In search of zero thermal expansion anisotropy in Mo_5Si_3 by strategic alloying

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Abstract

Reducing the thermal expansion anisotropy (TEA) of alloy compounds is one of the most important issues for their potential applications in high temperature environment. The Mo_5Si_3 (T1 phase) is known to be an important intermetallic compound with high melting temperature. Unfortunately, its large TEA renders it unsuitable for high temperature structural/coating applications. Many attempts have been made in the past to reduce TEA by substituting Mo by other transition metal ions such as V with little success and some unexpected observations. Here we use accurate *ab-initio* molecular dynamics (AIMD) simulations to obtain the TEA from thermal expansion coefficients for two T1 phase alloy systems $(\text{Mo,V})_5\text{Si}_3$ and $\text{Mo}_5(\text{Si,Al})_3$. We demonstrate that strategic alloying with Al substituting Si can achieve zero TEA for T1 phase. The microscopic origin of this outstanding thermomechanical properties in this alloy is explained by the calculation of higher order elastic constants in conjunction with atom and direction-resolved phonon density of states.

1. Introduction

Transition metal 5-3 silicides, particularly Mo_5Si_3 (T1 phase), are important structural phases due to its high melting point (2543 K), strength and excellent creep resistance at elevated temperatures [1]. The tetragonal crystal structure of T1 has two Wyckoff sites for Mo atoms; **4b** (chain site) and **16k** (non-chain site), and two sites for Si atoms; **8h** and **4a** (**Fig. 1a**). The major drawback of the T1 phase is its unusually high thermal expansion anisotropy (TEA) or α_c/α_a of 2.2[2], that results in micro-cracking, leading to mechanical failure. It has been suggested that the high TEA resulted from the anharmonicity originating from the unusually short Mo-Mo bond (2.46 Å) in the **4b** site along the c-axis within the T1 crystal structure [1]. Previous work addressed this issue[3] by selective substitution of Mo with another transition metal (ex. V/Nb) [2-4]. However, oxidation resistance of V/Nb alloyed Mo_5Si_3 is typically poor [5, 6]. An alternative strategy is to avoid the substitution of Mo and substituting Si by other metalloid elements such as Al. The multi-directional metallic bonds in Mo_5Si_3 could be altered by substituting Si (**8h**) atoms that are connected to the Mo (**4b**) atoms as indicated in **Fig 1(b)**. To the best of our knowledge no such study has been attempted.

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Al has been known to improve the oxidation resistance of metal silicides [7, 8] through formation of continuous alumina layer that prevents oxygen penetration [9]. It has also been shown to improve the ductility at room temperature [10]. There are indirect experimental evidences that Al alloying of the T1 phase may reduce the crack formation after solidification [11], which indicates a reduction in TEA[12]. A substitution of Si by Al in Mo-silicides has generally been known to weaken the Mo-Si bond and enhance the metallic nature of the system[13]. The substitution of Si by Al is limited to 32 atomic % for T1 phase according to the phase diagram [14]. However, no experimental thermomechanical properties of $\text{Mo}_5(\text{Si},\text{Al})_3$ alloys have been reported. We will first start with alloyed $(\text{Mo},\text{V})_5\text{Si}_3$ where experimental data are available to validate our approach and then proceed with more detailed investigation of Al alloying on the T1 phase.

Rawn *et. al.* [2] observed a TEA minimum in $(\text{Mo},\text{V})_5\text{Si}_3$ at 37.5% substitution of Mo with V. This is quite unusual as Mo_5Si_3 and V_5Si_3 are isomorphic and one would expect a monotonic change in the coefficient of thermal expansion (CTE) with V substitution. Rawn attributed the minimum in TEA to the site preference in substituting Mo by V [2]. At a lower level of substitution, the **4b** chain sites are preferred resulting in a large reduction in TEA. To better understand the microscopic origin of this intriguing thermomechanical properties of the T1 phase alloy and to engineer better high temperature alloys, we perform *ab-initio* molecular dynamics (AIMD) simulations on T1 phase alloys up to a temperature of 2000K. The AIMD method based on density functional theory (DFT) has an inherent advantage of having accurate potential as opposed to traditional classical MD methods. It can implicitly account for anharmonicity and is capable of directly observing the thermomechanical behavior at high temperatures [15-17]. Our goal is to first demonstrate the AIMD can explain the unusual alloying effect in $(\text{Mo},\text{V})_5\text{Si}_3$ and then make a more in depth analysis of the $\text{Mo}_5(\text{Si}, \text{Al})_3$ alloy via AIMD simulations. This is achieved theoretically by using second and third order elastic constants, and additional evidence via directionally resolved phonon density of states (DOS). Previous studies on the T1 phase $(\text{Mo},\text{V})_5\text{Si}_3$ show that the difference in third-order elastic constants C_{144} and C_{344} , may be the main reason for lattice anharmonicity[1, 4, 18]. To the best of our knowledge, no such studies have been presented before despite the tremendous importance and implication on its applications.

The outline of this paper is as follows. In the next section, we describe the methods used for the simulation in searching for and the verification of zero anisotropy in T1 phase by strategic alloying. In Section 3, we first present the results and discussions on the thermomechanical properties of $(\text{Mo},\text{V})_5\text{Si}_3$ showing good agreement with the experiment[2]. This is followed by a presentation of thermomechanical properties of $\text{Mo}_5(\text{Si},\text{Al})_3$ and detailed analysis on the atomistic origin of zero TEA in this new alloy. The paper ends with a brief conclusion.

2 Methodology

We employ Vienna *Ab initio* Simulation Package (VASP)[19, 20] for AIMD under a constant temperature and pressure (NPT) ensemble using the following specifications: (1) The PAW-PBE potentials[21] within the generalized gradient approximation(GGA); (2) electronic convergence criterion set at 10^{-5} eV with an energy cutoff of 350 eV; (3) simulation time step of 2 fs each with a total simulation time up to 12 ps; (4) a single Γ point sampling. We have tested the AIMD simulations at a higher energy cutoff, but no significant improvement was observed.

2.1 AIMD simulation

A 2x2x2 supercell of the T1 phase (256 atoms) in a tetragonal unit cell is used to construct the initial models for $(\text{Mo,V})_5\text{Si}_3$ and $\text{Mo}_5(\text{Si,Al})_3$ alloys. The concentration of V at each Wyckoff site is guided by the experimentally observed values of Rawn *et. al.* [2]. The vanadium atoms are randomly distributed on each site. We consider V concentration of 0% (Mo_5Si_3), 5.1%, 12.5%, 25.8%, 37.5%, 50% and 62.5% (V_5Si_3). For each composition, AIMD are carried out at five temperatures (300K, 700K, 1000K, 1300K and 1500K) for CTE estimation. In the 2x2x2 supercell of the T1 phase there are 96 Si atoms at both the **8h** and **4a** sites (Fig. 1a). We randomly distributed Al on the available Si sites. Four alloy models were constructed with 5.2%, 15.6%, 20.8%, 25% and 30.2% of Al substitution. The percentags are calculated with respect to the number of Si sites, not the total number of atoms. For example, the model with 5.2% has 5 Si atoms replaced with Al atoms in the cell. The total atomic percentage for this model is 1.9% Al. AIMD for $\text{Mo}_5(\text{Si,Al})_3$ alloys are carried out at four temperatures (300K, 1000K, 1500K and 2000K).

In the AIMD simulation, pressure, temperature, volume and lattice constants fluctuate throughout the simulation time. **Fig. 2** illustrates such fluctuations for pressure and temperature. However, after the initial ballistic stage (up to 1ps) their average values remain roughly constant. The thermodynamic parameters are taken from the average values excluding data from the initial ballistic stage. The CTE is obtained from the slope of lattice constants a and c variation vs. temperature from NPT simulations. The thermal expansion anisotropy is defined as the ratio of CTE in the crystallographic a and c directions ($\text{TEA} = \alpha_c/\alpha_a$).

2.2 Second and third order elastic constants

To better understand the effect of Al substitution in the proposed new $\text{Mo}_5(\text{Si, Al})_3$ alloy, it is necessary to analyze the elastic tensor of the equilibrium structure. To this end, we used the stress-strain method[22, 23] to calculate the elastic tensor for selected unit cell models of $\text{Mo}_5(\text{Si,Al})_3$ including the hypothetical “ Mo_5Al_3 ” phase (See section 3.2 for details). We apply $\pm 1\%$ strain to the fully relaxed unit cell structure. The stress tensor, σ_j 's is evaluated numerically from the stress data $(\sigma_j^+ - \sigma_j^-)/2$ of the stretched and compressed unit cell in 12 directions. The elastic tensor C_{ij} ($i, j = 1, 2, 3, 4, 5, 6$) are obtained by solving the system of linear equations $\sigma_j = \sum_{i=1}^6 C_{ij} \epsilon_i$. The resulting C_{ij} are then averaged over the symmetry equivalent elements. The Cauchy-Born stability criteria [24] is then checked for each of these crystals.

The third-order elastic constant is derived by fitting the second-order elastic constant (c_{ij}) as a function of the lattice parameter expansion in the a and c directions [4]:

$$c_{ij} = c_{ij}^o + 2 c_{1ij} \left[\frac{\delta a}{a} \right] + c_{3ij} \left[\frac{\delta c}{c} \right] \quad (1)$$

where c_{ij}^o is the second-order elastic constant of the crystal at its equilibrium lattice parameters and with relaxed internal parameters. We limited the lattice expansion for this purpose to a maximum of 2 % strain, to comply with the linear elasticity assumption[4].

2.3 Phonon density of states

The phonon density of states (DOS) in MD simulations can be obtained from the Fourier transform of the velocity autocorrelation function (VACF). We used a MD post processing package called "nMoldyn" [25] to obtain phonon DOS. The NPT simulation described above provides the optimal cell volume and the crystal parameters at the given temperature and 1 atm pressure. This information is used to perform an NVT (fixed volume and temperature ensemble) simulation to extract the vibrational behavior at equilibrium. The atom-resolved phonon DOS is extracted from VACF for individual atoms within the supercell according to:

$$C_{vv}(t) = \frac{1}{N} \sum_{\alpha=1}^N w_{\alpha} \frac{1}{3} \langle v_{\alpha}(0) \cdot v_{\alpha}(t) \rangle \quad (2)$$

where v_{α} and w_{α} are the velocity at a given time and the weighting factor (based on mass) for each atom α . The total phonon DOS can be estimated from the summation of the Fourier transform of the VACF of individual atoms:

$$G(\omega) = \int_0^{\infty} dt \cos[\omega t] C_{vv}(t) \quad (3)$$

For an illustration, **Fig. 3** shows the VACF of the NPT calculation for Mo_5Si_3 at 300K. In this study, VACF stabilizes after 1ps. thus the averaging of AIMD data after 1 ps is reasonable.

3 Results and discussion

This section is divided into two parts. In section 3.1 we show the results of CTE and TEA for $(\text{Mo,V})_5\text{Si}_3$ and $\text{Mo}_5(\text{Si,Al})_3$ alloys. The experimentally unusual TEA behaviour for the $(\text{Mo,V})_5\text{Si}_3$ alloys is well represented in our simulations. We employ the same procedure to $\text{Mo}_5(\text{Si,Al})_3$ alloys and observe the reduction in TEA. Section 3.2 is dedicated to identifying and explaining origin of the TEA in the T1 phase and to understand the effect of Al alloying by three different theoretical tools. Namely, Second and third order elastic constants and phonon DOS. The directionally resolved phonon DOS in particular, shows the origins of the anisotropic effect.

3.1 Coefficient of thermal expansion (CTE) and thermal expansion anisotropy (TEA)

The CTE and TEA for $(\text{Mo,V})_5\text{Si}_3$ and $\text{Mo}_5(\text{Si,Al})_3$ alloys are calculated using the method explained in section (2.1) above. The results for different V concentrations for $(\text{Mo,V})_5\text{Si}_3$ alloys are shown in **Fig. 4** together with the experimental data which exhibit unusual TEA behavior in $(\text{Mo,V})_5\text{Si}_3$ as observed by Rawn et. al. [2]. Indeed, in **Fig. 4(a) and 4(b)**, the variation of α_c and α_a as a function of V concentration is qualitatively reproduced. At low V

concentration, α_c decreases rather rapidly, reaching a minimum at 25.8% concentration, and increases thereafter. On the other hand, α_a increases only very moderately as V concentration increases with a slightly faster initial rate. The combined behavior for α_c and α_a resulted in a minimum of TEA shown in **Fig. 4(c)**. The minimum in TEA is located in the range of 25-40 % of V concentration in reasonable agreement with the experiment [2].

The data in **Fig. 4** not only show the capability of AIMD to capture the essential features of the CTE and the TEA in V substituted T1 phase models, but also show quantitative variations with experimental data. The α_a shows a deviation of 2×10^{-6} at low V concentrations but shows a better agreement with a smaller deviation of 1×10^{-6} at higher concentrations. There could be many reasons for the deviations, such as: (1) The data from AIMD simulations was based on a wider range of temperature (300K-1500K) than the range in experiment[2] (303K-873K), (2) A 2×10^{-6} deviation in CTE corresponds to a change in lattice parameters by at least 0.02 Å, which is beyond AIMD resolution in the present calculation. The standard deviations of a and c in our simulation were 0.07Å and 0.04Å respectively, (3) A 2x2x2 supercell (256 atoms) is of limited size for an alloyed system, especially for larger V concentration. Currently, using a larger supercell for AIMD will be computationally prohibitive, (4) There may be experimental uncertainty with respect to the CTE values themselves. For example, using a wider temperature range (up to 1400K), Rodrigues et al. [26] reported CTE values for V_5Si_3 closer to our results [**Fig. 4(b)**]. Despite these minor difference, the AIMD simulations using NPT ensembles do capture the unusual TEA behavior of $(Mo,V)_5Si_3$ and motivate us to explore the possibility of zero TEA in the T1 phase with other alloying elements.

With the validation of our AIMD technique for $(Mo,V)_5Si_3$ alloys, we now apply the same procedure to $Mo_5(Si,Al)_3$ alloys where no experimental data exist. Within the limit of Al solubility in the T1 phase, according to the reported Mo-Si-Al phase diagram at 1823K [14], we generate five $Mo_5(Si,Al)_3$ alloyed supercell models with different Al concentrations. As mentioned about Al atoms are randomly substituted on Si sites. We have tested several random models for each composition but found no significant change in CTE. The total free energy per atom, of the five models changed linearly from -9.225eV to -9.005eV. Although the stability cannot be known exactly because of the difference in compositions, the linear increase hints that they are stable structures. Furthermore, we have also calculated the cohesive energy to further confirm the stability of the supercell models. To calculate the cohesive energy, we followed the method described in ref. [27]. The Mo bcc crystal, Si in diamond structure and Al fcc crystal structures are taken as the reference states. The cohesive energies for the five models are -0.384, -0.358, -0.342, -0.331 and -0.319 eV/atom respectively. Therefore, the alloy models we studied are structurally stable according this criterion. The results of α_c and α_a from AIMD simulation as a function of % of Al substitution on the Si site are shown in **Fig. 5(a)**. There is an approximate linear decrease in α_c and a concomitant linear increase in α_a as Al content increased. The two lines intersect at 17.5% Al substitution, indicating an *isotropic* CTE (TEA=1) at a small Al substitution, well within the solubility limit is possible. Considering the fact that 60 % of V substitutions on Mo sites are required to yield a minimum TEA, Al should be a far more

effective alloying element than V in reducing TEA. It is highly desirable that experimental measurements be conducted to verify this exciting discovery.

3.2 Discussion on lattice anharmonicity in $\text{Mo}_5(\text{Si},\text{Al})_3$ models

In order to find the origin for the reduction of lattice anharmonicity associated with the Al substituted T1 phase, we performed additional static calculations on the elastic coefficients of four unit cell crystals with T1 structure corresponding to a 0.0% (Mo_5Si_3), 16.6%, 83.3%, and 100% (Mo_5Al_3) replacement of Si by Al. The last two crystals are hypothetical since they exceed the Al solubility limit in T1. For elastic coefficient calculations, the unit cell has to be used in contrast to a large supercell used in the AIMD because the crystal has to be at the equilibrium structure as explained in section 2.2. Table 1 shows optimized structures and the second-order elastic constants. For Mo_5Si_3 , the calculated values are in excellent agreement with the experimental data [28]. There is an overall decrease in elastic constants (C_{ij}) as a function of Al content due to an increase in the weaker Mo-Al bonding [13]. All calculated C_{ij} are positive and satisfy the Cauchy-Born elastic stability criteria, i.e. $((C_{11}-C_{12})/2 > 0)$. Mo_5Si_3 exhibits a large difference in C_{11} and C_{33} (~ 23 GPa) indicating a larger elastic anisotropy. This can be explained by the strong directional bonding in the basal plane (001) than those in the [001] direction (i.e. $C_{11}+C_{12} > C_{33}$ and $C_{66} > C_{44}$) [1]. The same trend can be observed in all 4 crystals of **Table 1**. The difference ($C_{11}-C_{33}$) however, is reduced to only 12GPa in Mo_5Al_3 . The message is that the Al substitution on Si sites reduces the elastic anisotropy in T1 phase structure by softening the directional bonding in the basal plane. This elastic anisotropy may have a direct correlation with CTE and TEA behaviour shown in **Fig. 5(a) and 5(b)**.

To gain an even better insight into the role of Al alloying, we computed the third order elastic constants of four crystalline models in **Table 1** within the linear elastic limit using a maximum strain of 2%. According to C-L Fu [4], a key to reducing TEA in T1 phase structure is to minimize the difference between the third order constants C_{144} and C_{344} , i.e. the rate of reduction of C_{44} as the lattice expands in a and c directions. In reference [4], it was shown that this difference is minimized with 20% V substitution for Mo in $(\text{Mo},\text{V})_5\text{Si}_3$ (i.e. $C_{144} - C_{344} \sim 100$ GPa). **Table 2** lists all calculated third order elastic constants for the four models and highlighting the C_{144} and C_{344} , including the data for Mo_4VSi_3 from ref. [4]. There is a large difference in magnitude initially between C_{144} and C_{344} for Mo_5Si_3 . With increasing Al substitution, the difference between the two third order elastic constants is reduced. In fact, only a relatively small Al substitution ($\sim 16.67\%$) is needed to reduce its difference to 169 GPa, which is slightly larger than the value of 100 GPa for 20% V substitution in $(\text{Mo},\text{V})_5\text{Si}_3$. This supports our finding that the Al is more effective in reducing the anisotropy in CTE for the T1 phase as observed directly from the AIMD simulations.

The Al effect shown above is quite surprising at first sight as no part of Mo-chain (**4b**) atoms are substituted by Al and thus one would expect its impact on the lattice anharmonicity to be minimal. However, as shown in **Fig. 1(b)**, the Mo-**4b** site is closely surrounded by the Si-**8h** sites as its first nearest neighbor (NN) forming Mo-Si and Mo-Al directional bonds. Thus, the

substitution of Si by Al may indirectly impact the vibrational behavior in the Mo atoms at the **4b**, sites due to the nature of multi-centered bonding, especially in the vicinity of Mo-Mo chains [1]. The occurrence or absence of the vibrational coupling between the two species can be detected by the degree of degeneracy in the atom-resolved phonon spectra in the T1 crystal structure. To support this hypothesis, we have evaluated and compared phonon DOS for both Mo_5Si_3 and the hypothetical Mo_5Al_3 compound with T1 structure using direct DFT phonon calculations [24], as well as from VACF via AIMD simulations. As shown in **Fig.6 (a)**, the phonon partial DOS (PDOS) from the Mo-**4b** site in Mo_5Si_3 at ground state shows a significant presence of high frequency peaks from Moatom in the $280\text{-}330\text{ cm}^{-1}$ range which overlap with the PDOS from the Si-**8h** sites. This feature is not as pronounced in Mo_5Al_3 as shown in **Fig. 6(b)**. In contrast, the phonon PDOS from Mo-**16k** site is at the same low frequency range in both crystals. We now go a step further to further resolve the PDOS in different directions in these two crystals. In **Fig. 7(a)-7(d)**, we display the directionally decomposed phonon PDOS for Mo_5Si_3 and Mo_5Al_3 which clearly indicates that the phonon structure in the high frequency range (**Fig.6(a)**) is largely due to the *c*-axis orientated vibration from the **4b** sites. These phonon modes are strongly coupled with the *c*-axis oriented phonon modes from the **8h** sites, as evident by the overlapping peaks.

We have also extracted the axially-resolved phonon PDOS of the four types of Wyckoff sites at 1500K from VACF of the AIMD simulations data for Mo_5Si_3 and Mo_5Al_3 (see section 2.3). They are shown in **Fig. 8(a-b)**) and **Fig. 8(c-d)** respectively. While the characteristics phonon peaks from the Mo- **16k** and Mo-**4b** sites along the *a*-direction are generally the same for both compounds, the respective component of the phonon spectra along the *c*-axis differ considerably. In the *a*-direction, the **16k** and **4b** site Mo atoms vibrate with a low frequency that is largely uncoupled with the phonon modes from the Si-**8h** atoms (see **Fig. 8**, upper panel). For the *c*-axis vibrations (**Fig.8**, lower panel), the atoms in Mo-**16k** sites still maintain the low-frequency phonon spectra similar to that in the *a*-direction, but the atoms in Mo-**4b** sites exhibit an additional phonon peak at the higher frequency range ($280\text{-}330\text{ cm}^{-1}$). This is especially true for Mo_5Si_3 (**Fig. 8(b)**). For Mo_5Al_3 , a much less distinctive feature at the low and high frequency phonon spectra is seen instead (see **Fig. 8(d)**). This explains why, despite the absence of a direct Mo substitution at the **4b** chain sites, the anharmonicity can still be altered significantly with Al alloying at 8h site. Obviously, the weakening of the Mo-Si bonding by an Al substitution, not only reduces the elastic anisotropy of the T1 phase, but also profoundly alters the vibrational characteristics of the adjacent Mo-**4b** sites.

4 Conclusion

In conclusion, we discovered the possibility of an isotropic T1 phase in $\text{Mo}_5(\text{Si},\text{Al})_3$ alloys with a considerably low level of Al substitution. The method and approach used is first validated by comparing data between theoretical and experimental values for $(\text{Mo},\text{V})_5\text{Si}_3$ alloys. Previous studies on V substituted T1 phase focused on the short Mo-Mo bond length of $2.46\text{ \AA}$ at the **4b** site as the primary source for anisotropy. Our finding shows this more related the Si-**8h** site attached to the chain, not as much due to Mo-Mo BL shortening. The origin of the Al

alloying effect in T1 is fully explained by the well-established second and third order elastic constant interpretations along with the decoupling of phonon modes pertaining to **4b** and **8h** sites in T1 structure. This finding of atomistic origin in explaining reduction in TEA in $\text{Mo}_5(\text{Al},\text{Si})_3$ will have a major impact in the application of Mo-based T1 alloys for high temperature applications. In principle, one can take advantage of this approach in addressing the TEA of a wider range of intermetallic compounds.

Table 1 Calculated second-order elastic constants (GPa) for a T1 unit cell substituting Al on Si sites. Number in the parenthesis is the experimental data^a.

%Al	C ₁₁	C ₃₃	C ₄₄	C ₆₆	C ₁₂
0.00	439(446 ^a)	394(390 ^a)	110(110 ^a)	137(140 ^a)	177(174 ^a)
16.67	426	388	109	129	160
83.33	370	359	96	96	113
100.0	360	347	94	94	113

^a ref [28]

Table 2 Calculated third-order elastic constants (GPa) of Mo₅(Si,Al)₃. Here C₁₁₁+ 3C₁₁₂ and C₁₁₃+ C₁₂₃ measure the ‘softening rate’ [18] of the tensile modulus C₁₁+C₁₂(GPa) with [100] and [001] expansions respectively.

%Al	(C ₁₁₁ + 3C ₁₁₂)	(C ₁₁₃ + C ₁₂₃)	C ₃₃₃	C ₁₃₃	C ₁₄₄	C ₃₄₄	(C ₁₄₄ - C ₃₄₄)	C ₁₆₆	C ₃₆₆
0.00	-4284	-1294	-4304	-993	-289	-569	280	-697	-317
16.67	-4016	-1675	-1886	-739	-300	-469	169	-516	-268
83.33	-3886	-1104	-2058	-859	-214	-166	-48	-190	-77
100.0	-4120	-950	-1945	-1133	-390	-343	-48	-363	-40
Mo₄VS₃[4]	-5200	-1300	-2500	-850	-350	-450	100	-600	-300

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Figure captions

Fig. 1 (a) Atomic structure of Mo₅Si₃ viewed from c direction; (b) Mo-2 chain (4b sites) viewed from *a*-axis direction

Fig. 2 Fluctuation of: (a) pressure and (b) Temperature as a function of AIMD run time in the model with 25% V concentration at 300K. Averages are taken from data after the 1ps time represented by the vertical line.

Fig. 3 Velocity autocorrelation function (VACF) for Mo and Si in Mo₅Si₃ at 300K.

Fig. 4 Simulated CTE for (Mo,V)₅Si₃ as a function of Vanadium concentration: (a) α_c , and (b) α_a ; (c) TEA. Experiment data are from Rawn et al (2005) shown in red open circles and Rodrigues et al (2009) shown in red open star symbols.

Fig. 5 Simulated (a) CTE and (b) TEA as a function of % Al substitution in $\text{Mo}_5(\text{Si},\text{Al})_3$ alloys.

Fig. 6 Calculated phonon DOS at the ground state using DFT for: (a) Mo_5Si_3 ; (b) Mo_5Al_3 .

Fig. 7 Ground state phonon PDOS projected along: (a) *a* direction and (b) *c* direction for Mo_5Si_3 ; and (c) *a* direction and (d) *c* direction for Mo_5Al_3 .

Fig. 8 Phonon PDOS from AIMD at $T=1500\text{K}$ for Mo_5Si_3 projected on the (a) *a-axis* (b) *c-axis* and for Mo_5Al_3 projected on the (c) *a-axis* (d) *c-axis*.

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Figure 1

Fig. 1 (a) Atomic structure of Mo_5Si_3 viewed from c direction; (b) Mo-2 chain (4b sites) viewed from a -axis direction

Figure 2

Fig. 2 Fluctuation of: (a) pressure and (b) Temperature as a function of AIMD run time in the model with 25% V concentration at 300K. Averages are taken from data after the 1ps tome represented by the vertical line.

Figure 3

Fig. 3 Velocity auto correlation function (VACF) for Mo and Si in Mo_5Si_3 at 300K.

Figure 4

Fig. 4 Simulated CTE for $(\text{Mo,V})_5\text{Si}_3$ as a function of Vanadium concentration: (a) α_c , and (b) α_a ; (c) TEA. Experiment data are from Rawn et al (2005) shown in red open circles and Rodrigues et al (2009) shown in red open star symbols.

Figure 5

Fig. 5 Simulated (a) CTE and (b) TEA as a function of % Al substitution in $\text{Mo}_5(\text{Si,Al})_3$ alloys.

Figure 6

Fig. 6 Calculated phonon DOS at the ground state using DFT for: (a) Mo₅Si₃; (b) Mo₅Al₃.

Mo1	Mo1
Mo2	Mo2
Si1	Al1
Si2	Al2

Figure 7

Fig. 7 Ground state phonon PDOS projected along: (a) *a* direction and (b) *c* direction for Mo_5Si_3 ; and (c) *a* direction and (d) *c* direction for Mo_5Al_3 .

Figure 8

Fig. 8 Phonon PDOS from AIMD at T=1500K for Mo₅Si₃ projected on the (a) *a*-axis (b) *c*-axis and for Mo₅Al₃ projected on the (c) *a*-axis (d) *c*-axis.