Defense Technical Information Center
Compilation Part Notice

ADP012213

TITLE: Nanoscale Compositional Changes Along Fast Ion Tracks in Equilibrium Solid Solutions: A Computer Simulation of Ultra-Fast Solidification and Thermomigration

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Nanophase and Nanocomposite Materials IV held in Boston, Massachusetts on November 26-29, 2001

To order the complete compilation report, use: ADA401575

The following component part numbers comprise the compilation report:
ADP012174 thru ADP012259

Mat. Res. Soc. Symp. Proc. Vol. 703 © 2002 Materials Research Society V6.26

Nanoscale compositional changes along fast ion tracks in equilibrium solid solutions: A computer simulation of ultra-fast solidification and thermomigration

Edmundo M. Lopasso, Alfredo Caro, Eduardo Ogando Arregui[1] and Magdalena Caro
Centro Atómico Bariloche - Instituto Balseiro, 8400 Bariloche, Argentina.
1 Dep. de Electricidad y Electrónica, UPV-EHU apdo. 644, 48080 Bilbao, España.

ABSTRACT

Starting from two equilibrium solid solutions in the Au-Ni system, we analyze the change in composition due to a 400 eV/Å fast ion track simulated by molecular dynamics in the Embedded Atom approximation. We aim at determining the influence of the thermodynamic forces derived from the large thermal gradients and the rapid solidification across the *solidus* and *liquidus* on the motion of solute atoms. One dimensional gradients as well as analytic models are used to quantitatively determine the domains of influence of these forces. Evidence shows that the *liquidus* and *solidus* equilibrium solidification predicted by the phase diagram is not reached during the track. The solute concentration is mainly determined by the combined diffusion and thermomigration mechanisms in the liquid stage.

INTRODUCTION

In the usual interpretation of radiation effects in alloys, equilibrium solid solutions are not expected to experience modification of solute distribution as a consequence of energetic collision cascades. However, the presence of huge thermal gradients and the rapid quenching across the two phase field delimited by the *solidus* and *liquidus* lines provide thermodynamic forces that may give rise to solute redistribution. In the short initial ballistic stage the atoms are displaced from their equilibrium positions, creating interstitials, vacancies and ion mixing near the cascade. The thermal stage that follows involves a liquid-like system, followed by a temperature drop that drives the system towards re-solidification; in these stages precipitation, dissolution, amorphisation, and diffusion (besides other possible transformations), influences the solute redistribution.

The diffusion mechanisms in the liquid phase are influenced by the thermomigration of solutes. The governing equation in this case is the diffusion equation with the heat of transport contribution [1]:

$$\frac{\partial C_s}{\partial t} = \nabla \cdot \left[D \left(\nabla C_s + \frac{Q^* C_s}{kT^2} \nabla T \right) \right] \qquad (1)$$

in which C_s is the solute concentration, t is the time, D is the diffusion coefficient, Q^* is the heat of transport, k is the Boltzmann constant and T is the temperature. Under a thermal gradient, the thermomigration effect would drive the solute to the cold region of the sample if Q^* is positive, and to the hot region of the sample if Q^* is negative.

Additional effects could appear as system cools down from the liquid, and the characteristics of the phase diagram affect the final solute distribution in the solid phase. In systems with *liquidus* and *solidus* lines with negative slopes, the solute is pushed towards the liquid as the solidification interface moves on cooling. If solid diffusion is neglected due to the rapid nature of the process under consideration, the complete or partial mixing by diffusion in the liquid phase produces a concentration profile. Standard results show that the first portion of matter that solidifies has a low solute concentration, while the last solid formed is solute enriched [2].

In a previous work [3] we determined the thermomigration effect on liquid dilute Au-Ni alloys. We found that Ni as a solute in Au has a tendency to move towards the hot core of the spike, while Au as a solute in Ni has the opposite tendency. The final solute concentrations under a fixed thermal gradient are shown in figure 1, for samples of 4.7 % initial solute content in the Au-Ni system. Figure 2 shows the Au-Ni system phase diagrams: the experimental (dotted lines) [4] and that determined in a previous publication [5], corresponding to the embedded atom potentials [6] used in this work. According to this phase diagram, during cooling from the melt the effect of the *liquidus* and *solidus* lines would drive the solute to the hot melted zone in both Ni 5% Au and Au 5% Ni systems: this would enhance (compensate) the thermomigration effect when Ni (Au) is the solute. This analysis would be correct if the solidification proceeds at thermodynamic equilibrium, a fact that we assess in the simulations reported here. Equilibrium solidification occurs when the concentration of solid and liquid phases close to the moving interface are given by the *liquidus* and *solidus* lines respectively. In this work we use molecular dynamics to study the combined effect of thermomigration and quenching during ultra-fast solidification in the Au-Ni system after a fast ion track event.

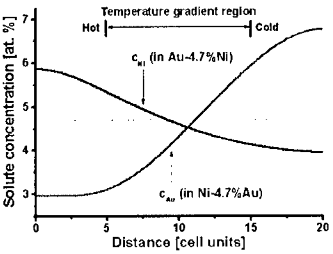

Figure 1: Solute distribution after 500 psec. under a fixed thermal gradient in initially 4.7% dilute alloys.

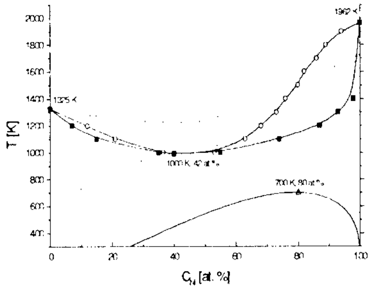

Figure 2: Experimental (dotted) [4] and calculated [5] Au-Ni phase diagram.

TRACK SIMULATION

A 400 eV/Å track in the [001] direction was simulated on dilute 5% Au-Ni and Ni-Au alloys, on 64x64x16 unit cells samples. This energy deposition is in the range usually attainable by swift heavy ions.

The Ni 5% Au sample is shown in figure 3, after 1 psec. from the track event. The melted zone reaches a maximum size and then the re-solidification interface moves towards the center of the track at a variable speed, which is shown in figure 4, and is estimated from the temperature profiles shown in figure 5. These figures show that the track effect extends over roughly ten cells. After about 16 psec. the system reaches the solid phase temperature.

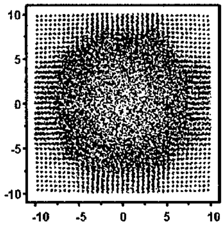

Figure 3: Ni 5% Au sample after 1 psec. from track event. Distances in cell units.

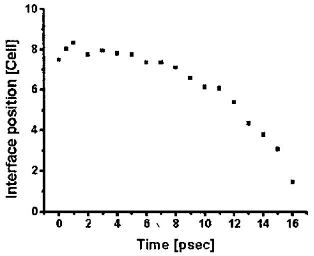

Figure 4: Interface position after track event in Ni 5% Au.

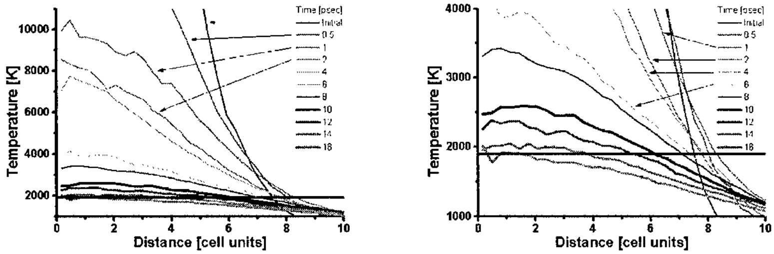

Figure 5: Temperature profiles after track event in Ni 5% Au.

Concentration profiles for Ni 5% Au and Au 5% Ni are shown in figure 6. From the figure it is observed that in the Ni 5% Au system the solute moves away from the center of the track, while in the Au 5% Ni system the solute moves to the track region. This observation is in agreement with the expected behavior when thermomigration is operative.

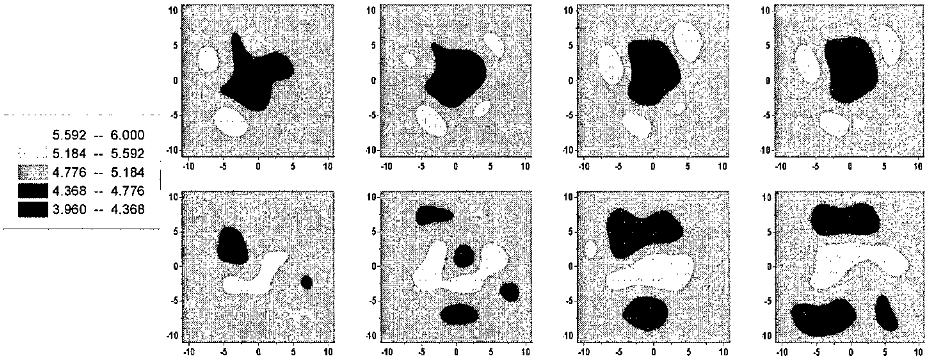

Figure 6: Au concentration during track cooling of Ni 5% Au system (above) and Ni concentration during track cooling of Au 5% Ni system (below). Distances in cell units. From left to right: at 2, 4, 10 and 20 psec. from track event.

From the track simulations we conclude that in the Ni 5% Au system the 20 psec. picture represents the sample back in its solid phase. In this time scale, the solidification is apparently not in equilibrium, as the thermomigration effect was not compensated by a solute enrichment in the final liquid in the center of the sample. In the Au 5% Ni system, the picture at 20 psec. still represents a sample with a liquid track core. However, further cooling up to 50 psec. did not raise the solute concentration at the center of the sample, as would be expected if solidification occurs at thermodynamic equilibrium.

To try to understand quantitatively these results, we proceed now to the analytic modeling of the processes.

ONE DIMENSIONAL SOLIDIFICATION MODELS

To verify the track results a molecular dynamics simulation and an analytical calculation were performed in one dimensional temperature gradient geometry under controlled temperature conditions. A thermal gradient was imposed to twenty cells long samples, with temperature control at both ends (cold ends) and at the center (hot center) and periodic boundary conditions in 3D. The cold ends were kept at 1000 K, while the hot center was initially at 11000 K and then cooled down. A fast cooling of 500 K/psec., similar to that observed during the track cooling, and a slow cooling of 10 K/psec., in an attempt to quench at thermodynamic equilibrium, are presented. The evaluation was performed in the Ni 5% Au alloy, which has a broad splitting of the two phase (liquid and solid) field and an evidence of the solidification solute redistribution is therefore expected.

Molecular dynamics results

The concentration profiles for the fast and slow cooling conditions after the samples reached an uniform temperature (1000 K) are shown in figure 7. In both cases the thermomigration effect is present at the beginning of the run. In the fast cooling, the concentration does not vary significantly, while in the slow cooling the solute is pushed towards the hot center of the sample, compensating the thermomigration effect at the end of the run. In the slow cooling a peak moves from the cold to the hot region, suggesting that some equilibrium is achieved. The interface position shown corresponds to the approximated point at which it should be according to the imposed temperature gradient.

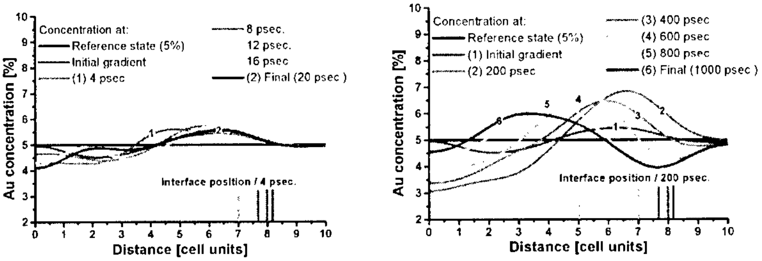

Figure 7: Concentration profiles for the fast (left) and slow (right) cooling down schemes. Molecular dynamics calculation in Ni 5% Au.

Figure 8 represents the sample configuration when the temperature at the center is 2000 K. The slow cooled sample is almost crystallized, while the fast cooled sample is still in a liquid like configuration. The observation is in agreement with the conclusion obtained from the concentration profiles, and also suggests that the slow cooling allows a partial thermodynamic equilibrium, while in fast cooling the equilibrium is not reached. When the fast cooled sample was left at 1000 K for a longer period, an ordered crystal structure was obtained, and there was no changes in the concentration profile.

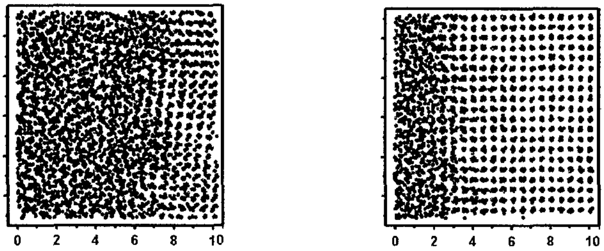

Figure 8: Samples obtained by molecular dynamics calculations for fast (left) and slow (right) cooling conditions in Ni 5% Au. Temperature in the center is 2000 K. The estimated interface position according to thermal gradient should be at the first cell. Distances in cell units.

Analytic results

The analytic model assumes the system is always at equilibrium solidification, and the diffusion equation including thermomigration (1) is solved as cooling down proceeds.

The results for fast and slow cooling are shown in figure 9 for the final (left) and transient (right) concentration profiles. In spite of the concentration values, the final slow cooling profile is similar to that obtained by molecular dynamics. The fast cooling profile has a peak at the center of the sample, resulting from the impingement of solute in the final stage, which is not observed in the molecular dynamics run. An equilibrium plateau at the initial 5% concentration is observed.

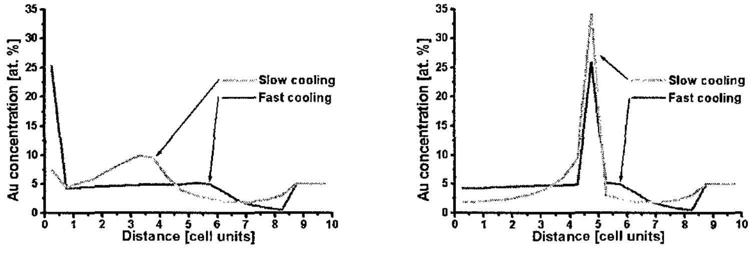

Figure 9: Concentration profiles from the analytical calculation, fast and slow cooling, in Ni 5% Au. Final profile (left) and transient (right).

The transient concentrations in figure 9 correspond to the same interface position for both cases. The fast cooling has a narrow concentration peak at the interface, while the slow cooling presents a diffusive profile. This allows the liquid to be enriched by solute, and as a consequence the center of the sample has an extended enriched zone in the final state. The zone of solute concentration below the initial 5% also differs. The slow cooling shows a broad zone, as the continuos build up of solute to the cold region, due to thermomigration, produces solidification at a composition close to the initial composition of the sample.

SUMMARY AND CONCLUSIONS

The concentration profiles obtained in the simulation of the track event indicate that the thermomigration effect is the main contribution to the solute re-distribution. The very fast cooling rate observed during the simulation does not allow a thermodynamic equilibrium in the system.

The observations in the Ni 5% Au system are verified with one dimensional thermal gradients in three dimensional molecular dynamics and an analytical model which assumes equilibrium solidification during quenching. A fast cooling rate, similar to the track cooling rate, reflects differences between the analytical simulation and molecular dynamics. This implies that equilibrium is not reached in the molecular dynamics simulation. In contrast, a slow cooling rate shows similar qualitative behavior in analytical and molecular dynamics results indicating some degree of equilibrium. There are differences in the concentration values for the slow cooling simulation and the analytical calculation, which are due to the strong assumption of equilibrium solidification in the analytic model, while in molecular dynamics there is no complete equilibrium. The average interface speed during the track and the fast cooling under the one dimensional temperature gradient is estimated to be 2 Å/psec., while in the slow cooling is about 0.04 Å/psec. These values are consistent with a 0.1 Å/psec. interface speed estimated as the upper limit at which equilibrium solidification should be operative, which was obtained with molecular dynamics and analytic models not presented here.

The Au 5% Ni system cools down at a slow rate after the track. The Au 5% Ni sample shown in figure 6 is still in the liquid phase, while the Ni 5% Au sample is solid. Concentration profiles in the Au 5% Ni system in later stages after the track event do not show further modifications. This is consistent with the above conclusions since, if the phase diagram equilibrium is supposed to occur, the center of the sample should be enriched with solute. However, due to the narrow splitting of the two phase (liquid and solid) field in the Au rich zone of the phase diagram, a relevant effect would not be expected even if equilibrium occurs during cooling.

One-dimensional thermal gradients in molecular dynamics calculations, and analytical results, suggest that the cooling rate should be much slower than is the case for Ni to allow for equilibrium solidification effects to become apparent. This may occur in heavier systems. These effects depend on the sign and magnitude of the heat of transport, and on the characteristics of the phase diagram.

REFERENCES

1. J.P. Stark, *Solid State Diffusion*, (John Wiley & Sons, 1976) p. 124.

2. D.A. Porter and K.E. Easterling, *Phase transformations in metals and alloys*, 2nd ed. (Chapman & Hall, London, 1992) pp. 208-214.

3. E.M. Lopasso, M. Caro and A. Caro, Phys. Rev. B **63**, 174105 (2001).

4. Thaddeus B. Massalski (editor), *Binary Alloy Phase Diagrams*, 2nd ed. ASM International (William W. Scott Jr., 1992) pp. 402-404.

5. E. Ogando Arregui, M. Caro and A. Caro: *Embedded Atom Model Prediction of the Au-Ni Phase Diagram*, submitted for publication.

6. S.M. Foiles, M.I. Baskes and M.S. Daw, Phys. Rev. B **33**, 7983 (1986).