Monte Carlo simulation of Pt-Al thin film diffusion

by R.A. Harris*, J.J. Terblans*, H.C. Swart†, and E. van der Lingen†

Synopsis

In this study Pt-Al thin films were prepared via electron beam physical vapour deposition (EB-PVD) with an atomic concentration ratio of Pt_{25}:Al_{75}. These films were heat treated at temperatures ranging from 150°C to 650°C for annealing times from 4 to 60 minutes. The resulting microstructure of these thin films were obtained via secondary electron imaging used in conjunction with depth profiling with the aid of scanning auger microscopy (PHI 700). Elemental maps of the micrographs were obtained. Simulations, based on a chemical potential Monte Carlo method[1], were run for various interaction parameters. From these simulations theoretical depth-profiles and proposed microstructures were obtained. These were compared to the experimentally measured depth profiles and elemental maps.

Keywords
Monte Carlo, chemical potential, depth profile, Pt-Al thin films.

Introduction

The concept of utilizing platinum, and the other platinum group metals as alloys and alloying constituents has been shown to enhance the oxidation and corrosion resistance properties of nickel-based super alloys. For this reason platinum-enriched and platinum-based alloys are being studied and developed for certain industrial and aerospace applications[2]. This is done by increasing efforts to tailor alloys with specific combinations of properties. These alloys have much to offer in industrial applications where corrosion resistance in high temperature environments is an important materials selection criterion. Application fields such as coal conversion and combustion, combustion and the petrochemical areas, suggest potential candidates. For this reason the study of the diffusion process that governs a Pt-based binary alloy (in a thin film system) is investigated. The aim of this study is to provide a better understanding of this process through computer simulations in order to design alloys with specific combinations of properties.

Theory

The regular solution model is a statistical model which is based on the following three assumptions:

- Atoms are randomly distributed over positions in a three-dimensional lattice
- No vacancies exist
- The energy of the system may be expressed as the sum of pairwise interactions between neighbouring atoms.

Consider a binary alloy composed of N_A atoms of component A and N_B components of atom B. In solid solution model three types of interatomic bonds can be present (shown in Figure 1.):

By counting only the closest neighbours, the co-ordination number, Z, is defined as the number of closest neighbours of A or B, because each atom A is included in Z pairs AA of AB. The summation over all A atoms is given by[3]

$$ZN_A = 2N_{AA} + N_{AB} \quad [1]$$

The factor 2 for N_{AA} is because each atom A is counted twice for the AA pairs. Similarly for atoms of type B,

$$ZN_B = 2N_{BB} + N_{AB} \quad [2]$$

Accordingly the total energy of the lattice is given by[4]

$$E = N_{AA}\gamma_{AA} + N_{BB}\gamma_{BB} + N_{AB}\gamma_{AB} \quad [3]$$

By making N_{AA} and N_{BB} the subjects of Equations [1] and [2] respectively and substituting that into Equation [3], the following equation is obtained.

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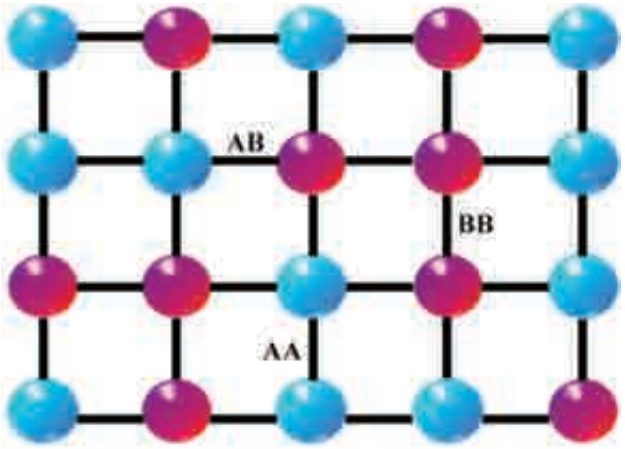

1. *A–A* bonds of N_{AA} pairs each with an energy γ_{AA}
2. *B–B* bonds of N_{BB} pairs each with an energy γ_{BB}
3. *A–B* bonds of N_{AB} pairs each with an energy γ_{AB}

Figure 1—Interatomic bonds in a solid solutio

$$E=\frac{1}{2}ZN_A\gamma_{AA}+\frac{1}{2}ZN_B\gamma_{BB}+N_{AB}\left[\gamma_{AB}-\frac{1}{2}(\gamma_{AA}+\gamma_{BB})\right] \quad [4]$$

Through Equation [4] it is seen that the expression $\frac{1}{2}ZN_A$ represents the total number of *AA* pairs in the pure solution of *A* before any mixing with component *B*. The expression $\frac{1}{2}ZN_A\gamma_{AA}$ therefore represents the total energy E_A of the N_A atoms of component *A* before mixing[5]. The same argument holds for element *B*. The expression for the total energy may thus be written as:

$$E=E_A+E_B+N_{AB}\left[\gamma_{AB}-\frac{1}{2}(\gamma_{AA}+\gamma_{BB})\right] \quad [5]$$

If a parameter ω_{AB} is defined as the difference between the *A-B* bond energy and the average of the *A-A* and *B-B* bond energies then an expression

$$E=E_A+E_B+N_{AB}\omega_{AB} \quad [6]$$

can be derived.

This can be expressed in terms of the molar Gibbs free energy of a binary system

$$G^P=\sum_{i=1}^{m}n_i^p\mu_i^p \quad [7]$$

with G^P the Gibbs free energy for phase *p*, n_i^p the number of moles of species *i* in phase *p*, and μ_i^p the chemical potential of species *i* in phase *p*. By minimizing this energy, the lattice state at equilibrium can be calculated and simulated by allowing for diffusion from initial, high energy state to final, low energy state. The detail of the Monte Carlo technique has already been published elsewhere[1].

Experimental setup

Pt-Al thin films (Pt_{25}:Al_{75}) were prepared using electron beam-physical vapour deposition. These films were heat treated with temperatures ranging from 150°C to 650°C. This was done for annealing times ranging from 4 to 60 minutes. Elemental maps and depth profiles were obtained with a PHI 700 nanoprobe. Simulations were run using the above mentioned model applied in a Monte Carlo technique[1] by using temperatures of 150°C to 650°C and compositions of Pt 25 at.% and Al 75 at.% as input parameters. Theoretical depth-profiles and microstructures, in the form of elemental maps where obtained from the simulations.

Results and discussion

The simulation was done for a binary thin film of 25 at.% Pt and 75 at.% Al. In this case the red colour represents Pt-rich areas and the blue colour represents Al-rich areas. Figure 2 shows a comparison between a simulated depth-profile, left (A) and an experimentally measured depth-profile, right (B). The red line represents Pt and the blue line Al. For the simulated depth profile the x-axis represents matrix depth and the y-axis the elemental concentration. It is important to note that the simulation does not include any of the effects of a substrate. Therefore (since there is only a Pt and Al layer) the elemental concentration of Al goes to 100% when the

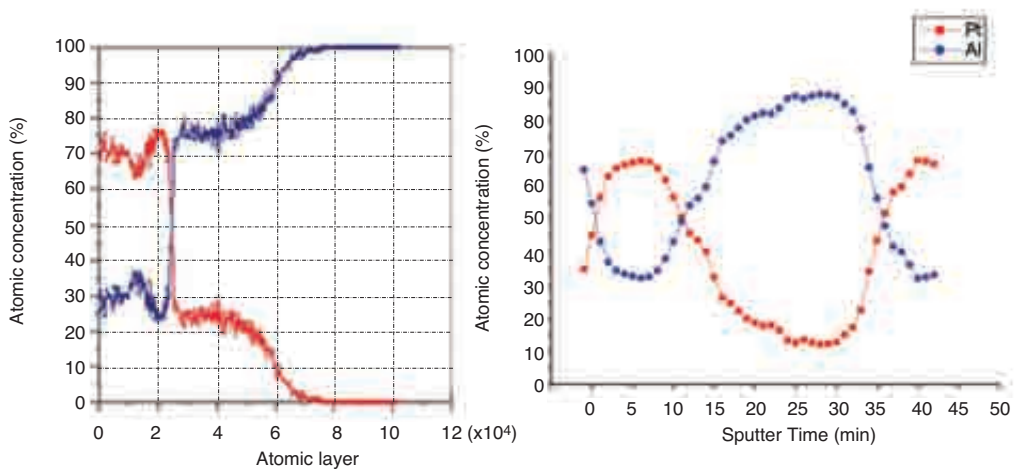

Figure 2—Comparison between simulated (left), A and measured (right), B depth profiles for Pt_{25}:Al_{75} thin films after 4 minutes annealing time

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depth-profile at the bottom of the matrix is calculated. Likewise the Pt concentration goes to 0% when the depth-profile at the bottom of the matrix is calculated. By comparing the general shape of the predicted depth-profile with the measured one, it is noteworthy that although the predicted and measured results do not correlate perfectly, a similar trend can clearly be seen. In both cases (the simulation and the experiment) the top Pt layer has a concentration of about 70 at.%. Thereafter it crosses over to about 25 to 20 at.%. Pt. At this point in the thin-film system the Al concentration has increased to about 75 to 80 at.%. It should be stressed that this is not an absolute comparison but rather the general trend of the depth-profile.

Figure 3 is a comparison between the simulated and measured depth-profiles after 20 minutes of annealing time. For this comparison a correlation is not as evident as for the correlation observed in Figure 2. However, a similar trend was observed, namely the simulation predicts a Pt concentration percentage around 60 at.% which should diminish to around 25 at.% in the Al layer. The aluminium should be around 25 to 30 at.% in the Pt-layer and then increase to approximately 70 at.%. As before, this comparison is general rather than absolute.

Figure 4 (i) shows a predicted/simulated microstructure (in the form of an elemental map) and Figure 4 (ii) shows the nanoprobe obtained elemental maps. For the Pt_{25}:Al_{75} sample it was observed that micron-sized Al-particulates nucleates in the top part of the prepared sample (A from Figure 4 (i) and 4(ii)). At a later stage (heat treated for longer times) it is observed that these particulates grow in size. This can be seen from a 20 minute sputter time-spectrum (Figure 5(i) and 5 (ii)). This results from a system that tends to evolve to

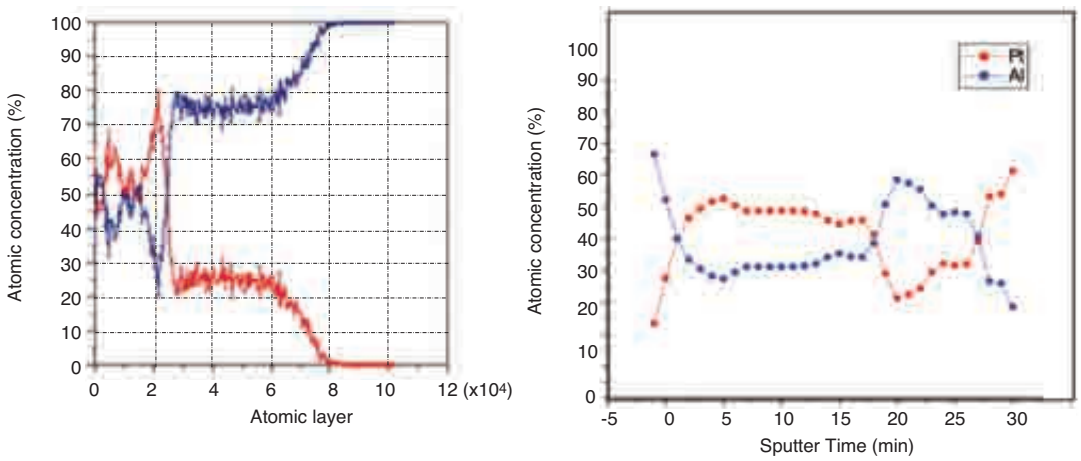

Figure 3—Comparison between simulated (left), A and measured (right), B depth profiles for Pt_{25}:Al_{75} thin films after 20 minutes annealing time

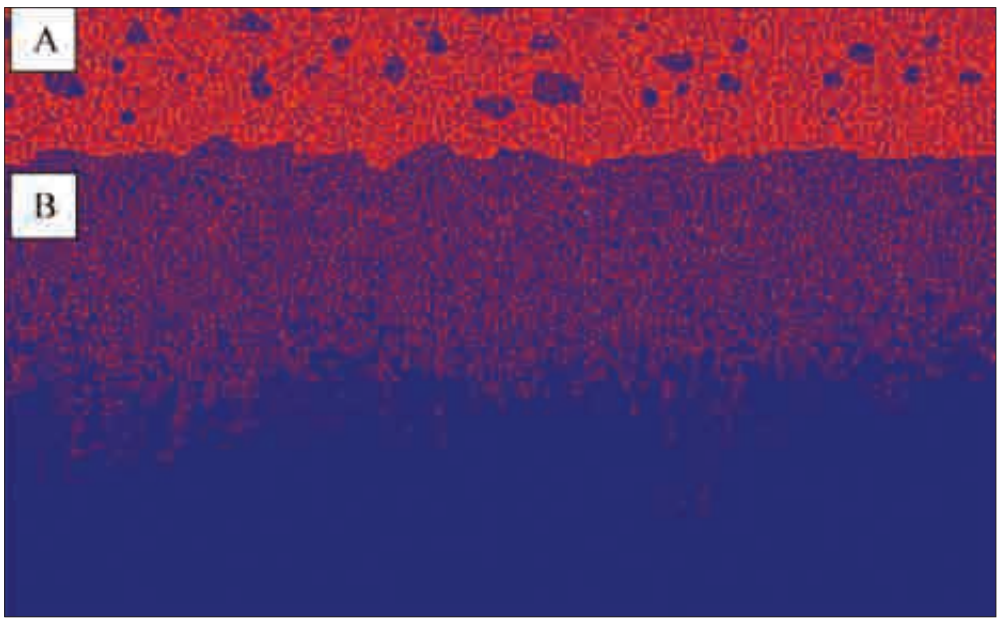

Figure 4 (i)—Pt_{25}:Al_{75}: The predicted microstructure consisting of Al-rich particulates (in blue) in the area, A (after 2 million Monte Carlo jumps)

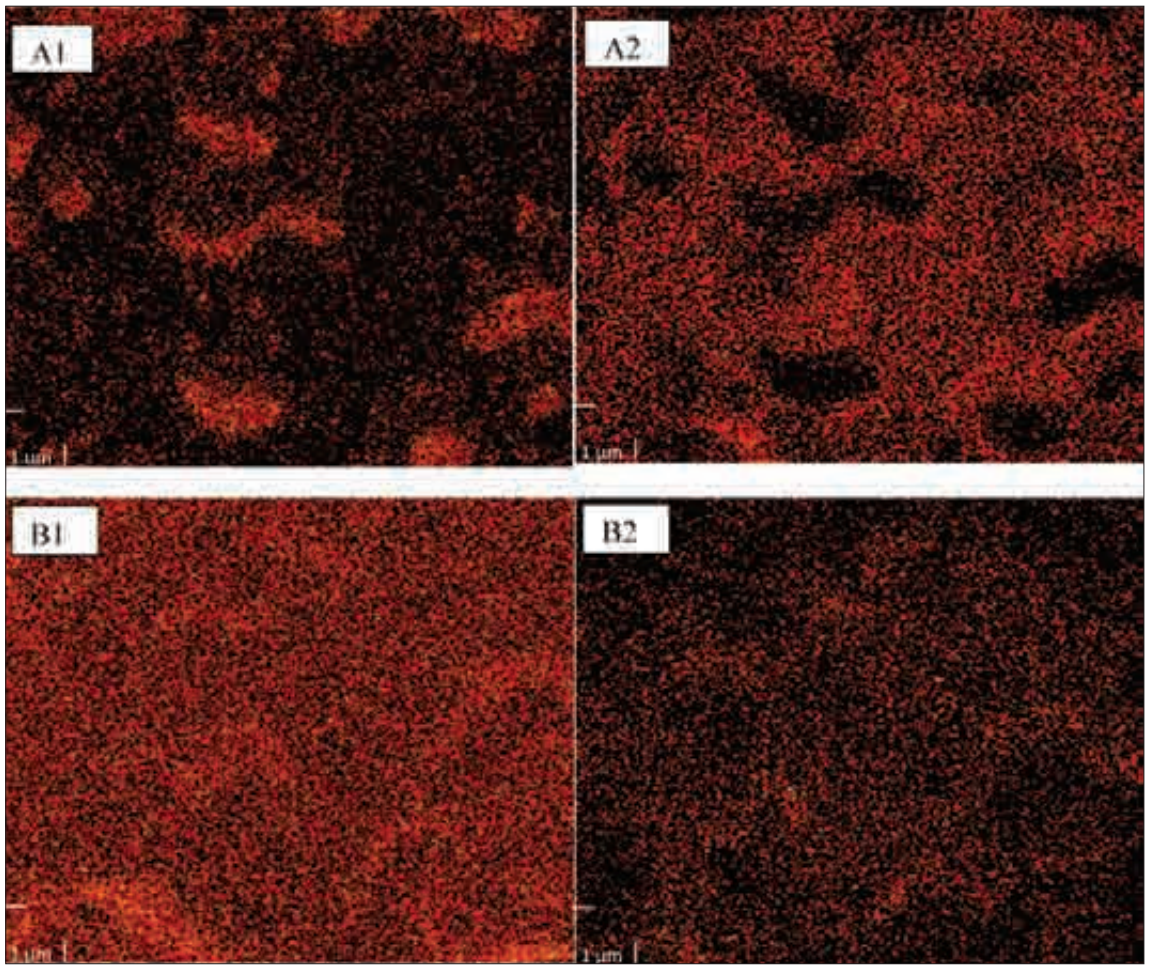

Figure 4 (ii)—Pt_{25}:Al_{75}. A1 and B1 are aluminium elemental maps. A2 and B2 are platinum elemental maps. The elemental maps A and B correspond to the areas A and B of the simulated microstructure of Figure 4 (i)

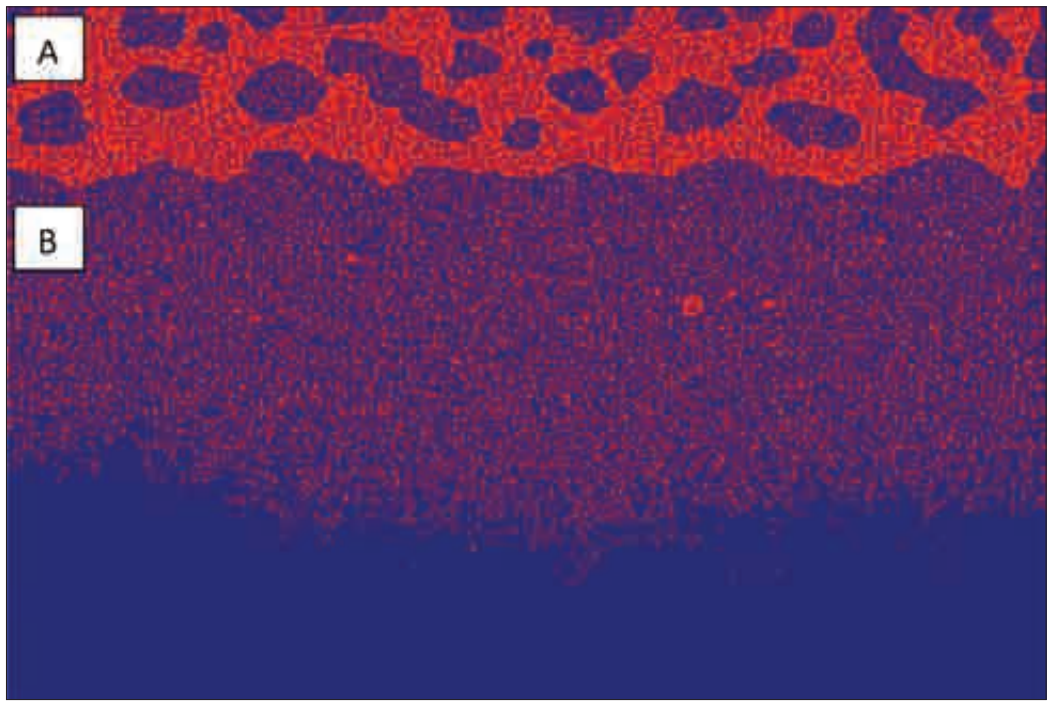

Figure 5 (i)—Pt_{25}:Al_{75}—The predicted microstructure consisting of Al-rich particulates (in blue) in the area, A (after 10 million Monte Carlo jumps)

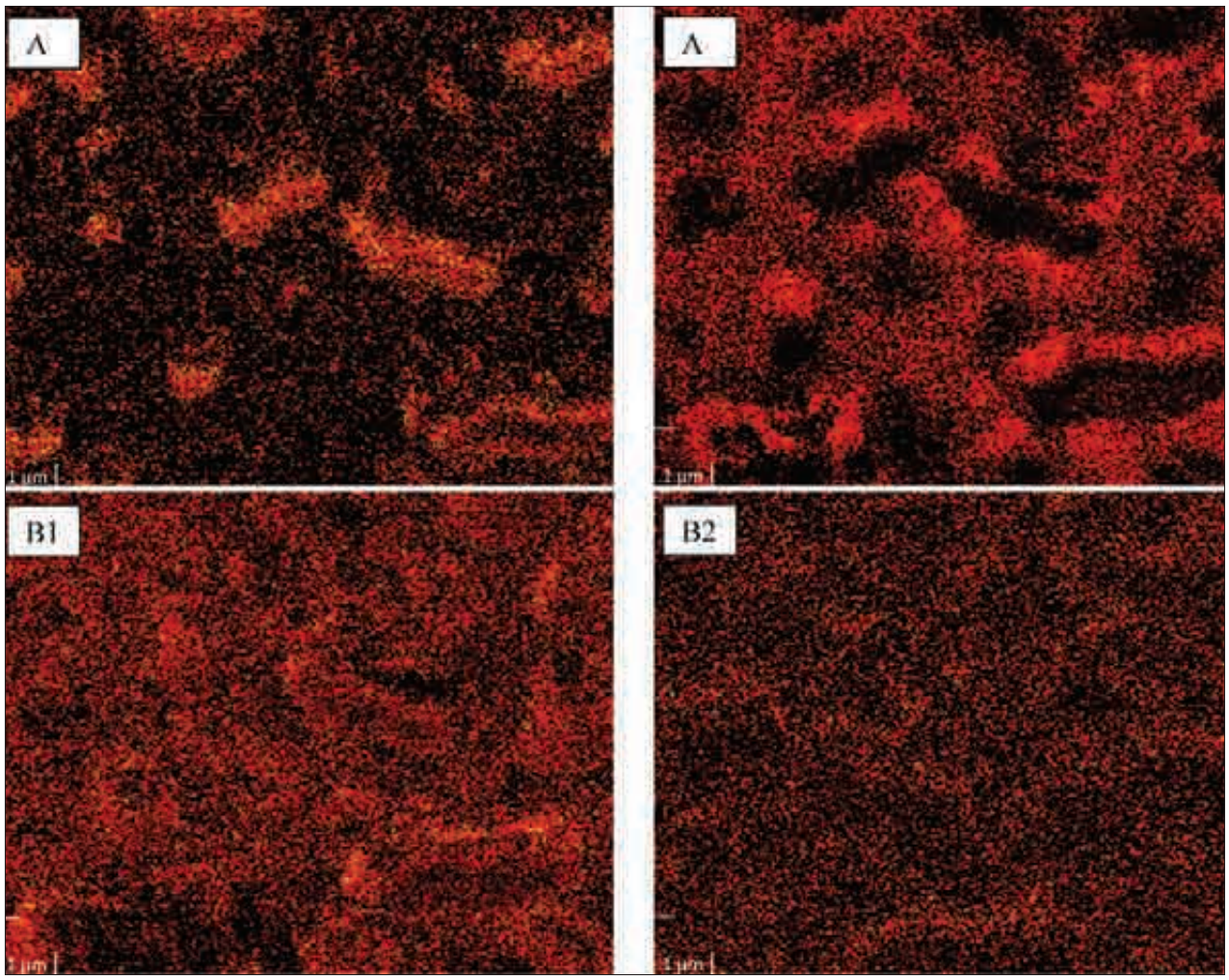

Figure 5 (ii)—Pt_{25}:Al_{75}. A1, B1 are aluminium elemental maps. A2, B2 are platinum elemental maps. The elemental maps A and B correspond to the areas A, B on the simulation of Figure 5 (i). This system was for a longer annealing time (after 20 minutes) than that in Figure 4 (ii))

a state where its energy is minimized. However, it is interesting to note what happens to the system before the state of minimization of energy is achieved. A question that arises is what happens if the thin films are not annealed for an indefinite period of time, but the annealing, and hence the diffusion, is interrupted? Figures 4 (i), (ii) and 5 (i), (ii) show two such interruptions in the diffusion process. The nucleation of the Al particulates is seen in Figure 4(ii). The increase in size and thus the growth of these Al particulates are seen in Figure 5(i) and Figure 5 (ii).

Figure 5 (i) shows the predicted/simulated microstructure (in the form of an elemental map) for Pt_{25}:Al_{75} after 10 million Monte Carlo jumps and Figure 5 (ii) shows the nano-probe obtained elemental map for this sample after 20 minutes of annealing. An increase in the size of the Al-rich particulates can be seen when compared to Figure 4 (i) and Figure 4 (ii). The similarity between the predicted/simulated elemental map and the nanoprobe obtained elemental map can clearly be seen in these two figures.

Conclusion

Comparisons between the simulated and experimentally measured depth-profiles show a good correlation. Likewise the comparison of the simulated microstructure and the elemental maps were shown to correlate. Therefore it is concluded that the theory presented and applied by using a Monte Carlo technique as published elsewhere[1] can be used as a good approximation to predict various Pt-Al binary thin film alloy particulate distribution profiles at different stages in a diffusion process.

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