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Reply to “Comments on ‘Modelling differential scanning calorimetry curves of precipitation in Al–Cu–Mg’” by M.J. Starink and S. Wang

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We recently published a short paper [1] on modelling DSC curves of AA 2024-T351 to which Starink and Wang [2] have made a number of critical comments. We recognize that some features of our paper were not fully developed initially and we now appreciate the opportunity of clarifying these points.

First, Starink and Wang write “In Ref. [1] only one experiment is considered, one DSC curve of the 2024-T351 (Al–Cu–Mg)” and then go on to compare this one curve with their extensive work on DSC of these alloy types. In fact, we conducted DSC experiments and simulations on this alloy at several different heating rates as part of a wider study of precipitation under non-isothermal conditions. Figure 1 gives an example of three simulated heat flow plots, at $5\text{--}20\text{ }^{\circ}\text{C min}^{-1}$, showing the expected behaviour of higher peaks at higher heating rates (as also measured experimentally). Note also that the peak temperatures shift to higher values with increasing heating rate, as usually observed. In this respect, we take note of the fact that the modelled differential scanning calorimetry (DSC) curves published by Khan and Starink [3] were effectively in error.

Starink and Wang then make the comment that “to test the real predictive capability of the model we need ... the predictions of precipitate size. From our experience ... we would expect that the model in Ref. [1] would fail to predict the precipitate size evolution in the over-ageing/coarsening stage by quite a substantial margin” and then “In contrast, with the interfacial energy in Ref. [1], which is 0.09 J m^{-2} at $190\text{ }^{\circ}\text{C}$, a KW type model would predict that no discernible coarsening occurs”. Here we agree entirely with them; after various simulations, we adopted the method suggested by Khan and Starink [3] of increasing the interfacial energy (of the temperature-dependent value for precipitation) by a

constant value of 0.2 J m^{-2} for the coarsening and dissolution stages. Khan and Starink effectively showed that this change in interfacial energy is required to correctly model the coarsening kinetics in Al–Cu–Mg where heterogeneous precipitation predominates. We regret that this value was not written explicitly in our paper, partly because of the possible length restrictions in a letters journal, but also because a more detailed paper is being written up on the applications of this type of modelling to precipitation during friction stir welding of this alloy. The intention was to develop these specialist points in more detail in the following paper.

In this context, it is worth noting that one can compare our calculated precipitate sizes with some of the transmission electron microscopy measurements given in the paper by Khan and Starink [3] on 2024 after a DSC-type heating cycle. For a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, Khan and Starink give experimental sizes of 4 and 45 nm at 300 and $420\text{ }^{\circ}\text{C}$, respectively. Our simulations predict sizes of 10 and 35 nm, respectively, at the above temperatures – which can scarcely be described as a failure by a substantial margin.

Nevertheless, it should be pointed out that the particle size effects on the integrated DSC peaks should be negligible. As shown in Ref. [1], the interfacial energies associated with particle size effects have no virtually influence on the integrated heat flow curves (the areas under the $dq/dt(T)$ plots), but will obviously affect the peak temperatures – particularly for the dissolution peaks.

Finally, Starink and Wang write that our assumption of rod-shaped pre-precipitates is “inconsistent with most work”. In fact, we simply assumed spherical Cu–Mg co-clusters, as is generally assumed for these alloys. In this case, the volume percentage of co-clusters is about 17%, which, given their unknown Al content, can be considered reasonably consistent with the alloy composition.

As a final comment, we greatly appreciate the contributions of Starink and colleagues to our understanding

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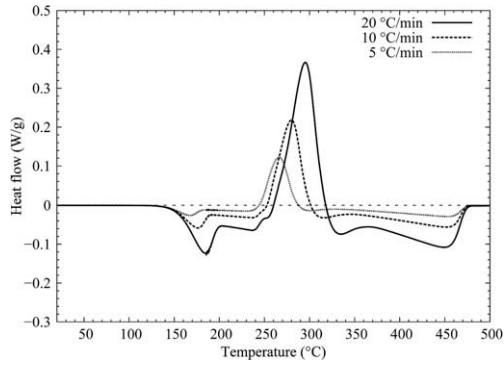


Figure 1. Simulated DSC curves of AA 2024-T351 at three different heating rates.

of precipitation in Al alloys and have therefore often employed their methods and many useful numerical val-

ues for the parameters. We feel, however, that to fully interpret DSC experiments it is important to write down the thermodynamic equations for the heat flow as clearly and rigorously as possible. In particular, their description in terms of Gibbs free energy helps basic understanding and can also be adapted to more complex alloys and heat treatments since thermodynamic databases are given in this form.

We express our gratitude to Christophe Sigli at the Alcan CRV Research Centre for several useful discussions on modelling precipitation in Al alloys.

- [1] E. Hersent, J.H. Driver, D. Piot, Scripta Mater. 62 (2010) 455.
- [2] M.J. Starink, S. Wang, Scripta Mater. 62 (2010) 720.
- [3] I.N. Khan, M.J. Starink, Mater. Sci. Technol. 24 (2008) 1403.