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TECHNICAL PAPER

Crystal–Melt Interface Growth Velocity of Ni–Zr Alloys Through Molecular Dynamics Simulations

R. Ramakrishnan[1,2] · **Gandham Phanikumar**[2] · **R. Sankarasubramanian**[1]

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Abstract In this investigation, crystal–melt interface growth velocities of Ni–Zr alloys are investigated at different undercoolings using molecular dynamics simulation. Ni, Ni–0.1 at.% Zr and Ni–1 at.% Zr are considered and free solidification approach is adopted to measure the interface growth velocity. Further, the anisotropy in growth velocity is studied by considering three different crystalline planes, viz., (100), (110) and (111), interfacing with the liquid. MD simulations are carried out using LAMMPS software and the Finnis–Sinclair interatomic potential developed by Wilson and Mendelev is used to describe the interatomic interactions. It is observed that addition of small amount of impurity (0.1 % Zr) increases the interface growth velocity of pure Ni during solidification. However, with further increase in the solute content (1 % Zr), interface growth velocity decreases. In all the cases, (100) is the fastest growing interface while the close packed (111) has the slowest velocity. Further, the calculated interface velocities are compared with the predicted ones from the theoretical model of Broughton–Gilmer–Jackson.

Keywords Crystal–melt interface velocity · Free solidification · Molecular dynamics

1 Introduction

Crystal–melt interface growth velocity during solidification is one of the important parameters that determine the growth morphology. Experimentally, many studies have been carried out to measure crystal growth rate in levitated droplets using capacity proximity sensor technique, photo-diode technique, high speed camera technique etc. [1, and references therein]. These measurements are actually for motion of the recalescence front and are of the scale of the sample size and do not resolve the orientation dependent growth rates. These experiments are also difficult to perform and measurement of anisotropic behaviour has not been reported so far. In this context, simulation techniques can be used as an alternative to the cumbersome experiments. Molecular dynamics (MD) simulation has been used in studying crystal-growth velocity of various elements [2]. However, very few MD studies have been done on alloy systems with most of them focusing on intermetallic compounds [3, and references therein]. A study by Lü [4] on the solidification kinetics of Ni-Si alloy (5 and 10 at.% Si) using MD simulations, reported the reduction in interface velocities with increasing Si content. Guerdane et al. [5] have studied the solidification and melting kinetics of $[Ni_cZr_{1-c}]_{liquid} - Zr_{solid}$ interface using MD and phase field simulations (PF) to address the applicability of bridging the two techniques. In this study, we employ MD simulations to study crystal–melt interface growth velocity of Ni–Zr alloys at the Ni rich end (Ni–0.1 at.% Zr and Ni–1 at.% Zr), as a function of different undercooling/superheating. Also, the anisotropy effect is investigated in these alloys by studying three interfaces, viz., (100), (110) and (111). Further, the effect of solute addition on the interface growth velocity of pure Ni is illustrated. A brief account of the computational details is given in the next section and the results are discussed subsequently.

✉ R. Ramakrishnan
rraghavan@dmrl.drdo.in

[1] Defence Metallurgical Research Laboratory, Hyderabad 500058, India

[2] Indian Institute of Technology-Madras, Chennai 600036, India

2 Computational Methodology

Molecular dynamics simulations are carried out using an open source software Large scale Atomic/Molecular Massively Parallel Simulator [6] (LAMMPS) and atomic interactions for the Ni–Zr system are described using the Finnis–Sinclair (FS) potential developed by Wilson and Mendelev [3]. The systems studied in the simulations are given in Table 1. In order to avoid any surface effect, periodic boundary conditions are applied in all the directions. Free solidification approach [2] is adopted in measuring the interface velocity and sandwich method is used in obtaining liquidus temperature [4]. Initially, Ni–Zr alloys are prepared by substituting the zirconium atoms randomly in FCC nickel lattice, as per the required composition. A solid–liquid interface is generated by melting one half of the system (perpendicular to Z direction) by equilibrating the portion at a temperature above the melting temperature (T_m), while the other portion is maintained at a temperature below T_m. Constant number of atoms, pressure and temperature (NPT) ensemble is used for this purpose and throughout the study a timestep of 1 femtosecond is maintained. Initial estimates of melting temperatures for these trials are made from simple calorific curve studies (which actually overestimate melting temperatures). Subsequently, the system is equilibrated in microcanonical ensemble (constant NVE). The conditions, for which both solid and liquid phases coexist, are the equilibrium melting conditions (i.e., combinations of pressure, P, and temperature, T). Such solid–liquid simulation cells are subsequently used in free solidification trials. In this study, for each free solidification simulation trial, at any particular undercooling, six different initial configurations are considered and the averaged interface velocity values are reported along with the standard deviations. A typical starting configuration depicting projected atomic positions in Ni–1 %Zr is shown in Fig. 1.

In the free solidification simulation, to allow the interface to grow, the solid–liquid system is equilibrated at different temperatures (using NPT ensemble with $P = 0$). The interface growth velocity can then be measured by two methods. In one method, the position of the solid–liquid interface is explicitly tracked with respect to time. In order to locate the interface position exactly, an order parameter is used in distinguishing atoms in solid and liquid phases. The order parameter [7] is defined as $\Phi = (1/12)\ \Sigma_i\ |r_i - r_{fcc}|^2$, where r_i and r_{fcc} are, respectively, the actual and the ideal distance (in fcc structure) between an atom and its nearest neighbours, i ($i = 1$–12). This definition ensures that $\Phi \sim 0$ for solid and $\Phi > 0$ for liquid. The order parameter is calculated for each atom at periodic time intervals. The entire system is divided into uniform bins perpendicular to Z direction, and the order parameter is averaged over all the atoms in each bin. In Fig. 1, the order parameter of Ni–1 %Zr is superposed on the projected positions of the atoms, and, the interface positions can be inferred to be at Z ~ 64 and 174 Å. Similar calculations are carried out at periodic intervals (at a particular undercooling) from which the interface velocity is obtained.

In the other method, the interface velocity is calculated from the rate of change of potential energy, $\mathrm{d}E/\mathrm{d}t$, using the relation, $v = (\Omega/2aL) \times (\mathrm{d}E/\mathrm{d}t)$, where, L is the latent heat of solidification, Ω is the atomic volume of the solid and a is the interface area [2]. Both methods are used in the present simulation to calculate the interface velocity and they yield close results within the error range (given by standard deviation).

3 Results and Discussion

3.1 Liquidus Temperature

The potential energy variation with temperature (calorific curve) for Ni–0.1 %Zr is shown in Fig. 2. Simulation starting from a solid phase shows a jump in potential energy at 2050 K (while heating), above which the system is entirely in liquid state. This is an overestimate of melting

Table 1 Systems studied in the simulation

	Ni	Ni–0.1Zr			Ni–1Zr		
	(001)/Liquid	(001)/Liquid	(110)/Liquid	(111)/Liquid	(001)/Liquid	(110)/Liquid	(111)/Liquid
Number of Zr atoms	0	39	31	61	360	320	600
at.% Zr	0	0.11	0.10	0.11	1.04	1.04	1.04
Total number of atoms	30720 to 57600						
System dimension							
(001) interface	~4.2 × 4.2 × 21.1 nm along X [100], Y [010] and Z [001]						
(110) interface	~3.9 × 4.2 × 19.9 nm along X [110], Y [001] and Z [1-10]						
(111) interface	~4.9 × 5.1 × 24.4 nm along X [1-10], Y [11-2] and Z [111]						

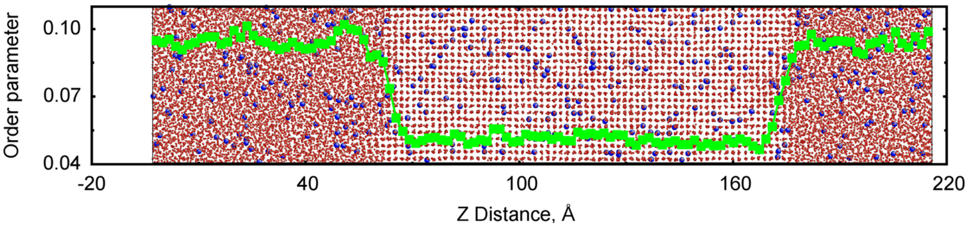


Fig. 1 A typical starting configuration for free solidification simulation (projected on XZ plane system: Ni–1 %Zr, Ni (*red*) and Zr (*blue*)). The average order parameter (averaged over bins parallel to XY plane) is superposed. (Color figure online)

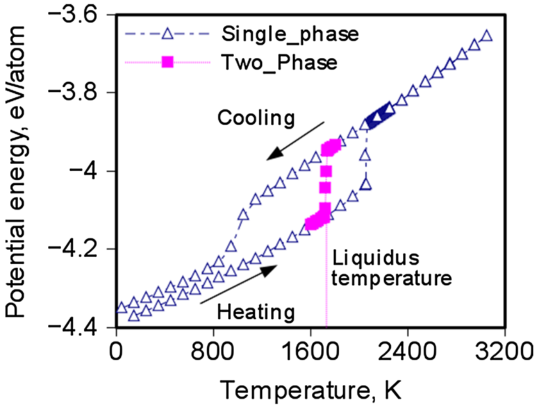


Fig. 2 Potential energy variation with temperature for Ni–0.1 %Zr. *Blue triangles* correspond to system where the starting configuration is homogeneous solid phase. *Red squares* correspond to the simulation in which solid + liquid is the starting configuration. (Color figure online)

temperature, as overheating is required to nucleate the liquid phase. However, when the starting configuration is a solid–liquid system, the steep change in potential energy occurs at 1730 K, which corresponds to the liquidus temperature. Similar analyses are carried out for Ni and Ni–1 %Zr and the results are given in Table 2. Further, liquidus temperatures calculated from thermodynamic calculations using ThermoCalc software with SSOL4 database are also reported in Table 2. It is observed that MD simulated liquidus temperatures match well (less than 2 % deviation) with the thermodynamic calculations.

3.2 Free Solidification Simulations

The potential energy variation against time at different temperatures (undercooling and superheating) for Ni–0.1 %Zr, (111) interface is shown in Fig. 3a. It can be seen that at a particular undercooling (for example T = 1665 K, ΔT ∼ 65 K), the potential energy gradually reduces with time (till ∼375 ps) and then reaches a plateau, indicating completion of solidification. The projected atomic configurations corresponding to 0, 200, and 400 ps are shown in Fig. 3b–d. Similarly, under superheating, melting is characterized by an increase in the potential energy. The interface velocities are measured for all the six different initial configurations and the averaged values as a function of undercooling for all the three systems are shown in Fig. 4. It can be seen that in all the cases, with increase in undercooling, the interface velocity increases.

Further, anisotropy in interface growth velocity is observed in both 0.1 and 1 %Zr cases with $v_{100} > v_{110} > v_{111}$. Similar anisotropic behaviour in nickel is well reported for MD simulations [2] and hence is not addressed in the present study. The anisotropy effect can be understood based on the density barrier explanation by Fredriksson and Akerlind [8]. The extent of anisotropy is quantified using a parameter, kinetic coefficient ($\mu = v/\Delta T$), which is the proportionality constant between interface velocity and undercooling (only solidification regime is considered in the present study). The calculated values for different systems are reported in Table 2. As mentioned above, the trend of $\mu_{100} > \mu_{110} > \mu_{111}$ is observed. Further, among the systems, it is seen that $\mu^{Ni\text{–}0.1Zr} > \mu^{Ni} > \mu^{Ni\text{–}1Zr}$.

Table 2 Liquidus temperature/melting temperature and other properties

	Ni	Ni–0.1Zr	Ni–1Zr
MD—liquidus (sandwich method) (K)	1735	1730	1690
Thermodynamic calculation (thermocalc)—liquidus (K)	1728	1727	1712
Latent heat (eV)	0.167	0.164	0.157
μ_{100} (cm/s K)	36.5 ± 1.0	39.2 ± 1.0	34.1 ± 2.7
μ_{110} (cm/s K)	–	31.0 ± 0.9	27.5 ± 0.9
μ_{111} (cm/s K)	–	25.7 ± 1.5	21.2 ± 1.2

Fig. 3 **a** Potential energy variation with time at different temperature for Ni–0.1 %Zr, (111) interface. Projected atomic configuration on XZ plane at different time **b** 0, **c** 200 and **d** 400 ps at a temperature of 1665 K corresponding to an undercooling of 65 K. Ni and Zr atoms are represented using *red and blue colour* respectively. (Color figure online)

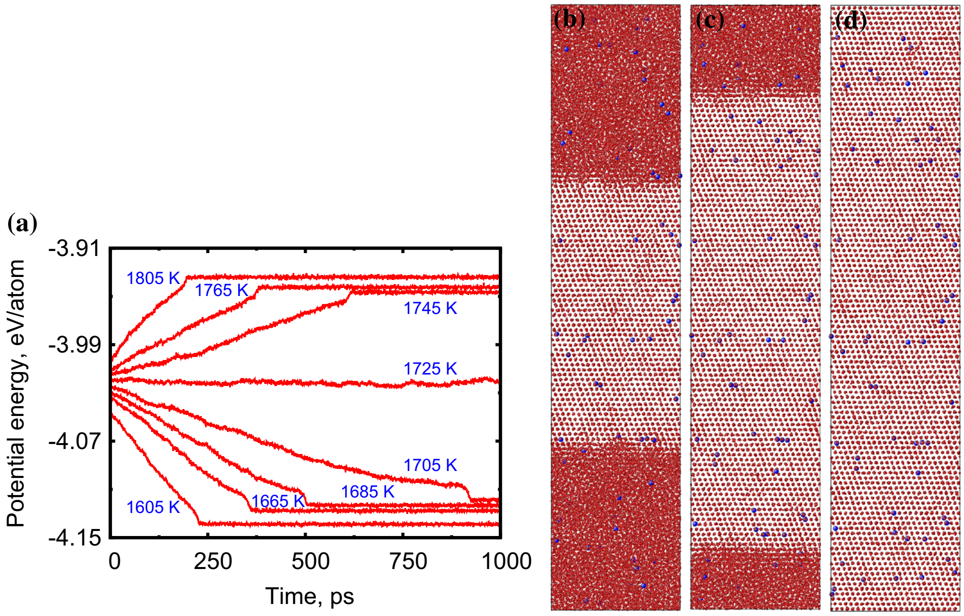
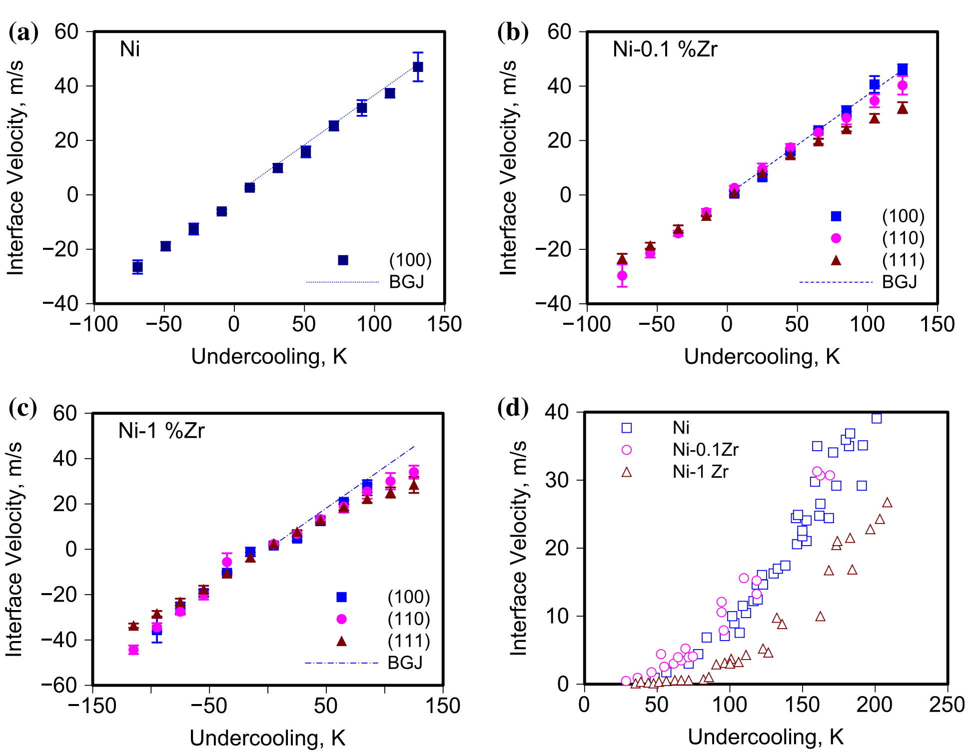


Fig. 4 Interface velocity variation with undercooling for **a** Ni, **b** Ni–0.1 %Zr and **c** Ni–1 %Zr along with theoretical BGJ prediction and **d** experimental [1] measurements



The dendrite growth velocities measured from levitation studies by Galenko et al. [1] are also shown in Fig. 4d. They have reported that the addition of small amount of impurity (0.1 %Zr) in nickel, enhances the dendrite growth velocity and further increase in the solute content (1 %Zr) reduces the growth velocity. The present study also captures these facts, though the simulated interface velocity values are different from that of the experimental measurements. The reasons for the enhancement or the reduction of the interface velocity on alloying may be due to a complex interplay between the availability of the driving force and the activation barrier for the interface growth. However, it needs further investigation (for example, using nudged elastic band (NEB) calculations and/or analysis of the liquid structure near the interface) to find the exact mechanism. The differences in velocity between the experiments and simulations can be easily understood. It is to be noted that the experimental measurements are carried out from the recalescence of the front motion. In such experiments, the velocity is obtained from the ratio of sample diameter to recalescence time. Also, the measurements are macroscopic in nature, and anisotropic measurement is not possible. More importantly, these measurements include contribution from other undercoolings such as curvature effect, whereas, the present simulation only addresses the kinetic undercooling. It can be seen from Fig. 4, that the kinetic undercooling (from MD) corresponding to the maximum interface velocity reported in experiments is about 40–60 % of the total undercooling. By deconvoluting the different undercoolings, it may be possible to find a good match between the experiments and simulations.

The simulated interface velocities are compared with those from theoretical prediction using Broughton–Gilmer–Jackson model (based on the collision based interface attachment mechanism). Figure 4a–c shows the interface velocity variation with undercooling from the simulations as well as the theoretical model. It can be observed that close to the melting temperature, simulated values matches well with that of BGJ prediction. Hence, it can be inferred that at low undercooling the interface controlled growth mechanisms is followed.

4 Conclusion

Crystal–melt interface velocity during solidification of Ni, Ni–0.1 %Zr and Ni–1 %Zr are calculated using MD simulations. Small impurity addition (0.1 %Zr) increases the interface velocity and with further increase in Zr content, the growth velocity reduces. The anisotropic effect on growth velocity is observed in both alloys with (100) interface being the fastest and (111) as the slowest. At lower undercooling, the interface velocities match well with the BGJ theory indicating interface controlled growth mechanism.

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