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Manipulating the Melting Behavior of Metal–Metal Eutectics

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Abstract Experiments were carried out in order to determine why a given eutectic sample approaches its state of equilibrium either rapidly or slowly during melting-curve determinations. The results of these experiments suggest that, when eutectic liquids are frozen, nonequilibrium solids normally form. The experimental results also suggest that the melting temperatures increase and the reproducibility of the melting curves improves considerably if the nonequilibrium solid is converted into the equilibrium eutectic solid lattice. As specific examples, Al–Cu and Al–Ag eutectic samples were studied.

Keywords Equilibrium solid · Eutectic · Melting point · Nonequilibrium solid

1 Introduction

It takes time to reach an equilibrium state after heating a partially melted substance for some time. The time to reach equilibrium is characterized by the so-called "relaxation time." The shorter this time, the faster the sample reaches its state of equilibrium. Equilibrium in thermometry may be defined as an isothermal state that is unchanging with time.

Figures 1 and 2 show how different the relaxation times and the melting temperatures of a given Al–Cu eutectic sample can be. Both curves show the drifting of the partially melted sample toward its state of equilibrium after a brief heating period

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Fig. 1 Example of long relaxation times as the sample drifts toward its state of equilibrium during a melting experiment

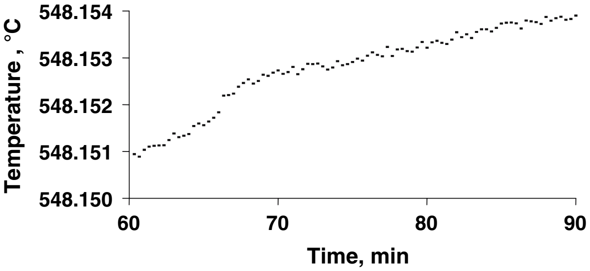


Fig. 2 Example of short relaxation times as the sample drifts toward its state of equilibrium during a melting experiment

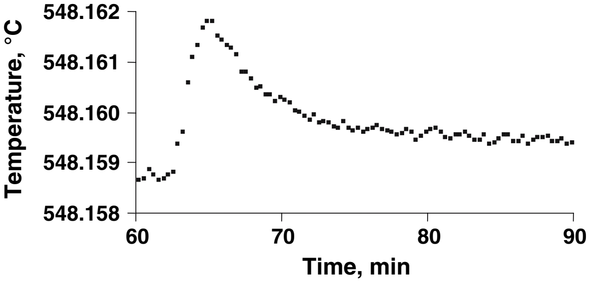
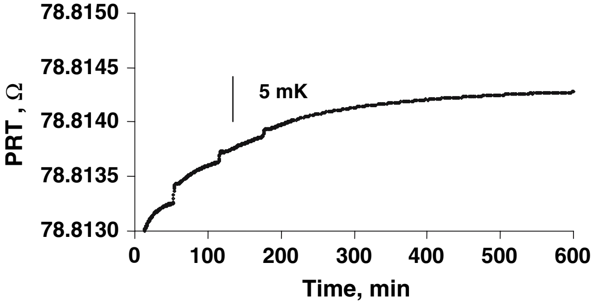


Fig. 3 Typical melting behavior of metal–metal eutectic substances in their states of long relaxation time



(at 62 min), during which it absorbed about 10% of its heat of fusion in both cases at the same solid/liquid ratio.

In Fig. 1, the liquid sample was frozen, kept within a few tenths of a degree Celsius below its melting range overnight, and then melted. This treatment kept the solid phase of the melting sample in a state that required very long relaxation times (several hours) to approach equilibrium during melting. The rest of the melting curve is shown in Fig. 3.

In Fig. 2, the same sample was partially melted and then slowly frozen overnight (8 h). The solid state of the sample, using such a procedure, was brought into a state of short relaxation time, i.e., the sample was able to reach its state of equilibrium rapidly during melting after heating it for a while.

Figure 3 shows the long drift of a partially melted sample toward its state of equilibrium during a melting experiment. On several occasions, the sample was kept slightly below its melting range for several days and the results were similar to Fig. 3, suggesting that the diffusion of atoms in the solid state from their nonequilibrium states to their equilibrium states is negligibly small. In this melting experiment, the total melting time was about 15 min. The accumulated melting times were 1.5, 3, 4.5, and 6 min. After the sixth melting minute (at 180 min), the sample was allowed to drift in order to see how long it would take to reach its equilibrium state at this liquid/solid fraction (37% liquid, 63% solid). This long drift curve holds the explanation for the short and the long relaxation times during a melting experiment; for pure metals, the time to reach stable thermal equilibrium at any solid/liquid fraction along the melting curve depends on their thermal conductivity. The higher the thermal conductivity, the faster a sample can reach a uniform temperature throughout its entire volume.

However, for eutectics to achieve their equilibrium states, it is not only the temperature gradients that have to be minimized, but also an equilibrium distribution must be reached between the two different metals that make up the eutectic. In the liquid state, at equilibrium, the Al and Cu atoms are uniformly distributed. Concentration gradients in liquids, in general, tend to gradually disappear, apart from some minor gravitational segregation that can be eliminated by stirring. In fact, the liquid samples (no solid phase present) were stirred by rapidly moving the thermometer well up-and-down before freezing them in order to ensure a uniform atomic distribution.

If a eutectic liquid of uniform component distribution is rapidly solidified, then the solid phase will also have a near-uniform component distribution. However, uniform component distribution on a microscopic scale within the eutectic solid lattice does not necessarily correspond to equilibrium locations of the Al and Cu atoms. McAllen [1] gave a very clear metallographic picture of the distribution of the Al and the Cu phases in the solid phase of this eutectic substance: the location of the Al and Cu atoms is far from uniform within the solid lattice. This will be confirmed later in this paper. The diffusion of Al and Cu atoms from their initial meta-stable state toward their final stable equilibrium states takes much longer than the time to eliminate the temperature gradients.

2 Developing a Hypothesis

If the sample is kept solid, then it will take a very long time for the atoms to diffuse into their equilibrium locations within the solid lattice, and the relaxation times during melting will be very long. However, if the substance is kept in a partially molten state, then equilibrium rearrangement of atoms along solid–liquid phase boundaries will be much quicker than deep within the solid phase where the atoms are locked into their lattice locations.

It is important to note that if Fig. 3 shows how the sample drifts from its nonequilibrium toward its equilibrium lattice structure, then the melting temperatures of the nonequilibrium lattice must be lower than that of the equilibrium lattice. As the temperature of the sample spontaneously rises along the drift curve (as seen in Figs. 1 and 3), the temperature will gradually become higher than the melting temperature of the existing nonequilibrium lattice and, therefore, it will gradually begin to melt. Then, atomic rearrangement along the newly created solid–liquid phase boundaries will follow. However, as the liquid formed is below the freezing temperature of the equilibrium lattice corresponding to the current liquid/solid fraction, the atoms re-solidify, apparently, into their equilibrium lattice sites. This re-solidification releases the associated heat of fusion at this location (possibly causing some local overheating), further warming the sample. Thus, the atoms throughout the bulk of the sample gradually reach their equilibrium distribution, by way of such intermediate phases. Once this stage is reached, the temperature of the sample stabilizes.

If this indeed happens, then one would expect the nonequilibrium to equilibrium lattice transformation to take place at the solid/liquid interfaces. The rest of the solid should remain in its nonequilibrium state because its melting temperature is higher than the current sample temperature and the atoms are locked into their nonequilibrium lattice locations. If this sample was now slowly refrozen, then the equilibrium solid lattice layer at the interface will grow in its equilibrium form (much like single crystals grow). Later, if the melting experiment was repeated, there should be no need for atomic re-arrangement, while the equilibrium lattice melts. The relaxation times should be short following heating periods, just as for pure metals, as seen in Fig. 2. However, once the melting reaches the nonequilibrium lattice portion of the sample, the relaxation times should become long during the rest of the melting curve. However, if there was some local overheating in the immediate vicinity of the released heat of fusion, then some equilibrium lattice may form at a slightly higher temperature than that corresponding to the current solid/liquid fraction.

It should be mentioned that Ivanova et al. [2], using Ga–Sn eutectic, also observed that samples frozen from partially molten states yielded higher melting temperatures than samples frozen from entirely liquid states.

2.1 Observations Concerning the Hypothesis

Now, let us take a closer look at the temperature changes within the sample as it drifts toward its equilibrium states.

All of these melting experiments were carried out in the furnace of Fig. 4, which was specifically built to study high-temperature melting properties of substances under adiabatic conditions. A detailed description of its use can be found in [3]. The experiments shown in Figs. 5 and 6 illustrate the contrast between the melting behaviors of, presumably, equilibrium and nonequilibrium lattices: A liquid Al–Cu eutectic sample was frozen and then melted till the seventh melting minute, liquefying about 45% of it. Then, at 300 min in Fig. 5, the furnace temperature was lowered 2°C below the sample temperature. Yet, the sample temperature kept increasing for about five more hours before it began to decrease and then the sample gradually solidified.

The question now arises: How can the temperature of such a small sample (67 g) persistently increase for several hours while constantly losing heat to its surroundings? This is possible only if the sample itself generates some heat. Such heat can be generated if some heat of fusion is released at the solid–liquid interface as the Al and the Cu atoms re-solidify from their initially unstable, nonequilibrium state into their final, stable equilibrium lattice locations, as discussed above.

A melting experiment was then carried out on this frozen sample. However, the sample now had short relaxation times along its melting curve, reaching its equilibrium

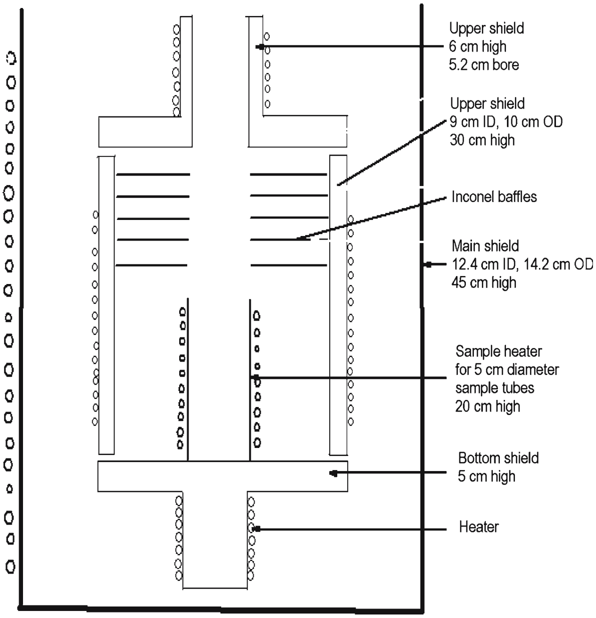


Fig. 4 Diagram of the adiabatic furnace

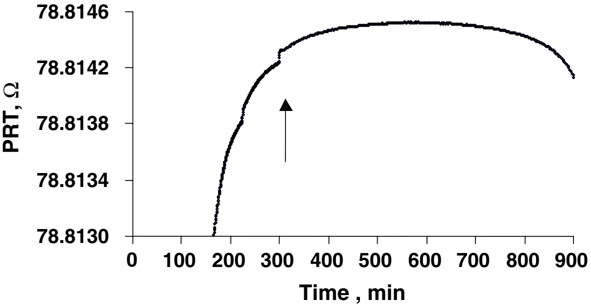


Fig. 5 Initial melting data obtained after freezing a liquid Al–Cu eutectic sample. The sample was heated at 160 min (3rd melting min), 220 min (5th melting min), and 300 min (7th melting min). Relaxation times along the melting curve are very long. Arrow indicates the time when the furnace temperature was lowered 2°C below the melting range of the sample

state quite rapidly after periods of heating. After the 7.5th melting minute, the furnace temperature was lowered as in Fig. 5, but, this time, the sample immediately noticed the temperature change of its surroundings, and its temperature began to drop within a few minutes, as seen in Fig. 6. This is exactly what one would expect if the solid phase of the sample was in an equilibrium lattice state because there should be no nonequilibrium-to-equilibrium transformation heat liberated, warming the sample, keeping it above the temperature of its surroundings. A melting of this frozen sample produces a carbon copy of this melting curve.

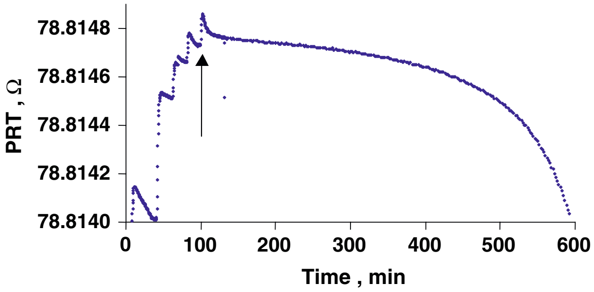


Fig. 6 Melting the frozen sample in Fig. 5. Sample was heated at 0 min (1st melting min), 40 min (3rd melting min), 60 min (4.5th melting min), 80 min (6th melting min), and 100 min (7.5th melting min). Relaxation times along the melting curve are quite short. Arrow indicates the time when the furnace temperature was lowered 2°C below the melting range of the sample. In Figs. 5, 6, 7 and 8 one unit in the last digit along the vertical axis is about 1 mK

The experiments described above suggest that, when a eutectic liquid is solidified, nonequilibrium eutectic solid forms. Similar behavior was observed during experiments carried out using Cu–Ag and Al–Sb eutectics. The observed melting temperatures of nonequilibrium solid eutectics differ from that of equilibrium solids. The reason for the large irreproducibility of the melting temperatures of Al–Cu eutectic reported by McAllan of ±5 mK was most likely due to the use of nonequilibrium samples, i.e., samples of long relaxation times. In those experiments, transient rather than equilibrium temperatures were measured; hence, the relatively large uncertainties in the observed melting temperatures.

An Al–Ag eutectic has similar features: an Al–Ag eutectic liquid sample was frozen and then about 30% of it was melted. The furnace temperature was then lowered below the temperature of the sample, yet, the sample temperature kept increasing for several hours before it began to decrease and then the sample gradually solidified (see Fig. 7).

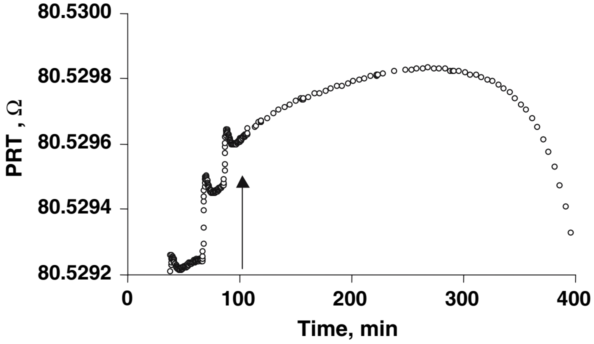


Fig. 7 Initial melting data obtained after freezing a liquid Al–Ag eutectic sample. Sample was heated at 30 min (1st melting min), 60 min (2nd melting min), and 80 min (3rd melting min). Relaxation times along the melting curve are similar to Fig. 1. Arrow indicates the time when the furnace temperature was lowered 2°C below the melting range of the sample, yet, as seen in the figure, it took several hours before the temperature of the sample began to decrease, as expected

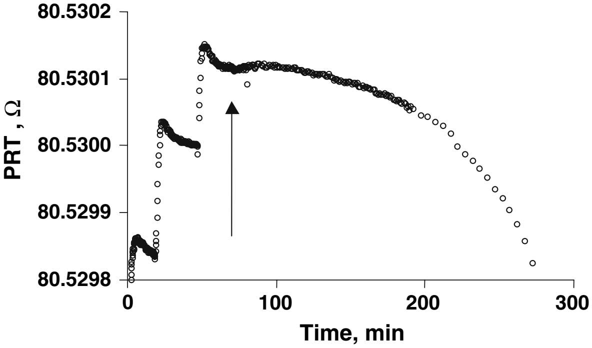


Fig. 8 Melting of the frozen sample in Fig. 7. The sample was heated at 0 min (1st melting min), 20 min (2nd melting min), and 40 min (3rd melting min). Relaxation times along the melting curve are quite short, similar to that shown in Fig. 2. Arrow indicates the time when the furnace temperature was lowered 2°C below the melting range of the sample, and shortly afterwards, the temperature of the sample began to decrease, as expected

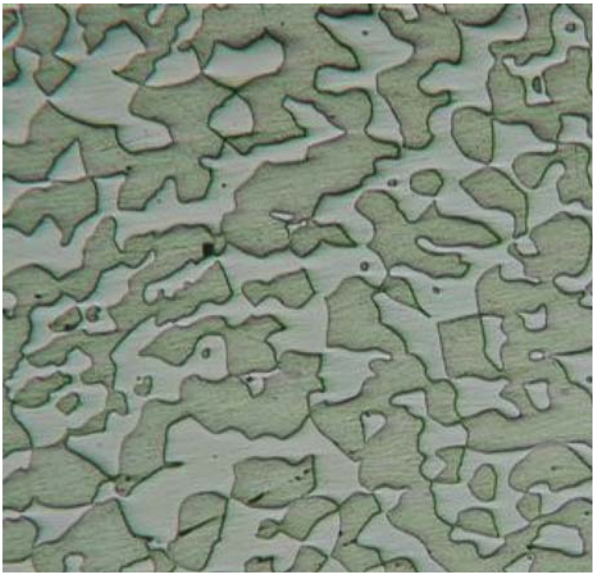


Fig. 9 Photograph of the microstructure of a slowly frozen sample from the partially melted state (equilibrium Al–Cu eutectic solid). Its melting behavior is shown in Fig. 2. Actual size of the sample is about 400 μm × 400 μm

The subsequent melting experiment carried out on this equilibrium-frozen sample had short relaxation times (see Fig. 8), and quite reproducible melting curves.

2.2 Microstructures

Several Al–Cu eutectic samples were analyzed using an inverted metallurgical microscope. Figures 9–11 show examples of some of the photographs of the microstructures of equilibrium and nonequilibrium solid eutectic samples.

Fig. 10 Photograph of the microstructure of a rapidly frozen Al–Cu eutectic sample. Its melting behavior is shown in Fig. 1. Actual size of the sample is about 400 μm × 400 μm

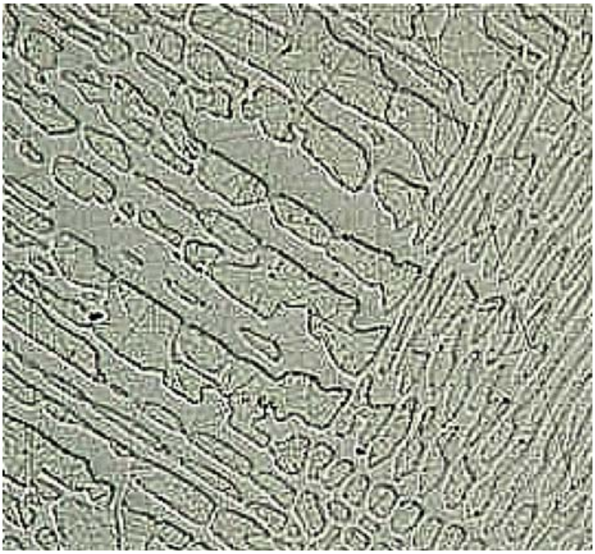


Fig. 11 Photograph of the microstructure of a slowly frozen Al–Cu eutectic sample from entirely the liquid state. Its melting behavior is similar to that of Fig. 1. Actual size of the sample is about 400 μm × 400 μm

Figure 9 shows the microstructure of an equilibrium solid Al–Cu eutectic obtained by slowly freezing a sample (9 h) from 90% liquid to 10% solid state by keeping the furnace about 2°C below the melting temperatures of the sample. A multitude of Al and of Cu micro phases is clearly seen throughout the sample.

Figure 10 shows a nonequilibrium solid obtained by removing the liquid sample from the furnace and rapidly solidifying it at ambient temperature. When a homogenous liquid sample is rapidly solidified, the resulting solid phase is also expected to be fairly homogenous. This solid phase differs considerably from that seen in Fig. 9 that has short relaxation times (as seen in Fig. 2) and yields reproducible melting curves. The sample of Fig. 10 has long relaxation times, as seen in Fig. 3.

Figure 11 shows a nonequilibrium solid obtained by slowly freezing the entirely liquid eutectic sample (10 h) by keeping the furnace about 2°C below the melting temperature of the sample. This sample also shows a multitude of distinct, microscopic Al and Cu solid phases just like the equilibrium solid (Fig. 9).

Superficially, the difference between them (Figs. 9 and 11) appears to be in their shapes only. However, Fig. 9 likely consists of continuous channels and Fig. 11 consists of a set of discrete, well-separated islands. The reason for these conclusions is as follows: when melting an equilibrium solid Al–Cu eutectic, the PRT overheats right from the very start of the melt, as seen in Fig. 6, when there is plenty of solid surrounding the well. Now, liquids can supercool but solids do not overheat. How can the PRT possibly overheat from the very beginning of the melt? The PRT can only overheat if continuous, convoluted, highly conductive channels shunt the heat between the sample heater and the thermometer well. Some of the heat is absorbed at the interfaces but some of it reaches the well along the heat-conductive channels.

Why would the PRT monitoring the melting of the nonequilibrium sample begin to overheat only near the end of the melt (compare Figs. 5 and 6)? Because there must be isolated islands consisting of the solid phases of components that have to be melted at the contact surfaces, arresting the heat flow toward the well until a continuous liquid channel is formed between the heater and the well.

3 Conclusion

The above experiments suggest that nonequilibrium eutectic solids form when metal–metal eutectic liquids solidify. The melting temperatures of nonequilibrium solid eutectics are lower and are far less reproducible than those of equilibrium solids. Equilibrium solid eutectics can be obtained by slowly freezing partially melted samples.

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