dynamic and physical properties of silicate melts. The local dynamics of atoms are better understood and show strong decoupling at the microscopic scale. The macroscopic descriptions of crystal nucleation and growth have now to take into account these microscopic properties to reconcile theory and experimental data. This is especially true at large degrees of supercooling where the mobility of various cations may be very different. Indeed, our results demonstrate that the high mobility of network-modifying cations can directly affect the compositions of nucleating phases and might quantitatively explain the failure of classical theories when predicting nucleation rates. In particular, the importance of mobile network modifiers questions the use of the bulk shear viscosity of the parent melt as a scaling property for kinetic factors controlling crystal nucleation. The same may be true for crystal growth.[13]

Finally, from the standpoint of materials engineering, these studies demonstrate that it is possible to predict the composition of metastable subsolidus phases if the glass transition temperature of the parent melt is known. This in turn may offer new opportunities to design advanced composite and glass-ceramic materials.


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An Atomic and Mesoscopic Study of Precipitation Kinetics in Al-Zr-Sc Alloys**

By Emmanuel Clouet,* Maylise Nastar, Alain Barbu, Christophe Sigli and Georges Martin

Zirconium and scandium are added to aluminium alloys because they allow to control recrystallization and lead to an
increase of the tensile strength, the better effect being obtained for a combined addition. This is a direct consequence of the formation of small ordered precipitates having the L12 structure and the efficiency of the solute addition depends on the density and on the size of these precipitates. An accurate knowledge of the precipitation kinetics is thus necessary so as to optimise the alloy properties.

At the atomic scale, kinetic Monte Carlo (KMC) simulations are the suitable tool to study precipitation kinetics. Thanks to a precise description of the physical phenomenon leading to the evolution of the alloy, such simulations allow to predict the kinetic pathways in full details. Nevertheless, one drawback of this atomic approach is the needed computational time: only the early stages of precipitation and the high super-saturations can be simulated. To circumvent this difficulty, we develop mesoscopic models of precipitation for Al-Zr-Sc alloys, using the cluster dynamics (CD) approach and the classical nucleation theory (CNT). The corresponding mesoscopic input parameters are directly deduced from the atomic model.

Kinetic Monte Carlo

We developed an atomic diffusion model for Al-Zr-Sc alloys.[1–3] It relies on a rigid lattice with interactions between first and second nearest neighbours and uses a thermally activated atom-vacancy exchange mechanism to describe thermodynamics and diffusion. Parameters of the model were deduced from experimental data (Zr and Sc solubility limits and diffusion coefficients in aluminium) and from ab-initio calculations (Al3Zr and Al3Sc enthalpy of formation as well as Zr-Sc interaction in aluminium). Details of the KMC algorithm are briefly recalled in Ref.[4] In agreement with experimental observations, atomic simulations predict that the L12 Al3Zr0.5Sc0.5 precipitates are inhomogeneous: their core is richer in Sc than in Zr whereas this is the opposite for the external shells (Fig. 1 of Ref.[4]). This arises from the fact that Sc diffuses much more faster than Zr in aluminium.[4]

In agreement with TEM observations,[5–8] the KMC simulations show that a Zr addition to an Al-Sc alloy leads to a higher density of precipitates, these precipitates being smaller (Fig. 1(a)). Indeed, a Zr addition increases the nucleation driving force and thus the number of precipitates. As these ones mainly grow by absorbing Sc, one obtains smaller precipitates because the number of growing clusters is higher and there is less Sc available for growth at the end of the nucleation stage. The precipitate growth by Zr absorption is really slow but plays an important role too as it leads to the formation of an external Zr enriched shell which is responsible for the good resistance against coarsening. On the other hand, KMC simulations predict that a Sc addition to an Al-Zr alloy has quite distinct effects (Fig. 1(b)). As Sc atoms play a key role for nucleation and growth, such an addition leads to an increase of the precipitate density as well as to an increase of the precipitate size.

Cluster Dynamics

So as to extend the range of super-saturations and annealing times that can be simulated, we built a mesoscopic model of precipitation in Al-Zr and Al-Sc alloys using CD approach.[9] In such a modelling, precipitation is described by the time evolution of the cluster size distribution. Rate equations governing this evolution consider the absorption by a cluster and the evaporation from a cluster of monomers. All the different stages of precipitation, i.e. the nucleation, the
growth and the coarsening stages, are described by the same set of equations. The only required input parameters are the cluster interface free energies.

Comparing the precipitation kinetics obtained with KMC and CD simulations, one sees that a good agreement can be obtained between both modelling for the variations of the precipitate density and of the mean size of the observed particles (Fig. 2). The comparison can be made too with experimental data\cite{10,11}. CD model manages to reproduce the variation with time of the mean precipitate radius (Fig. 2). Despite the fact that the time scales in real experiments are several order of magnitude larger than those in KMC, CD reproduces atomics simulations at short times and gives a safe extrapolation thereof to the range of annealing times corresponding to experimental data.

CD can be used so as to simulate the evolution of the electric resistivity during annealing kinetics\cite{3}. A good agreement is obtained with experimental data\cite{12,13} (Fig. 3); CD manages to reproduce the fast decrease of resistivity during the nucleation and growth stages as well as the slower variation which follows during the coarsening stage.

**Classical Nucleation Theory**

CNT allows to predict the nucleation rate in a supersaturated binary solid solution, using one more input parameter than CD, the nucleation free energy. For Al-Zr and Al-Sc alloys, comparisons with KMC simulations\cite{2} show that its predictions are correct. But, to obtain a good agreement, one has to take into account the ordering tendency of the binary alloy when calculating the nucleation free energy. This requires the use of the cluster variation method or of low temperature expansions\cite{3} to compute this parameter from the atomic model, and exclude the use of more widespread models like the ideal or regular solid solution models.

An extension of the CNT to the Al-Zr-Sc alloy has been proposed\cite{3}. Going from the binary to the ternary alloy, the main difficulty is that the precipitates have the composition Al\(_3\)Zr\(_x\)Sc\(_{1-x}\), where \(x\) is not known a priori. Therefore, the theory has to predict this composition. In this purpose, a nucleation rate \(J_{st}(x)\) depending on the composition \(x\) of the nucleus is computed using the fact that Sc diffuses faster than Zr. This allowed us to assume that any critical nucleus is growing by absorbing a Sc atom and to neglect Zr absorption. The nucleation rate is then defined as the maximum of the function \(J_{st}(x)\) and the composition of the nucleus as the corresponding value of \(x\). The comparison with KMC simulations (Fig. 4) shows that this mesoscopic model reproduces the variation of the nucleation rate with the zirconium concentration of the solid solution when the Sc super-saturation is high. The mesoscopic
evaluation of the nucleation rate worsens a little bit when the Zr concentration becomes comparable to the Sc one and when the Sc super-saturation becomes too low. Nevertheless, the key point is that this extension of CNT manages to predict the increase of the nucleation rate with a Zr addition to an Al-Sc alloy, this increase being in reasonable agreement with atomic simulations.

Conclusions

This study illustrates how a quantitative multiscale modelling of the precipitation kinetics can be performed. Using a very limited number of experimental data and ab-initio calculations, we built for the Al-Zr-Sc alloy an atomic model from which mesoscopic quantities like the interface free energy or the nucleation free energy could be deduced. For the two binary Al-Zr and Al-Sc alloys, it was shown that a good agreement can be obtained between the KMC simulations, different mesoscopic models (CD and CNT) and experimental data. For the ternary alloy, CNT could be extended leading to predictions of an increase of the nucleation rate in agreement with atomic simulations and with experimental data.

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Reconciling the Classical Nucleation Theory and Atomic Scale Observations and Modeling**

By Georges Martin*

In the early 90’s, dramatic improvements of two techniques made it possible to observe and to simulate the early stages of phase separation at the atomic scale, on significant volumes of similar sizes: the efficiency of data collection by the Tomographic Atom Probe (TAP) on the one hand and the increase of computational efficiency on the other hand, make it possible respectively, to observe, locate and analyze atoms in several $10^3$ nm$^3$ (with 60% efficiency), and to simulate, using the Lattice Kinetic Monte Carlo method (LKMC), the...