Polytetrahedral short-range order and crystallization stability in supercooled Cu$_{64.5}$Zr$_{35.5}$ metallic liquid

R.E. Ryltseva,b,c,∗, N.M. Chetchelkatcheva,c,d,b

*a Institute of Metallurgy, Ural Division of Russian Academy of Sciences, Amudsena str. 101, 620016 Ekaterinburg, Russia
b Ural Federal University, Mira str. 19, 620002 Ekaterinburg, Russia
c Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Russia
d Moscow Institute of Physics and Technology, 141700, 9 Institutskiy per., Dolgoprudny, Moscow Region, Russia

Abstract

Development of reliable interatomic potentials is crucial for theoretical studies of relationship between chemical composition, structure and observable properties in glass-forming metallic alloys. Due to ambiguity of potential parametrization procedure, some crucial properties of the system, such as crystallization stability or symmetry of the ground state crystal phase, may not be correctly reproduced in computer simulations. Here we address this issue for Cu$_{64.5}$Zr$_{35.5}$ alloy described by two modifications of embedded atom model potential as well as by ab initio molecular dynamics. We observe that, at low supercooling, both models provide very similar liquid structure, which agrees with that obtained by ab initio simulations. However, deeply supercooled liquids demonstrate essentially different local structure and so different crystallization stability. The system, which demonstrate more pronounced icosahedral sort-range order, is more stable to crystallization that is in agreement with Frank hypothesis.

Keywords: Cu-Zr alloys, glass-forming ability, nucleation, molecular dynamics, embedded-atom model, icosahedral short-range order

1. Introduction

Understanding relationship between chemical composition, short-range order (SRO) and nucleation stability in supercooled metallic liquids is crucial to fabricate bulk metallic glasses. One of the generally accepted paradigm suggests that icosahedral SRO (ISRO) is responsible for stability of supercooled metallic liquids. Such SRO provides local minima of potential energy but it is incompatible with translational order that causes so-called geometric frustration. Following the pioneering work by Frank, years of research have established that this idea can explain dynamical arrest in supercooled liquids as well as glass-forming ability of metallic alloys.

Among other glass-forming metallic alloys the Cu-Zr-based ones are of special interest due to their high glass-forming ability. Moreover, simulated Cu-Zr alloys have become model systems demonstrating pronounced ISRO.

Molecular dynamics (MD) is the main theoretical tool for investigating SRO in supercooled liquids and glasses because it provides direct information regarding atomic-level structure. The key point of any MD simulation is the choice of interaction potential determining all the system properties at microscopic level. The most relevant type of potentials for describing metallic alloys is Embedded Atom Model (EAM), which usually provides good description of structural properties of both liquid and glassy metallic alloys. However, development of EAM potentials is a rather complex task due to the fact that many independent parameters need to be determined. Such parameters are usually obtained via fitting procedure, during which some properties calculated by EAM match to those either experimentally measured or calculated by ab initio methods. This procedure is often ambiguous one: some properties (especially those involved in fitting procedure) may be described rather
well while others may not [18] [19]. In regard to glassforming systems that means that, despite of good description of structure, some crucial properties of the system, such as crystallization stability or symmetry of the ground state crystal phase, may not be correctly reproduced in simulations [20] [17]. For example, recently we showed that, despite of pronounced ISRO, Cu_{64.5}Zr_{35.5} alloy described by widely accepted EAM potential [15] nucleates in sufficiently lengthy simulations with the formation of Cu_{2}Zr intermetallic compound with structure of C15 Laves phase. Moreover the alloy is actually unstable to crystallization for large system sizes (N > 20,000).

Such problems can be in principle overcome within the framework of ab initio molecular dynamics (AIMD). This method does not require any fitting and, in principle, can provide comprehensive information regarding structural properties of a system under consideration. However, strong limitations on time and spatial scales available in AIMD simulations raise concerns about applicability of the method for describing supercooled liquids and glasses.

Here we address these issues for Cu_{64.5}Zr_{35.5} alloy described by two modifications of EAM potential as well as by AIMD. We show that, at low supercooling, both models provide very similar liquid structure, which is in good agreement with that obtained by AIMD. However, deeply supercooled liquids demonstrate essentially different SRO and so different crystallization stability. The system, which demonstrate more pronounced ISRO, is more stable to crystallization that is in agreement with Frank hypothesis.

2. Methods

For MD simulations, we use LAMMPS Molecular Dynamics Simulator [21]. Periodic boundary conditions in Nose-Hoover NPT ensemble at P = 0 were imposed. The number of particles was N = 50,000. The MD time step was 2 fs that provides good energy conservation at given thermodynamic conditions.

Even though many properties of metals can be satisfactorily described with using pair potentials [22] [23] [24] [25], many-body effects are usually important for describing crystallization (see, for example, Ref. [26]). Thus, EAM potentials are applied in classical MD simulations of Cu-Zr alloys. We use two versions of EAM potential developed in the group of M. Mendelev from Ames Laboratory. The first one (hereinafter referred to as EAM-2008) is a widely accepted model [15] [27], which has been specially designed to describe liquid and glassy states of the Cu-Zr alloys. The second one (hereinafter referred to as EAM-2017) is modified version of EAM-2008 developed by the same group [28]. The main difference between two models is due to pair interaction between Cu and Zr; the embedded function F(ρ) for Zr and electron density functions ρ(r) for Zr-Zr and Cu-Zr are also slightly different; other functions are the same for both models.

Initial configurations were prepared as hcp-lattices with random seeding of the species in the lattice sites. These configurations were melted, completely equilibrated at T = 1200 K for 1 ns, then immediately cooled down to T = 850 K and isothermally annealed at this temperature for 0.2 µs. Note that annealing of N = 50,000 particles for 0.2 µs (∼10^6 MD steps) requires about a month of calculations in 128 supercomputer cores.

To study the structure of liquid, glassy and crystalline phases, we use radial distribution functions g(r), Voronoi tessellation (VT) [29] and visual analysis of the snapshots. Detailed description of these methods is presented in Refs. [30] [11] [17].

The classical MD results for the high-temperature liquid state (at T = 1200 K) were compared with those obtained by AIMD. To perform AIMD, we use open source quantum chemistry and solid state physics software package, CP2K. Projector augmented-wave (PAW) pseudopotentials and Perdew-Burke-Ernzerhof gradient approximation to the exchange-correlation functional were used. The simulations were performed at the Γ point only, with a time step of 2 fs. Cubic supercell of 512 atoms with target composition was built. Initial configuration was a random distribution of the atoms, which were subsequently equilibrated at 3000 K and 1200 K for 10 ps at each stage. Additional simulations for 10 ps were performed to collect data for calculating structural properties.

3. Results

Our first purpose is to compare two versions of EAM potential for Cu-Zr and to check how closely both models describe structure of the Cu-Zr liquids in comparison with AIMD. In Fig. [1] we show partial radial distribution functions g(r) of Cu_{64.5}Zr_{35.5} alloy calculated by using both versions of EAM as
well as by AIMD. We see that both EAM models demonstrate practically the same structure at \( T = 1200 \) K, which corresponds to slightly supercooled liquid (Fig. 1(a)-(c)). Comparison with AIMD reveals good agreement. However, for deeply supercooled liquid at \( T = 850 \) K, \( g(r) \) for the EAM models under consideration are noticeably different (Fig. 1(d)-(f)). Such difference is probably caused by difference in \( U_{\text{Cu-Zr}} \), which becomes important and low temperatures.

In Fig. 2 we show histograms of the most popular Voronoi polyhedra for Cu\(_{64.5}\)Zr\(_{35.5}\) alloy at \( T = 1200 \) K. We see again that both EAM potentials demonstrate practically the same results. Comparison with AIMD reveals qualitative agreement; the list of the most popular Voronoi polyhedra is the same for EAMs and AIMD but they fractions are essentially different. For example, fraction of icosahedra for AIMD is greater by a factor of two.

Our main purpose it to study crystallization stability of simulated Cu-Zr alloys. Recently we reported that Cu\(_{64.5}\)Zr\(_{35.5}\) alloy described by EAM-2008 is actually unstable to crystallization for large system sizes (\( N > 20,000 \)); it nucleates with the formation of Laves phases [20]. Here we perform the same annealing for Cu\(_{64.5}\)Zr\(_{35.5}\) with EAM-2017. In Fig. 3 we show time dependencies of the potential energy \( E_p \) for both systems mentioned. We see that average \( E_p \) is constant for EAM-2017 but decreases essentially for EAM-2008. That means the former is stable to crystallization on the simulation timescales.

To compare structural evolution of the systems under consideration, we perform Voronoi analysis. In Fig. 4 we demonstrate time dependencies of the fractions of the most popular Voronoi polyhedra. All the polyhedra presented are ZCN Kasper polyhedra (including icosahedron Z12) and their distorted modifications (CN is coordination number) [31]. Note that the increase of the fraction of both icosahedra and Z16 in Cu\(_{64.5}\)Zr\(_{35.5}\) with EAM-2017 is due to the growth of C15 Laves phase, which is build of these polyhedra [20]. Comparison of the pictures reveals that Cu\(_{64.5}\)Zr\(_{35.5}\) with EAM-2017 has more pronounced ISRO order than that with EAM-2008. Indeed the latter has only 6% of icosahedral clusters in the supercooled liquid state (before the crystal growth starts) whereas the former has 10% of icosahedra. We suggest that causes crystallization stability of Cu\(_{64.5}\)Zr\(_{35.5}\) EAM-2017 alloy that is in agreement with Frank hypothesis.

Analysis of Fig. 4(a,b) allows making important conclusions regarding growth of crystal nuclei in Cu\(_{64.5}\)Zr\(_{35.5}\) with EAM-2008. First, we see that
fraction of Z16 polyhedra in supercooled liquid is order of magnitude less than fraction of icosahedra. That suggests the Z16 polyhedron is an useful indicator of the growth of Laves phases. In the insert for Fig. 3 we show spatial distributions of the centers of Z16 polyhedra for Cu$_{64.5}$Zr$_{35.5}$ alloy described by both EAM-2008 (a,b) and EAM-2017 (c,d) at $T = 850$ K. Panels (a,c) and (b,d) correspond to Cu-centered and Zr-centered polyhedra, respectively.

4. Conclusions

Doing molecular dynamics simulations we compare structure and crystallization stability of two Embedded Atom Models for Cu$_{64.5}$Zr$_{35.5}$ alloy developed by M. Mendelev and co-authors (EAM-2008 [15] and EAM-2017 [28]). Exploring their structural evolution at isothermal annealing near the glass transition temperature for 0.2 $\mu$s, we observe that crystallization stability of supercooled Cu-Zr liquids is closely related to ISRO that is in agreement with Frank hypothesis. Indeed, the alloy with EAM-2017 demonstrating more pronounced ISRO (about 10% of ico-like clusters) is stable to
crystallization at simulation timescales. Whereas, the one with EAM-2008 having about 6% of ico-like clusters nucleates with the formation of C15 Laves phase. In general, SRO of Cu-Zr alloys is polytetrahedral that means it is mainly presented by Kasper polyhedra. Thus, besides icosahedra, other Kasper polyhedra, such as Z13 and Z11, can play important role in crystallization stability.

We observe that systems demonstrating similar structure in both equilibrium and slightly supercooled liquid states can have noticeably different structure and crystallization stability being deeply supercooled. That conclusion may be important for developing interatomic potentials procedure. Indeed, our findings rise a question if an EAM potential developed with using fitting of high-temperature structure properties is suitable for simulating deeply supercooled liquids and glasses.

We also observe that crystallization of the system at high supercooling level (i.e., at temperatures comparable to and below the glass transition temperature) occurs through polynuclear scenario that is in agreement with recent studies.

5. Acknowledgments

The authors gratefully acknowledge M. Mendelev for helpful discussion and providing EAM potentials. This work was supported by Russian Science Foundation (grant RNF 18-12-00438). Molecular dynamic simulations have been carried out using "Uran" supercomputer of IMM UB RAS and computing resources of the Federal collective usage center "Complex for Simulation and Data Processing for Mega-science Facilities" at NRC Kurchatov Institute.

References

[1] G. Tarjus, S. A. Kivelzon, Z. Nussinov, P. Viot, The frustration-based approach of supercooled liquids and the glass transition: a review and critical assessment, J. Phys.: Condens. Matt. 17 (2005) R1143.

[2] L. Berthier, G. Biroli, Theoretical perspective on the glass transition and amorphous materials, Rev. Mod. Phys. 83 (2011) 587–645. doi:10.1103/RevModPhys.83.587.

[3] H. Shintani, H. Tanaka, Frustration on the way to crystallization in glass, Nature Phys. 2 (2006) 200. doi:10.1038/nphys235.

[4] F. Frank, N. Mott, Supercooling of liquids, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences 215 (1952) 43–46. doi:10.1098/rspa.1952.0194.

[5] C. P. Royall, S. R. Williams, The role of local structure in dynamical arrest, Phys. Reports 560 (2015) 1 – 75. doi:10.1016/j.physrep.2014.11.004.

[6] J. E. Hallett, F. Turci, C. P. Royall, Local structure in deeply supercooled liquids exhibits growing lengthscales and dynamical correlations, Nature Communications 9 (2018) 3272.

[7] Y. Q. Cheng, E. Ma, H. W. Sheng, Atomic level structure in multicomponent bulk metallic glass, Phys. Rev. Lett. 102 (2009) 245501. doi:10.1103/PhysRevLett.102.245501.

[8] R. Soklaski, Z. Nussinov, Z. Markow, K. F. Kelton, L. Yang, Connectivity of icosahedral network and a dramatically growing static length scale in cu-zr binary metallic glasses, Phys. Rev. B 87 (2013) 184203. doi:10.1103/PhysRevB.87.184203.

[9] Z. W. Wu, M. Z. Li, W. H. Wang, K. X. Liu, Correlation between structural relaxation and connectivity of icosahedral clusters in czzr metallic glass-forming liquids, Phys. Rev. B 88 (2013) 054202. doi:10.1103/PhysRevB.88.054202.

[10] D. Wang, S.-J. Zhao, L.-M. Liu, Theoretical study on the composition location of the best glass formers in cu-zr amorphous alloys, J. Phys. Chem. A 119 (2015) 806–814. doi:10.1021/jp512006x.

[11] R. E. Ryltsev, B. A. Klumov, N. M. Chtchelkatchev, K. Y. Shunyaev, Cooling rate dependence of simulated Cu64.5Zr35.5 metallic glass structure, J. Chem. Phys. 145 (2016) 034506. doi:10.1063/1.4958631.

[12] D. Xu, B. Lohwongwatana, G. Duan, W. L. Johnson, C. Garland, Bulk metallic glass formation in binary cu-rich alloy series cu100-xzr x (x=34, 36, 38.2, 40 at.%), and mechanical properties of bulk cu62zr38 glass, Acta Mater. 52 (2004) 2021–2024. doi:10.1016/j.actamat.2004.02.009.

[13] D. Wang, Y. Li, B. B. Sun, M. L. Sui, K. Lu, E. Ma, Bulk metallic glass formation in the binary cu-zr system, Appl. Phys. Lett. 84 (2004) 4029–4031. doi:10.1063/1.1751219.

[14] B. A. Klumov, R. E. Ryltsev, N. M. Chtchelkatchev, Simulated cu-zr glassy alloys: the impact of composition on icosahedral order, JETP Lett. 104 (2016) 546–551. doi:10.1134/S0021364016020007.

[15] M. Mendelev, M. Kramer, R. Ott, D. Sordelet, D. Yogodin, P. Popel, Development of suitable interatomic potentials for simulation of liquid and amorphous cu-zr alloys, Philos. Mag. 89 (2009) 967–987. doi:10.1080/14786430902832773.

[16] S. Wilson, M. Mendelev, Anisotropy of the solid-liquid interface properties of the ni-zr b33 phase from molecular dynamics simulation, Philos. Mag. 95 (2015) 224–244. doi:10.1080/14786435.2014.995742.

[17] B. A. Klumov, R. E. Ryltsev, N. M. Chtchelkatchev, Polytetrahedral structure and glass-forming ability of simulated ni-zr alloys, J. Chem. Phys. 149 (2018) 134501. doi:10.1063/1.5041325.

[18] J. R. Vella, F. H. Stillinger, A. Z. Panagiotopoulos, P. G. Debenedetti, A comparison of the predictive capabilities of the embedded-atom method and modified embedded-atom method potentials for lithium, The Journal of Physical Chemistry B 119 (2015) 8960–8968. doi:10.1021/jp507775z.

[19] K. N. Lizd, N. Jakse, A. Pasturel, How closely do many-body potentials describe the structure and dynamics of glass-forming alloy?, J. Chem. Phys. 146 (2017).
R. E. Ryltsev, B. A. Klumov, N. M. Chctchellkatchev, K. Y. Shmyaev, Nucleation instability in supercooled cunral glass-forming liquids, J. Chem. Phys. 149 (2018) 164502. doi:10.1063/1.5054631.

S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, J. Comput. Phys. 117 (1995) 1 – 19. doi:10.1006/jcph.1995.1039.

N. Dubinin, A. Yuryev, N. Vatolin, Straightforward calculation of the wca entropy and internal energy for liquid metals, Thermochimica Acta 518 (2011) 9 – 12. doi:https://doi.org/10.1016/j.tca.2011.01.041.

N. Dubinin, V. Filippov, A. Yuryev, N. Vatolin, Excess entropy of mixing for binary square-well fluid in the mean spherical approximation: Application to liquid alkali-metal alloys, J. Non-Cryst. Solids 401 (2014) 101 – 104. doi:10.1016/j.jnoncrysol.2014.01.046.

M. Dzugutov, K.-E. Larsson, I. Ebbsjö, Pair potential in liquid lead, Phys. Rev. A 38 (1988) 3609–3617. doi:10.1103/PhysRevA.38.3609.

R. M. Khusnutdinoff, B. N. Galimzyanov, A. V. Mokshin, Dynamics of liquid lithium atoms, pseudopotential and emt-type potentials, JETP 126 (2018) 83–89. doi:10.1134/S1063776118010041.

M. I. Baskes, Many-body effects in fcc metals: A lennard-jones embedded-atom potential, Phys. Rev. Lett. 83 (1999) 2592–2595. doi:10.1103/PhysRevLett.83.2592.

Y. Zhang, C. Z. Wang, M. I. Mendelev, F. Zhang, M. J. Kramer, K. M. Ho, Diffusion in a cu-zr metallic glass studied by microsecond-scale molecular dynamics simulations, Phys. Rev. B 91 (2015) 180201. doi:10.1103/PhysRevB.91.180201.

M. Mendelev, Y. Sun et al., private communications (????).

J. Finney, Modelling the structures of amorphous metals and alloys, Nature 266 (1977) 309–314. doi:10.1038/266309a0.

R. Rybtsev, B. Klumov, N. Chctchellkatchev, Self-assembly of the decagonal quasicrystalline order in simple three-dimensional systems, Soft Matter 11 (2015) 6991–6998. doi:10.1039/C5SM01397F.

Y. Cheng, E. Ma, Atomic-level structure and structure-property relationship in metallic glasses, Prog. Mater. Sci. 56 (2011) 379 – 473. doi:10.1016/j.pmatsci.2010.12.002.

B. N. Galimzyanov, D. T. Yarullin, A. V. Mokshin, Change in the crystallization features of supercooled liquid metal with an increase in the supercooled level, JETP Letters 107 (2018) 629–634. doi:10.1134/S0021364018080099.

B. N. Galimzyanov, D. T. Yarullin, A. V. Mokshin, Structure and morphology of crystalline nuclei arising in a crystallizing liquid metallic film, Acta Materialia 169 (2019) 184 – 192. doi:10.1016/j.actamat.2019.03.009.