Measuring the effect of surface evaporation on the segregation process

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Abstract. Metallurgical products play an important role in everyday life. The search for alloys with better material properties such as strength, wear and corrosion resistance continues to this day. In addition to these desirable properties, the search for ways to reduce production costs and time has led to a large amount of research being conducted on the processes which determines the material properties of metals and alloys. One of these processes is known as segregation. To improve segregation studies the influence of surface evaporation should be considered. As experimental segregation studies are performed under high vacuum conditions, certain elements are prone to this neglected phenomenon. Although some attempts have been made to develop segregations models that take surface evaporation into account, these models can only predict segregation in either the kinetic region or when equilibrium has been reached. In addition the effect of evaporation has received little attention in previous experimental studies. In this study surface evaporation during segregation of a Sb/Cu system was measured. These results together with the modified Darken model will be used to simultaneously predict kinetic and equilibrium segregation including the effects of surface evaporation. A first approximation will be discussed as well as modifications made to an Auger system in order to measure the actual surface evaporation that takes place during segregation.

1. Introduction

Metallurgical products play an important role in everyday life. The search for alloys with better material properties such as strength, wear and corrosion resistance continues to this day. In addition to these desirable properties, the search for ways to reduce production costs and time has led to a large amount of research being conducted on the processes which determines the material properties of metals and alloys. One of these processes is known as segregation.

Segregation of one or more components of an alloy to interfaces and surfaces can influence both the chemical and physical properties of the alloy. Surface segregation is commonly regarded as the redistribution of solute atoms between the surface and the bulk of the material, resulting in a solute surface concentration that is generally higher that the solute bulk concentration. The redistribution comes about so that the total energy of the crystal is minimized.

In previous investigations a typical surface segregation study might have had the following procedure:

- Prepare binary alloys of single crystals doped with a foreign element
- Measure the concentration of the segregant on the surface using Auger Electron Spectroscopy (AES) with the method of linear temperature ramp (LTR).
- Extracting the segregation parameters by doing simulations of the experimental data.

The segregation models commonly used in the above mentioned type of study are based on the macroscopic transport equations. These are the Fick, Bragg-Williams, Guttman and the Darken models.

1.1. Segregation model modifications. The models in one way or another describe the change in atom flux between the surface layer and the first atom layer as:

$$J_{10} = N_s X_1 \vartheta_1 \exp[\Delta G_s / RT] \qquad (1)$$

Where N_s is the total number of available surface sites, X_1 is the surface concentration of segregant, ϑ_1 is the effective jump frequency, ΔG_s is the segregation energy as shown in figure 1. This equation is not taking any possible evaporation into account. A modification by Stinespring *et.al* [1] suggests a third flux of atoms from to surface layer into the vacuum as:
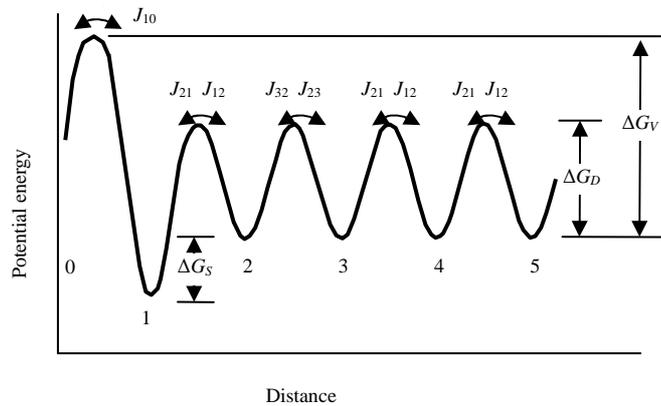
$$J_{10} = N_s X_1 \vartheta_1 \exp[-(\Delta G_v - \Delta G_s / RT] \qquad (2)$$

where ΔG_v is the evaporation energy.
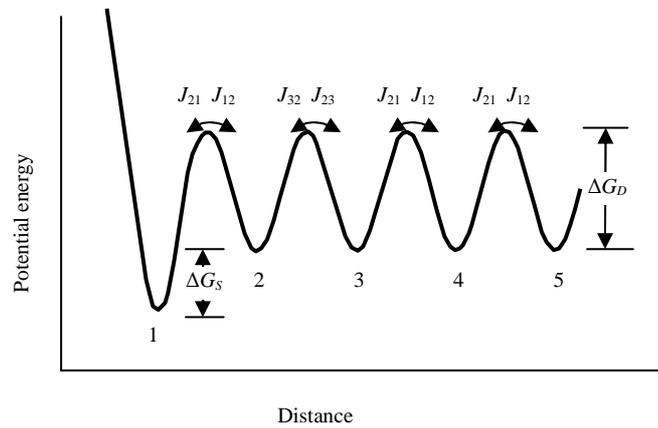
Figure 1. The potential energy diagram as a function of depth into the crystal indicating a very steep potential barrier for atoms escaping into the vacuum.

The evaporation process is incorporated into the models by ΔG_v which is illustrated in figure 2. The potential barrier between the surface layer and vacuum is thus finite, making evaporation possible. For evaporation to take place the energy barrier ΔG_v - ΔG_s has to be exceeded. Remember that the conventional thermodynamic definition of zero energy is the minimum of the interior free energy. Therefore ΔG_v will be positive and ΔG_s be negative. The Gibbs free energy necessary for this additional flux of atoms is illustrated in figure 1b. Expanding the segregation model the experimental challenge is to measure this third flux of atoms leaving the surface into the vacuum under various conditions of temperature and pressure. As AES is an ultra high vacuum technique (~10^{-9} Torr) it is possible that at high temperatures (>400K) certain elements might evaporate from the surface. From literature [2] it is known that a common element used for segregation studies namely antimony (Sb) falls well within the region where surface evaporation can be expected.

Figure 2. The potential energy diagram as a function of depth into the crystal indicating a finite potential energy barrier between the surface layer (1) and vacuum (0) allowing evaporation to take place.

By qualifying and quantifying the amount of segregant that evaporates off a crystal surface during a segregation run, the accuracy of the segregation parameters obtained from such a measurement for the specific system can be improved upon.

2. Experimental Setup

An AES system was modified to allow the user to perform standard segregation measurements, but also to measure the evaporation rate of any material that might evaporate from the surface of a sample during a temperature ramp. This was done by employing an Inficon XTC/3s Deposition Controller which utilizes a gold coated crystal to detect any material that is deposited onto the crystal surface. This thickness monitor was mounted in the AES system in such a way that the specimen mounted on a resistance heater could be repositioned from in front of the electron gun/analyzer to a position underneath the gold coated crystal. This was achieved by making use of a manipulator. See figures 3 and 4
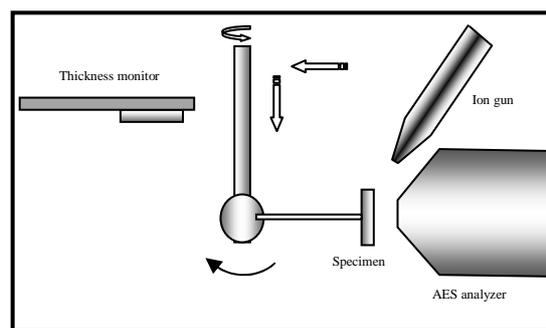
Figure 3. A schematic of the thickness monitor and AES analyzer. The arrows indicate the movements necessary to align the specimen for evaporation measurements.
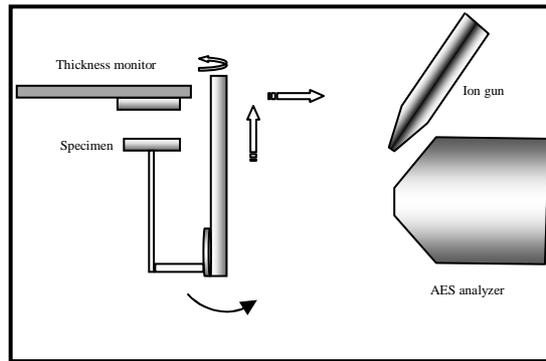
Figure 4. A schematic of the evaporation monitor and AES analyzer. The arrows indicate the movements necessary to align the specimen for AES measurements.

A Cu(110)crystal doped with Sb was used in this experiment. After performing a LTR to confirm that segregation of Sb did indeed take place, the sample was sputtered at room temperature for a few minutes using 2 keV Ar^+ ions and rastered over an area of 3 mm × 3 mm. This was done to rid the sample surface of any contaminants, as well as to remove any residual Sb. The sample was then positioned below the gold coated crystal, and a temperature ramp was performed. This ramp was performed by increasing the temperature in steps of 20K every 5 minutes from room temperature up to 830K, while simultaneously monitoring the evaporation rate of any material deposited onto the gold coated crystal of the thickness monitor. At this stage it was assumed that any material deposited onto this surface would be Sb which evaporated from the sample surface.

3. Results and discussion
The evaporation rate measured is shown in figure 5.
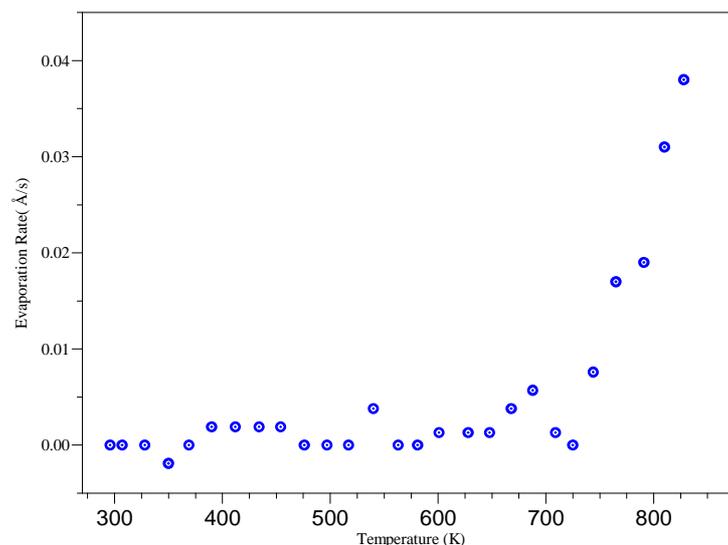
Figure 5. Change in evaporation rate as a function of temperature measured by the thickness monitor during a segregation run.

A typical exponential increase in the flux rate of atoms escaping from the surface can be seen. According to evaporation graphs [2] for pure Sb at a pressure of 10^{-8} Torr Sb sublimates at approximately520K. The evaporation run was repeated several times indicating a start of evaporation

Because evaporation at lower temperatures is controlled by the segregation term (see equation 2) the high sublimation temperature is a result of very low surface concentrations of Sb at lower temperatures. AES segregation runs show a sufficiently high concentration of Sb only at a temperature of 700K. Adding to this, the Sb escaped from a Cu substrate suggesting stronger interaction between Sb-Cu than between Sb-Sb atoms on the surface. This positive Sb-Cu interaction was measured by Asante [3].

The gold coated crystal was then removed from the thickness monitor and transferred to a PHI Versaprobe XPS spectrometer. To identify the deposited material, XPS analyses were performed on the used and unused gold coated crystals in the flux monitor. It is clear from the XPS results shown in figure 6 that the deposited material was Sb. It can thus be concluded that the change in flux measured by the thickness monitor was due to Sb evaporating off the sample surface.
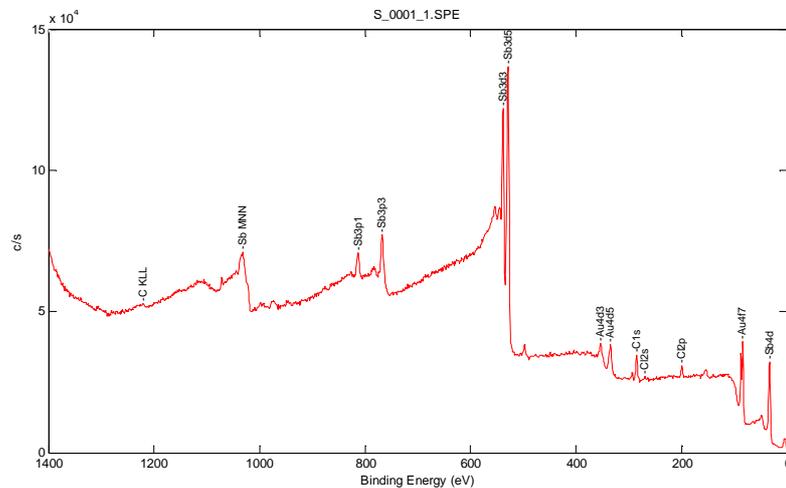
Figure 6. XPS spectrum of the gold coated crystal used in the monitor after a segregation run

Conclusion

An AES system was successfully modified to not only perform standard segregation experiments, but also to monitor any segregant which evaporates from the sample surface during such an experiment. This additional evaporation data may change the exiting segregation parameters obtained so far and give a more realistic model for segregation in metal substrates.

References

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[2] Honig R E and Kramer D A 1969 *RCA Rev.* **30** 285
[3] Asante J K O 2005 Surface segregation of Sn and Sb in the low index planes of Cu *PhD Thesis*