

Solidification of silver–germanium alloys under microgravity conditions

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SOLIDIFICATION of any melt occurs by the process of nucleation and growth. The driving force arising from cooling the melt below its equilibrium freezing temperature (undercooling) drives the process of nucleation. Depending upon the magnitude of the driving force, equilibrium phases or competing metastable phases get nucleated. In case nucleation is completely prevented, the melt freezes into a non-crystalline phase – the glass. The presence of insoluble foreign material, the container wall and impurities promote nucleation by providing the substrates. Therefore, any attempt to achieve high degrees of undercooling must remove such nucleation sites and several methods like the glass-slag techniques are available to facilitate the removal of extraneous nucleants.

Most of the thermodynamic parameters that characterize and control the nucleation process such as free energy of the liquid and solid phases and the interface energy, are not affected by gravitation. However, the absence of convective currents in the microgravity environment of space, increases the tendency towards nucleation. In contrast, the possibility of levitating the melt and containerless solidification reduce the possibility of heterogeneous nucleation and promote undercooling. In view of these opposing tendencies, it is difficult to predict the nucleation behaviour of a melt under microgravity conditions. Any attempt to quantify the extent of undercooling achieved in a space experiment must be based on an alloy which is otherwise well characterized with respect to its thermodynamic properties, undercooling behaviour under terrestrial conditions and likely phases that may arise through nucleation.

In our experiments conducted in the *MIR* space station in association with Regel *et al.* of Space Research Institute, Academy of Sciences, USSR (1984), we have chosen alloys of the eutectic silver–germanium system for investigating the undercooling behaviour. The aim of the experiment is to evaluate the extent of undercooling in space and compare the same with terrestrial results to estimate the effect of convection on the nucleation behaviour. Experiments on the ground have shown that it is possible to heavily undercool these alloys resulting in changes in microstructure, production of a novel metastable phase, extended solid solubility and even expect the formation of glass. These changes could be reasonably well correlated to the extent of undercooling and could thus be used as markers for characterizing the magnitude of undercooling. Besides, many physical, structural and thermodynamic properties of these alloys have been well established.

Three silver–germanium alloys representing hypo-eutectic, hyper-eutectic and the eutectic composition (25.9 wt% Ge) were prepared from super purity metals (> 99.999% pure). The alloys were then subjected to undercooling studies under the cover of a low melting glass slag by repeatedly heating them to above the melting temperature and cooling. The undercooling achieved was monitored with the aid of a suitably embedded thermocouple. The thermal cycling process was conducted until the undercooling achieved was largest and consistently produced. At the end of such experiments, the alloy formed a spherical bead of about 3 mm in diameter. It was then taken out of the glass slag, ion etched and mounted in a specially designed quartz cage. The cage had a provision for introducing glass-coated thermocouples in the form of circular loops at different levels. The alloy sphere could be mounted between the two loops to confine it to space

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within the cage. The cage was in turn placed in an isothermal container fitted with vacuum-shielded insulation developed at the Patan Space Research Institute for the ISPARITEL-M apparatus. This apparatus was already available on the *SALYUT-7* space station. The sample (suitably shielded) was placed by the astronauts in the ISPARITEL-M apparatus and the chamber was depressurized. Heating and melting of the specimen was accomplished with the aid of an electron beam and a molybdenum reflector. Analogue ground experiments were carried out under a vacuum of 3×10^{-4} mm Hg. Both the experiments used a heating and cooling cycle which took the samples to 800°C, held for 5 min and cooled down to temperatures in the solid state at 70°C/min.

After the experiments were performed in space, the samples were first examined for surface features in a scanning electron microscope. Subsequently, they were cut into slices of ~ 0.15 mm thickness and polished for X-ray diffraction and optical metallographic studies. Results obtained indicated the following:

- (i) Both ground and space specimens contained the silver-solid solution (α) and the germanium phases.
- (ii) The space sample of the hypo-eutectic alloy showed peculiar surface pitting which was not observed in any other sample.
- (iii) The microstructure of the hypo-eutectic alloy consisted of α -phase crystals which were uniform in size with about 10 μm diameter and were surrounded by much finer grains of germanium. Such a microstructure was observed in all the slices indicating that there was complete homogeneity in respect of the microstructure. This was in

notable contrast to the microstructure of the ground specimen, which showed the conventional dendritic α -phase with a eutectic microstructure in the space between α crystals.

(iv) In the eutectic and hyper-eutectic alloys, there were insignificant differences in microstructure.

(v) Extensive X-ray diffraction studies indicated that there were no metastable phases. All reflections corresponded to either the silver-rich α phase or germanium. No significant extension of solid solubility was found.

(vi) The X-ray diffraction studies also indicated that there was considerable texture in the polycrystalline α and germanium phases.

In summary, it can be said that the hypo-eutectic alloy containing 20 wt% germanium exhibited vastly refined microstructure that was very different from that observed on solidification on the ground. The most striking features of the microstructure of the space specimen were the uniformity of structure over the entire volume, the fine size of the particles and nearly isotropic nature of growth as well as the formation of germanium at the boundaries. These features can be attributed to a fairly large degree of undercooling and homogeneous nucleation over the entire volume. The extent of undercooling was, however, insufficient to produce any metastable phases in the system.

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