Scandium overtakes zirconium

Nanoscale core–shell precipitates within multicomponent alloys are known to confer strength and thermal stability beyond that expected from the constituent materials. Their formation mechanism has finally been revealed to involve a combination of thermodynamic and kinetic processes.

Core–shell nanoparticles are made of a core of one material surrounded by a thin shell of another. Their combination of small size and heterogeneous composition leads to novel optical, magnetic and electronic properties. In addition to the standard chemical routes for synthesizing discrete core–shell nanoparticles, it has become apparent that analogous core–shell structures can form spontaneously within Al-Sc-Zr alloys by controlling alloy composition and processing conditions.\(^1-^3\) The structures consist of a core that is rich in Sc and a thin, 1–2 nm shell that is rich in Zr, see Fig. 1. When these heterogeneous nanoparticles precipitate in an Al alloy, the material exhibits surprisingly superior properties, which includes a high strength and excellent thermal stability that cannot be expected simply on the basis of the properties of the constituent elements themselves.\(^4-^6\) Such strength and thermal stability are essential for high-temperature aluminium alloys that are used for structural applications. Until now, the formation process of these core–shell precipitates has been poorly understood, but a study reported in this issue by Clouet et al. now reveals the mechanism, and shows it to be dependent on both kinetic and thermodynamic factors.\(^7\)

To elucidate the mechanism of how the precipitate core–shell structures form, Clouet et al. used a broad range of experimental and computational techniques that allowed them to probe the particle formation and evolution process over length scales from the atomic to the micrometre. Ab initio calculations were used to determine the interactions between the constituent atoms, and these interactions were used as inputs in a Monte Carlo model for atomic motion, which had already been verified to produce accurate results when modelling the formation of precipitates in Al-Sc and Al-Zr binary systems. The authors then simulated the formation of the structures in the Al-Sc-Zr alloy at their earliest stages. An advantage of this approach is that it is not necessary to make any assumptions on the manner in which the composition of the precipitate structure evolves during the nucleation and growth process. A unique aspect of this work is that these simulations were tested using a wide array of experimental techniques: three-dimensional atom probe tomography, high-resolution electron microscopy and small-angle X-ray diffraction. In agreement with the simulations, all three techniques find a core–shell nanostructure with a composition of the shell in reasonable agreement with the simulations.

The simulations and experiments point to a novel nucleation and growth mechanism of the precipitates, with Zr playing a crucial role in both processes. When Zr is added to an Al,Sc compound it disrupts the regularity of the lattice and results in an increase in entropy. This increase leads to a large free-energy change on the formation of the Al-Sc-Zr precipitates, and thus to a high density of very small Al-Sc-Zr domains — or nuclei, the centre of the core–shell precipitates. Owing to the large diffusion coefficient of Sc relative to that of Zr, after the nuclei are formed the precipitates grow by primarily absorbing Sc. This leaves the slower-diffusing Zr atoms in the matrix. As the growth process continues and...
all the Sc is absorbed, the Zr is all that is left to precipitate on the Sc-rich core, creating the Zr-rich shell.

This coating of slow-diffusing Zr then acts as a barrier to the atomic transport that is required for particles to shrink if the others are to grow into larger particles, a process known as ‘coarsening’. The shell therefore slows this coarsening process. The high number density of core–shell nanoparticles increases the strength and high-temperature creep resistance of the alloy and the low coarsening rate gives rise to a high degree of thermal stability.

The kinetics of the diffusion process obviously plays an important role in the development of the core–shell nanoparticles, however, in the calculations of Clouet et al. it is assumed that the atoms lie on a rigid lattice. It is therefore not possible from this work to determine the role of elastic stress, that is, deformations of the lattice, in the core–shell formation process. The formation of the Zr-rich shell will relieve some of the stress associated with the misfit between the lattices of the Sc-rich precipitate and the Al matrix (refs 2, 8, also V. Radmilovic, private communication); there is therefore an additional driving force for the formation of the shell in these alloys that was not considered by Clouet et al. Nevertheless, elastic stress can only further promote the formation of the shell.

By bringing together the novel computational techniques and a vast array of experimental methods, Clouet et al. have provided new insights into the mechanism by which core–shell nanoparticles can form spontaneously in alloys. Using this insight, one can now design other alloys that form core–shell nanoparticles and, as a result, create new alloys with greatly enhanced properties.

REFERENCES