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Molecular-dynamics simulations of binary Pd-Si metal alloys: Glass formation, crystallisation and cluster properties

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ABSTRACT

Using Quantum Sutton-Chen potentials, Molecular Dynamics was used to obtain an atomistic description of melting, glass formation and crystallisation processes for palladium metal, metallic silicon and their alloys, from PdSi to Pd_5Si. Glass formation and crystallisation were investigated using different cooling rates, by analysing the radial distribution function, enthalpy, density, volume, and diffusion coefficient. As expected, glass forms at high cooling rates, while crystallisation occurs at slower rates. The glass transition temperature was estimated from the Wendt-Abraham parameter vs temperature curves and the splitting of peaks in the radial distribution function. The effect of the Pd/Si ratio on the glass transition was studied by analysing the volume change during cooling of the Pd-Si alloys. The glass forming ability was found to increase with increasing Pd concentration in the alloys. Overall, our results reveal that Quantum Sutton-Chen potentials allow good descriptions of the melting, glass transition, and crystallisation during the heating and cooling processes.

1. Introduction

Cooling rate plays an important role in the amorphisation of a material. When a liquid metal is cooled to a low temperature from melt, depending on the cooling rate, either crystalline or amorphous structures can be obtained. If the cooling rate is greater than the critical cooling rate or sufficiently high, homogeneous nucleation of crystalline phases can be avoided, and metastable amorphous/glass structure is formed. Metallic glasses were first reported by Duwez and colleagues [1] in 1960, wherein they demonstrated the preparation of $Au_{75}Si_{25}$ metallic glass by rapid quenching of the $Au_{75}Si_{25}$ liquid to avoid the crystallisation of the alloy. Recently, a significant attraction in metallic-glass research has been assumed to the essential factors that play a role in glass formation [2]. For pure metals, the theoretical glass transition temperature is taken as $T_g = 0.25T_m$ (T_m is the melting temperature), whereas for various glass-forming metallic alloys, it has been observed experimentally that T_g varies from 0.5 to $0.8T_m$ [3]. Accordingly, the structural changes in the liquid that occur during the cooling process are small and therefore, the transformation from the liquid into the amorphous solid phase can be investigated by examining atomic motions [4]. It is noteworthy that determining the nature of the glass formation from experiments is a rather difficult task.

Molecular dynamics (MD) can provide important insights into such complex processes by allowing the determination of quantities that are difficult to assess in real experiments and/or beyond the reach of first-principles methods. Currently, MD is one of the most powerful tools for investigating the glass formation and crystallisation processes of liquids on the atomic scale. Moreover, it is reliable for the study of short-range structural order in amorphous and glassy semiconductors. The first ab initio MD (AIMD) effort was made by Car and Parrinello [5], who adopted the so-called plane wave MD method to study the short-range order in amorphous silicon. Subsequently, the investigation of metallic glasses has turned into the foremost areas of MD simulation.

MD interest in metallic glasses covers various properties, such as statistic structures (i.e. pair correlation function) and transport (i.e. diffusion and viscosity) properties. Until the 19th century, the metalloid was referred to originally as non-metals or semi-metals. The term “metalloid” was reported initially by Pinkerton in 1800, to depict a mineral group of pyroxene with metallic magnificence [6]. Extension of the MD simulations into metal-metalloid systems are more challenging due to the complexity of describing the interaction potentials associated with directionality. In addition to successful MD simulation using Quantum Sutton Chen (Q-SC) potential of various metals and metallic alloys, e.g. face-centred-cubic (FCC) metals palladium, nickel, copper, silver and their binary alloys [7–9], more recently, efforts have been made to study the physical and structural properties of metalloid

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elements and their alloys with metals; for example, Silicon [10] and Pd-Si alloys [11–13]. In 1988, Stillinger and Weber (SW) [14] developed a new potential model to describe the interactions in solid and liquid forms of silicon. The outcome had revealed the structural and thermodynamic properties of amorphous silicon, which concurred with experimental data. To obtain an in-depth analysis of the disordered silicon phases along with its structural properties, "ab initio" MD study was conducted by Car and Parrinello, wherein an amorphous silicon was prepared by rapid cooling from the melt [15]. The results predicted during the simulation studies were in line with the observed experimental data.

Recently metalloid alloys such as silicon-germanium (SiGe) [16], have been studied using AIMD to investigate their structural and electronic properties. The results indicated that the total pair correlation function for the amorphous phase of silicon germanium (a-SiGe) was in line with the experimental data. It was demonstrated that the metallic character of the liquid phase of silicon germanium (l-SiGe) by evaluating its conductivity and derived semiconductor nature for the amorphous phase (a-SiGe). To extend MD systems for the metal and metalloid alloys, such as $Pd_{80}Si_{20}$, studies were conducted using the Yukawa pair potentials by Takagi et al. [11]. These revealed that a similar structural factor was found as observed in the experimental data obtained by Takagi et al., and the same number of the nearest neighbours of Pd around Si as the Gaskell proposed a structural model [13]. MD simulation for various Pd-Si alloy compositions using the Lennard–Jones pair potentials [11] investigated the local atomic structure based on the analysis of Voronoi polyhedra, which demonstrated that the medium range order (MRO) increased rapidly, as the composition of Si decreased.

Since the 1980s, great achievements have been made in the formulation of the interatomic potential with the consideration of some many-body effect with the inclusion of volume or density dependence to describe metallic bonding; for example, the effective medium theory [17], the embedded atom method (EAM) [18], Finnis-Sinclair (FS) [19] and Sutton-Chen (SC) [20] type potentials. In fact, Sutton-Chen potentials have been used widely due to their simple mathematical formulation and long-range characteristics; in particular, they have been used successfully in MD studies of thermal and mechanical properties of transition metals and metal alloys. In addition, Quantum Sutton–Chen potentials (Q-SC) [7], which involves parametrisation from fitting to first-principles properties, were used successfully in various investigations of metallic systems; glass formation, crystallisation, surface phenomena, clusters, nanowires, single crystal plasticity and transport properties.

Owing to better reproducibility of metallic systems properties with QC potential over the simpler pair-potential, Kart et al. [21] studied melting, cooling, and crystallisation of binary Pd_xAg_{1-x} alloys, and they obtained a wide range of accurate values for physical properties of the liquid, crystal, and glass phases. The resultant Q-SC potentials provided a satisfactory prediction of temperatures for melting, glass transition, and crystallisation during heating and cooling processes. Various efforts were also made to study the metalloid silicon materials using classical potentials, such as the simple Lennard-Jones pair-wise potentials [12], three-body potentials [22], Stillinger and Weber, [14] Tersoff [23], and EAM potentials [24].

While many researchers have used the SC potentials to study FCC metals such as Pd, Cu, Ni, Ag, Au, Ir, Pb, Al, Pt, Rh and their alloys, to the best of our knowledge, no one has previously attempted to use (Q-SC) to study metallic alloys containing Si. In this work, we have conducted a comprehensive study of the Pd-Si system; including its structural properties, glass transition & crystallisation temperatures, transport properties and cluster properties of metallic glasses. Firstly, we have derived the Q-SC many-body potentials, and then applied them to simulate the important materials phenomena associated with cooling and heating, in the temperature range from 0 to 2000 K.

Table 1
Q-SC potential parameters for the Pd-Si system.

Element	ε (eV)	a (Å)	n	m	c
Pd-Pd	0.003967	3.9382	12	7	113.14
Si-Si	0.064310	3.7653	6	5.25	12.76
Pd-Si	0.016304	3.8838	9	6.125	–

2. Computational details

2.1. Density functional theory calculations

First-principle calculations, within density functional theory (DFT) and the generalised gradient approximation (GGA) for the exchange-correlation energy, as implemented in the Vienna Ab-Initio Simulation Package (VASP) code [25], were used to fit the Sutton-Chen potentials. The cohesive energy and lattice parameters of palladium, metallic silicon and their alloys were calculated using a 7 × 7 × 7 Monkhorst–Pack grid [26] for the Brillouin zone sampling and a 300 eV energy cut-off. The plane-wave basis sets energy cut-off, and k-point grid was selected to ensure energy convergence to less than 1 meV per atom. The total energy (E) of the crystal was calculated for a set of chosen volumes (V), and the resulting E vs V data was then fitted to an integrated 3rd-order Birch–Murnaghan equation-of-state (EOS) [27] to calculate the bulk modulus of the Pd-Si system. The GGA functional, used throughout this work, generally provides an accurate description of closed-packed, metallic and intermetallic systems [28]. Electronic properties (transport, magnetism) might require a more accurate treatment of non-local effects (correlation, exchange) in some cases, but are not within the scope of the present work.

2.2. Derivation of interatomic potentials

The DLPOLY MD package [29], along with Q-SC potentials, were used to gain insights into melting and solidification processes at the atomic scale. Çağin et al. [8] to reproduce experimental properties such as density, cohesive energy, bulk modulus, and phonon frequencies, while including zero-point energy (quantum) effects, first introduced quantum corrections to SC-type potentials by fitting them to DFT results. In the current research, Q-SC potential parameters for palladium and metallic silicon were obtained by fitting to some experimental data; for example, lattice parameters, cohesive energy, and bulk modulus.

The Sutton-Chen interaction potential comprises a pair potential V (r_{ij}) between atoms i and j, responsible for the Pauli repulsion between the core electrons, and a local energy density ρ_i term accounting for the cohesive interactions with atom i. The total potential energy takes the following form:

$$U_{tot} = \sum_i U_i = \sum_i \left[\sum_{j \neq i} \frac{1}{2} \in_{ij} V(r_{ij}) - c_i \in_{ij} (\rho_i)^{1/2} \right] \tag{1}$$

where,

$$V(r_{ij}) = \left(\frac{a_{ij}}{r_{ij}} \right)^{n_{ij}} \tag{2}$$

and

$$\rho_i = \sum_{j \neq i} \varnothing_{ij} (r_{ij}) = \sum_{j \neq i} \left(\frac{a_{ij}}{r_{ij}} \right)^{m_{ij}} \tag{3}$$

In Eqs. (1)–(3), r_{ij} is the distance between atoms i and j, a_{ij} is a length parameter leading to dimensionless V(r_{ij}) and ρ_i; c_i is a dimensionless parameter scaling the attractive vs repulsive terms, $\in_{ij}$ sets the overall energy scale, and n, m are positive integers such that $n > m$. Interatomic terms $\in_{ij}$ are derived from one-centre terms $\in_i$ and