In this case, the system porosity does not exceed $\phi = 35\%$. The resulting pores are stable and have a shape close to spherical. Average linear size of the closed pores is $\sim 2$ nm, which is a low threshold value for porous alloys belonging to the class of nanoporous materials [31]. To obtain the porous structure with open pores and the percolating amorphous matrix, the fraction of argon must be above 18%. Here, the argon fraction from $f \sim 18\%$ to 23% is optimal. In this case, the porosity of the system varies in the range $\phi \in [40; 70]\%$. It is important to note that the fraction of the injected argon should not exceed $\sim 23-25\%$ at the considered thermodynamic conditions. The structure of the system is destroyed with an increase in the argon fraction above this value: the liquid melt is decayed by overheated argon. Thus, the optimal fraction of the injected argon required to obtain the highly porosity system with open pores is about $\sim 20\%$ at the considered thermodynamic conditions.

We find that the dependence of the system porosity on the injected argon fraction can be reproduced by the exponential law

$$\phi(f) = \phi_0 \left[ e^{f/f_0} - 1 \right], \quad f \geq f_0. \quad (7)$$

Here, $\phi_0$ is the fraction of the free volume in the system without pores; this parameter is related to the packing fraction $f_p$, $\phi_0 \approx 1 - f_p$ [32, 33]. The parameter $f_0$ characterizes the minimum fraction of the injected argon that is sufficient for the formation of stable pores. Expression (7) is an empirical result and it is realized at $f \geq f_0$. In fact, Eq. (7) indicates that the density of the porous system $\rho$ is related to the fraction of injected gas $f$ according to the exponential law

$$\rho(f) = \rho_0 (1 + \phi_0 - \phi_0 e^{f/f_0}), \quad f \geq f_0. \quad (8)$$
Figure 2: Dependence of the porosity $\phi$ on the injected argon fraction $f$. Regions corresponding to the amorphous system with different porous structures (with open pores, with closed pores) are identified. The system instability region is shown, where the addition of Ar atoms leads to the destruction of the system.

Both Eqs. (7) and (8) take into account the physical effect associated with the fact that there is a minimum fraction of injected gas $f_0$, at which stable pores are formed in the system and the system is not able to “heal” these pores. The values of the parameters $f_0$ and $\phi_0$ were determined by fit of Eq. (7) to the simulation data. For the considered system, the found value $f_0 = (7.6 \pm 0.8)\%$ determines the minimum argon fraction that should be injected into nitinol melt to obtain the minimum porosity $\phi(f_0) \approx 1.72\phi_0 \approx 6.9\%$, where $\phi_0 = (4.0 \pm 1.0)\%$. The formed pores will coalesce after removal of Ar atoms from the system if value of the parameter $f_0$ is less than $7.6\%$. We find that for the case minimal porosity with $\phi(f_0)$ it is satisfied the correlation relation $f_0 \approx 1.9\phi_0$.

Then, from expression (8) at $f = f_0$ we find

$$\rho(f_0) \approx \rho_0(1 - 0.9f_0).$$

Expression (9) shows the ultimate density of the system, at which the formation of stable pores
becomes possible.

Figure 3 shows the fragment of the amorphous matrix of porous nitinol with the porosity 70%. As can be seen from this figure, the so-called spongy porous structure is formed at injected of more than 20% argon. The reason for formation of such spongy structure is the thermal expansion of the liquid melt due to the large fraction of overheated noble gas. In this spongy porous structure, the average thickness of the interpore walls is much less than the average linear size of the pores: average thickness of interpore walls is $\sim 5\,\text{nm}$, while the average linear size of the pores is $\sim 20\,\text{nm}$.

We note that nitinol is in the state of viscous liquid at the considered temperature $\simeq 1890\,\text{K}$, while argon at this temperature is in strongly overheated gas phase (the melting temperature of solid argon is $\sim 88\,\text{K}$). Despite the high fraction of argon, the high viscosity of liquid nitinol does not allow the gas phase to be completely separated from the melt. Thus, the partial coalescence of the formed gas bubbles and foaming of liquid nitinol are occurred. The high viscosity of the melt also contributes to formation of the percolating matrix at the cooling procedure [see Figure 3]. It is noteworthy that such the spongy porous structure almost completely corresponds to the structure of organic foams, aerogels and metallic foams, the porosity of which ones usually is larger than 70% [34, 35, 36, 37, 38]. Average value of the linear size of the pores in the considered system is also close to the pore size in aerogels, where pores can have sizes from $\sim 10\,\text{nm}$ to $\sim 100\,\text{nm}$ [39].

Figure 3: Snapshot of the system with porosity $\sim 70\%$ prepared by injecting 23% argon.
Such the spongy porous structure could be of great interest for various practical applications: for example, for the design of filter elements, fuel reservoirs and battery electrodes [40].

4. Conclusion

Based on the results of molecular dynamics simulations, we have shown the possibility of obtaining porous amorphous nitinol by injecting argon into the corresponding melt. The energies and forces between Ni, Ti, and Ar atoms were correctly calculated using the hybrid interparticle interaction potential, which made it possible to obtain the porous system whose structure is close to experimentally synthesized aerogels and metallic foams. A relationship between the fraction of the injected argon and the system porosity has been determined, which is well reproduced by an exponential function. We have determined the optimal fraction of the injected argon, which makes it possible to obtain the porous amorphous nitinol with the spongy structure and with the stable amorphous matrix without crystalline inclusions. The limiting fraction of the injected argon was also found, the excess of which leads to the complete extrusion of argon from the liquid melt and to destroy of the system. It is shown that for formation of stable porous structure, the minimum fraction of the injected argon should not be less than ~ 7.6% at the considered thermodynamic conditions. The obtained results show that well-known method of direct melt foaming by gas injection [21, 22] can be adapted for the synthesis of porous amorphous nitinol if the rapid cooling protocol will be implemented.

The results of the present study are practically significant and can be applied to improve the foaming protocols of metal melts. For example, based on the results presented in Figure 2, it is possible to determine the optimal ratio of foaming gas and metal melt to obtain a sample with the required porosity and pore morphology. This makes it possible to simplify the procedure for synthesizing samples with desired mechanical properties for specific applications, for example, for the manufacture of construction materials or implants [41, 42]. Moreover, the ultimate value of the argon fraction necessary to obtain a highly porous system with the porosity ~ 70% was determined for the first time. At such porosity, we have a sponge-like porous structure as in the case of aerogels, organic and metal foams. This result is of great importance in production of porous filters and biocompatible porous nanoparticles, for example, for the delivery and storage of drugs in humans [43, 44, 45].
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