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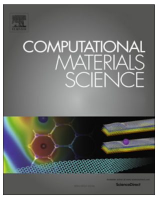

Editor's Choice

Structure and properties of liquid Al–Cu alloys: Empirical potentials compared

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ABSTRACT

We report on the structure and mass transport properties of liquid Al–Cu alloys predicted by two recently-developed empirical many-body potentials: MEAM (Jelinek et al., 2012) and EAM-ADP (Apostol and Mishin, 2011), and by the well-known Gupta potential. Total and partial pair correlation functions, angular distribution functions, densities, coordination numbers and self-diffusion coefficients are compared with published experimental and *ab initio* results for a number of temperatures above the liquidus. Prevalent local orderings are characterized by means of Voronoi analysis. Densities and the temperature coefficient of density are compared with experiment for different compositions of the alloy. All three studied potentials, and EAM-ADP and MEAM in particular, display marked difficulty in describing mixed (Al–Cu) interactions. EAM-ADP mispredicts Cu-rich alloys to re-solidify at all temperatures studied, while MEAM's predictions for the density and its temperature dependence are poor for Al-rich compositions. Overall, the best description of liquid Al–Cu is offered by the Gupta potential, which is found to give a reasonable picture of short-range order and predicts mass transport coefficients and densities in moderately good agreement with experiment.

1. Introduction

Aluminum alloys are ubiquitous. Owing to their low density, good forgeability and high thermal conductivity, they are used extensively in the aircraft industry [1], both as bulk structural materials (fuselage frames, chassis), and for high-performance mechanical parts and devices (engine cylinder heads and impellers, propellers, hydraulic systems) [2]. A high yield-strength-to-density ratio, low corrosibility and weldability contribute to their prevalence in shipbuilding (hulls, deckhouses, bilges, tanks) [3] and, coupled with high temperature resistance, in the automotive industry (engine cylinder blocks, truck frames, suspension struts) [4,5].

The addition of copper as main alloying element can serve to improve the hardness and strength of an aluminum alloy through precipitation hardening [4,6]. High-strength Al–Cu alloys thus find applications in aerospace engineering [7], and their high fracture toughness and resistance to crack propagation are desirable in the construction of light-weight armoured systems [8,9].

The thermophysical properties of the melt from which Al–Cu alloys are obtained and the conditions under which solidification proceeds in an undercooled alloy fundamentally influence the resultant structure of the solid alloy [10]. A number of experimental investigations of the solidification of Al–Cu shed light on how the microstructure depends on the solidification rate (e.g. Ref. [5]) and how it is influenced by dynamical processes on the micro-scale (e.g. melt convection [6]). However, a thorough atomic-scale understanding of solidification in Al–Cu alloys remains elusive, as scattering and diffraction experiments lack necessary atomic-level resolution [11].

Another route to the elucidation of structure and dynamics of liquid Al–Cu is through atomic-scale computer simulation. Classical particle-method (molecular dynamics (MD) and Monte Carlo (MC)) simulations of metallic systems enjoy a steady gain in popularity since the introduction of many-body empirical potentials (sometimes referred to as pair functionals [12]) in the 1980s. Most notable examples include the Gupta potential [13], the Finnis–Sinclair model [14], the Sutton–Chen potential [15–17], the effective medium theory (EMT) approach [18,19], Ercolessi's glue potential [20] and the embedded atom method (EAM) [21–23]. The above-mentioned "metal" potentials all set out to describe metallic bonding by including a local volume or density dependence [24], thereby circumventing known deficiencies of simple pair poten-

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tials, such as poorly predicted vacancy formation energies and mispredicted isotropy of elastic constants [12].

Direct application of atomic-scale simulations to dynamical processes (nucleation, diffusion, quenching, age hardening, crack propagation) that are of interest in Al–Cu alloys face a number of considerable difficulties. The limited (sub-μs) timescales accessible to MD calculations pose problems in simulating processes that require statistical averaging of long trajectories, such as melting or re-crystallization [25,26]. Such simulations, out of sheer necessity, employ heating or cooling rates in the order of 10^{11} K/s or higher [11], far in excess of experimental values. In model calculations time-dependent nucleation effects have been observed to lead to nucleation rates that are orders of magnitude off compared to experiment [27]. Finite-size effects, a consequence of length-scale limitations of atomic-scale simulations, also lead to uncertainties regarding the convergence of obtained results with respect to the size of the simulation cell [27]. Finally, and perhaps most importantly, all empirical potentials assume particular functional forms as models of the electronic interactions that are not accounted for explicitly in classical methods. This is known to lead to their poor transferability, i.e. empirical potentials give qualitatively wrong predictions when they are confronted with phases they have not been parameterized for. Occasionally even common structures pose unexpected difficulties for seemingly reasonably-transferable potentials (see Refs. [28,29] for discussion).

All the above difficulties notwithstanding, some ambitious efforts have been undertaken very recently in the field: Yanilkin et al. [7] studied dislocation mobility in Al–Cu alloys under load, and Singh et al. [30] examined the interactions of dislocations with precipitates known to occur in age-hardened Al–Cu alloys. The fact that both of these investigations had to resort to multiscale modeling to properly describe the relevant phenomena serves to illustrate difficulties faced by direct application of MD to the study of dislocation dynamics in these systems.

Some computational efforts have been devoted to the study of the liquid metallic state either for pure Al and Cu [31], or for alloys containing Cu [32,33]. The only computational study of liquid Al–Cu is due to Wang et al. [34], who give insight into the structure of liquid Al–Cu from *ab initio*-driven molecular dynamics, their results compare favorably with experimental results, where these are available. An overview of approaches for calculating thermophysical properties of undercooled alloys and a discussion of limitations of both experimental and computational approaches is given by Lv et al. [10]. Morris et al. [29] give a short summary of challenges faced by atomic-scale simulations of alloy melts, including an observation that inhomogeneities in the melt can apparently persist well above the eutectic temperature.

Another reason why metallic alloys pose considerably more difficulties for computer simulation compared to pure metals, is due to the complexities of the unlike-atom interactions that are often crucial for correctly modeling chemical ordering. It is not always obvious how to consistently treat these "mixing" interactions [28,35], which are precisely the interactions that usually play a crucial role in metallic [30] and non-metallic [36] binary systems alike. A systematic approach in the form of a composition-dependent potential for treating mixed systems has been proposed [37].

The difficulties associated with poor transferability of empirical functional forms can be overcome by using *ab initio* MD (AIMD), whereby electronic effects are modeled directly through explicitly considering the electronic wavefunction (e.g. Hartree–Fock, HF), its radically simplified expansion in terms of atomic orbitals (tight-binding), or the electronic density (density-functional theory). Such approaches require a significantly larger computational effort compared to empirical potentials, and usually scale unfavorably ($O(N^3)$ or worse) with system size. This, in turn, necessitates the use of radically small simulation cells and short timescales, exacerbating the finite-size [27] and finite-time [26,29] artifacts.

With the above points in mind, it is no surprise that considerable effort is being expended into improving upon existing potentials – by seeking new parameterizations through fits to *ab initio*-derived properties (e.g. Ref. [25]), by identifying and including physically relevant components missing from the description (such as long-range forces [38] in standard EAM), or by generalizing existing formalisms to include angular dependence (modified EAM (MEAM) or EAM-ADP potentials) [1,35,39,40], and second-nearest-neighbor effects [28] (2NN-MEAM).

Although newly-developed potentials are usually diligently tested by comparing selected properties with experiment or with *ab initio* calculations, the scope of such tests is typically limited to structures and properties that are of interest to the group developing the potential. How well, or whether at all, the potential transfers to other structures or phases and reproduces different properties is not typically assessed.

The aim of this work is to compare the predictions of three markedly distinct potentials for the Al–Cu system with available experimental and *ab initio* data. In this paper we focus entirely on the liquid state, anticipating future work devoted to the simulation of quenching in the Al–Cu system, for which a reliable description of the initial liquid state will be indispensable.

The paper is organized as follows. In Section 2 we briefly review available experimental and *ab initio* data that were available to us as references to compare against. We devote Section 3 to a more detailed description of the three potentials that we set out to compare. Section 4 summarizes the details of the set-up of our simulations. Results are presented in Section 5, while Section 6 is devoted to conclusions.

2. Reference data

We now turn to the justification of the choice of experimental and *ab initio* data that we used to compare the empirical potentials against. Experimental data on Al–Cu alloys that would be directly usable for comparison against computer simulation is admittedly scarce. Below we list relevant experimental work, with a rationale for using, or not, particular results as experimental reference in this work.

Mass transport properties of liquid Al–Cu have been investigated recently – with Brillo et al. [41] and Plevachuk et al. [42] reporting viscosity measurements, while quasi-elastic neutron scattering (QNS) [41,43] and cold neutron inelastic scattering [44] have been used, with varying success, to measure the dependence of the self-diffusion coefficient, D, on temperature. The significant scatter (in excess of 50%) in reported experimental values of the self-diffusion coefficient for Al–Cu has been blamed on non-negligible fluid flow in the liquid (an excellent review of available results and a detailed analysis of experimental difficulties is given by Lee et al. [45]), at the same time model assumptions used to derive $D(T)$ from QNS data are disputed [41,43]. Time-resolved X-ray radiography has been used to derive interdiffusion coefficients in Al–Cu melts [46]. These uncertainties in the experimental determination of the self-diffusion coefficient are too large to allow meaningful comparisons of $D(T)$ between simulation and experiment.

Electrical conductivity (measured by Plevachuk et al. [42]) is not accessible to classical molecular dynamics simulations.

Viscosities reported by Plevachuk et al. [42] are valuable; however, we found through repeated numerical experiments that obtaining sufficiently-converged viscosities from simulations is