

Surface composition of Pt-Rh alloys : the role of lattice vibrational entropy

Citation for published version (APA):

van Langeveld, D., & Niemantsverdriet, J. W. (1986). Surface composition of Pt-Rh alloys : the role of lattice vibrational entropy. *Surface Science*, 178(1-3), 880-887. [https://doi.org/10.1016/0039-6028\(86\)90364-X](https://doi.org/10.1016/0039-6028(86)90364-X)

DOI:

[10.1016/0039-6028\(86\)90364-X](https://doi.org/10.1016/0039-6028(86)90364-X)

Document status and date:

Published: 01/01/1986

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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SURFACE COMPOSITION OF Pt–Rh ALLOYS; THE ROLE OF LATTICE VIBRATIONAL ENTROPY

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Received 13 March 1986; accepted for publication 21 May 1986

The bulk and surface composition of a polycrystalline Pt–Rh alloy, equilibrated at 1000 K, have been analysed by use of Auger electron spectroscopy. The results are discussed in relation to experimental data in the literature. Although the enthalpy of sublimation and the atomic diameters of Pt and Rh do not differ very much, a significant enrichment of Pt in the surface is observed. It is shown that the surface segregation behaviour in atomically clean Pt–Rh alloys can be understood quantitatively by taking into account the difference in vibrational entropy of bulk and surface atoms of the constituent metals.

1. Introduction

Presently, it is accepted as a rule rather than an exception that the composition of alloy surfaces may differ substantially from that of the bulk. Various models have been developed to predict, in many cases successfully, the surface composition of alloys [1–7].

Pt–Rh alloys form a particularly interesting system for various reasons. First, there exists a controversy in the literature on which of the metals segregates to the surface of equilibrated alloys [8–11]. Second, none of the experimental data on surface segregation in Pt–Rh alloys can satisfactorily be explained by the models referred to above. Third, the Pt–Rh system is of great practical interest. Pt–Rh alloys are used as a catalyst for the production of nitric acid from ammonia [12], and both metals are essential components in catalytic converters used for emission control of automotive exhaust gases [13,14]. Pt–Rh alloys are furthermore known for their resistance to corrosion and deformation at high temperatures, and are therefore widely applied in

equipment for glass manufacture, in thermocouples for high-temperature measurement, and in heating elements [15].

In this paper we show that Pt segregates to the surface of Pt-Rh alloys equilibrated at temperatures in the range of 1000–1500 K, and that this segregation can be attributed to the influence of lattice vibrational entropy.

2. Experimental

The experiments were performed in a Perkin-Elmer PHI 550 UHV system, equipped with a double-pass cylindrical mirror analyzer. A base pressure of 2×10^{-10} Torr could routinely be obtained in this system. The Auger spectra in the 0–1000 eV range were measured by exciting the sample with a $4.5 \mu\text{A}$ beam of 2 keV electrons, using a 2 eV modulation amplitude. For recording the high-energy Auger spectra, the sample was irradiated with a beam of 5 keV electrons, and a 6 eV modulation amplitude was used. In order to maintain reproducible analytic conditions, the sample position and CMA settings were tuned in for an optimum intensity and symmetry at the proper position of the elastic peak of reflected primary electrons.

The alloy and pure metals used in this investigation consisted of polycrystalline foils of specpure quality which were mounted on a tantalum hairpin. The temperature was monitored by use of chromel–alumel thermocouple spotwelded on the sample.

The samples were cleaned by Ar^+ ion bombardment at 1000 K until no more contaminants could be observed by an Auger analysis after equilibration. By monitoring Pt and Rh Auger signals as a function of time during sputtering and annealing, it was seen that the surface of the alloy sputtered at 350 K was depleted in Pt as compared to the alloy equilibrated at 1000 K. However, a subsequent annealing of the Pt–Rh alloy at 1000 K for about 1 min was sufficient to establish a surface segregation close to thermodynamic equilibrium. The standard equilibration procedure was to anneal the sample at 1000 K for at least 5 min, since a prolonged annealing resulted in no significant changes of the Auger spectra recorded.

The Auger spectra were evaluated by use of the Gallon model [16,17]. Generally, Auger transitions of both constituent metals are used in the analysis of a binary alloy. However, the Rh 302 eV Auger transition is neither very useful for a surface analysis, nor for a bulk analysis. On the one hand the monolayer intensity of it is too low for an accurate surface analysis, whereas on the other it is sufficiently high to induce effects in the bulk analysis. Hence, for reasons of accuracy, the surface and bulk sensitive Auger transitions of Pt have been used in the data evaluation. In this evaluation the intensity of the Pt 1967 eV transition was used to calculate the bulk composition of the alloy, and the intensities of the surface sensitive Pt 64 eV and 168 eV transitions as

Table 1
Auger parameters of Pt

	Auger transition (eV)		
	64	168	1967
Monolayer intensity	0.47	0.43	0.08
Backscattering factor in Pt	2.32	2.28	1.88
Backscattering factor in Rh	2.07	2.02	1.71
Matrix density (atoms/nm ²)	15.16 (Pt)		16.08 (Rh)

compared to that of the Pt 1967 eV transition were used to calculate the composition of the outermost atomic layer of the alloy. It was assumed that only the composition of the outermost atomic layer differed significantly from that of the bulk, and corrections were made for differences in the matrix density and the backscattering factor. All data of relevance have been collected in table 1. The backscattering factors have been calculated by use of the empirical relation of Reuter [18], and the monolayer intensities of the surface sensitive Auger transitions have been derived from the literature [19,20].

3. Results and discussion

3.1. Experimental data on the surface composition of Pt–Rh

The Auger analysis of the polycrystalline Pt–Rh alloy resulted in a bulk content of 62 at% Pt and a surface content of 84 at% Pt. A slightly lower surface concentration in Pt was found after annealing the alloy at 1500 K. Analogous results on Pt–Rh have been reported by Williams and Nelson [8]. Hence, the Pt–Rh alloy exhibits a significant surface enrichment in Pt. The result is indicated in fig. 1, along with other data on the surface composition of PtRh alloys from the literature [8–11].

The experimental data of Ahmad and Tsong [10] (open circles) have been obtained on the (001) planes of alloys equilibrated at about 1000 K by use of the time-of-flight atom probe, and indicate a surface segregation of Rh. Since the surface of their alloys is contaminated by 20–50% of a monolayer of sulfur, we will disregard these data in our further discussion. Williams and Nelson [8] (filled circles) analysed the surface composition of alloys equilibrated at 1300 K by use of low-energy ion scattering, and concluded that a Pt enrichment in the alloy surface occurs. This result is consistent with data based on an AES analysis by Holloway and Williams [9] (filled triangle) on a (111) alloy surface equilibrated at 1100 K. Also the data of Van Delft and Nieuwenhuys [11] (filled square) on the (100) surface of an alloy equilibrated at 1000 K indicate a surface enrichment in Pt. Notwithstanding some scatter

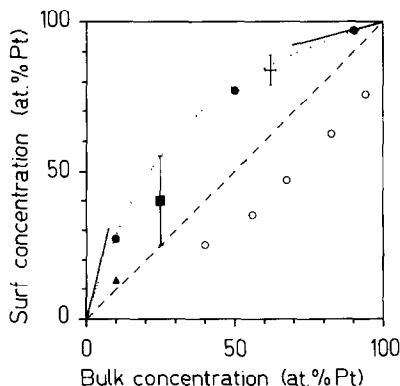
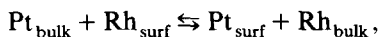


Fig. 1. The composition of the outermost atomic layer of Pt–Rh alloys as a function of their bulk composition. (\dagger), present work (1000 K); (\bullet), Williams and Nelson [8] (1300 K); (\blacktriangle), Holloway and Williams [9] (1000 K); (\circ), Ahmad and Tsong [10] (973 K); (\blacksquare), Van Delft and Nieuwenhuys [11], (1000 K). The dashed line indicates the relation between the surface and the bulk composition when no segregation occurs. The dotted curve indicates the calculated relation between the bulk and the surface composition; the drawn lines are predicted relations for dilute solutions based on the work of Miedema [2].

in the data, all results on atomically clean Pt–Rh alloys equilibrated in the temperature range of 1000–1500 K agree on a significant surface segregation of Pt.

3.2. Theory of surface segregation in Pt–Rh

When considering the process of surface segregation as an exchange reaction between bulk and surface atoms of Pt and Rh:



it is easy to understand that the position of the equilibrium of the segregation reaction is determined by the minimum of the Gibbs free energy of the system. Whatever the assumptions of the model to describe the alloy system may be, the Gibbs free energy can be formulated in general terms as follows:

$$G = U + PV - TS,$$

in which U represents the cohesive energy, PV stands for the pressure–volume contribution, and S for the entropy content of the system under consideration; T is the temperature of equilibration.

Now, we will discuss the relevance of the various contributions for solid solutions. For solid solutions, the contribution of PV to the Gibbs free energy is negligible.

The cohesive energy, U , can be related to the following parameters [1–7]: (i) the enthalpy of sublimation of both components (or the surface free energy),

Table 2
Parameters of importance for the surface segregation behaviour

	Pt	Rh
Enthalpy of sublimation at 298 K (kJ/mol) [21]	568.3	558.6
Atomic radius (nm)	0.138	0.134
Surface free energy at 0 K (kJ/mol) [2]	101.0	102.6
Enthalpy of mixing [22]	Slightly negative	

(ii) the enthalpy of mixing.

(iii) the radii of the constituent atoms.

The various parameters have been collected in table 2. No actual data on the enthalpy of mixing have been found in the literature. However, calculations of Niessen et al. [22] suggest that the formation of Pt–Rh alloys will be accompanied by only minor heat effects. Consequently, the system can be described by a model assuming a random distribution of the atoms over the various lattice sites in which the enthalpy of mixing is neglected. Also, on the assumption that bond strength surface relaxation effects are absent, only compositional deviations in the outermost atomic layer have to be taken into account [23]. Considering the difference in the enthalpy of sublimation, one would expect a surface enrichment of 7 at% Rh in the equimolar alloy. On the other hand, the slightly larger atomic radius of the Pt atoms will counterbalance or, perhaps even overcompensate the difference in enthalpy of sublimation. Based on a combined action of these two effects, as is the usual procedure in models of surface segregation, we estimate that the surface of the equimolar Pt–Rh alloy is enriched in Pt for about 1–2 at% [2,7]. Data on the surface free energy of Pt and Rh (table 2) also suggest a small Pt enrichment at the surface of Pt–Rh alloys, corresponding to 4 at% for the equimolar alloy. The experimental data in fig. 1, however, show a pronounced enrichment in Pt of about 25–30 at% for the equimolar alloy.

Evidently, the usual segregation models cannot explain the experimental data on Pt–Rh alloys. Hence, consideration of the entropy terms in the expression for the Gibbs free energy seems appropriate. Support for the involvement of an entropy contribution also comes from the literature; Williams and Nelson [8] reported an increasing surface excess of Pt with increasing equilibration temperature in the temperature range of 800–1100 K, in agreement with data of Van Delft and Nieuwenhuys [11]. Notice, that the observed temperature dependence of the Pt surface excess is in striking contrast with experience from the usual models of surface segregation in which the process is dominated by the cohesive energy. According to these models the surface excess of the segregating component decreases with increasing temperature (see, e.g., ref. [23]). The temperature dependence of the surface composition of Pt–Rh will be discussed in a forthcoming publication [24].

The entropy contribution of solutions can be subdivided into the following categories:

(i) The ideal entropy of mixing, referring to entropy effects upon the formation of a solution in which the atoms of both components are randomly distributed. Clearly, this entropy contribution will always be present in solutions. However, its relative contribution to the Gibbs free energy will depend on the temperature of equilibration, T .

(ii) The excess entropy of mixing, representing a non-ideal behaviour of the solution formed. The numerical importance of this contribution can be related qualitatively to enthalpy effects upon the formation of the solution. Generally, this contribution can be neglected in moderately exothermic alloy systems. According to predictions of Niessen et al. [22] the formation of Pt–Rh alloys should be accompanied by mild exothermic heat effects. Hence, our conclusion is that no important effect due to this entropy contribution can be expected.

(iii) The electronic and magnetic entropy. For a discussion on this point we refer to Swalin [25].

(iv) The vibrational entropy of the constituent atoms, representing vibrational properties of the atoms of both components in the surface and the bulk. Various authors (see, e.g. ref. [26], and references therein), most of which used the Einstein model for lattice vibrational properties, verified the possible role of this entropy contribution. Generally, the contribution of this effect was calculated to be of only minor importance. However, in the specific case of the Pt–Rh alloy system this contribution will predominate all other contributions at the temperature of equilibration of the present investigation, 1000 K, as we will show below.

The relevant quantity is the difference in vibrational entropy between both situations shown in the quasi-chemical reaction above. The major problem here is how to obtain reliable data in order to calculate the entropy balance sufficiently accurate. In the present approach we have used the relation between the vibrational entropy, the Debye temperature and the actual temperature, as derived within the framework of statistical thermodynamics for a monoatomic three-dimensional crystal [27]. Of course, the application of this relation to surface vibrations and to vibrations in an alloy is questionable [28]. Hence the results of the calculations can only be considered as a first-order approximation. Bulk and surface Debye temperatures have been obtained from the literature [29]. Using standard tables [30] the corresponding vibrational entropies at 1000 K have been determined. The vibrational entropy balance in the temperature range of 500 to 1500 K is $11.5 \pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$ in favour of Pt surface segregation. The various Debye temperatures and their corresponding vibrational entropies at 1000 K are given in table 3. Notwithstanding the constant value of the vibrational entropy of segregation over a wide range of temperatures, its contribution to the Gibbs free energy is

Table 3
Bulk and surface Debye temperatures of Pt and Rh and their corresponding vibrational entropy at 1000 K

	Θ_D (K) surface	Θ_D (K) bulk	S (J/mol·K) surface	S (J/mol·K) bulk
Pt	110	234	88	70
Rh	260	350	67	60

essentially temperature dependent. At low temperatures the cohesive energy and the ideal entropy of mixing will determine the position of the equilibrium of surface segregation, as in the usual models for surface segregation. With increasing temperature of equilibration the vibrational entropy contribution will become more important, and at high temperatures the vibrational entropy and the ideal entropy of mixing will predominate the process.

On the assumption that the vibrational entropy of both types of atoms in the alloy behaves ideally, and neglecting all other effects except for the ideal entropy of mixing, the relation between the surface and the bulk composition of the (111) plane of the Pt–Rh alloys has been calculated. The results of the calculations have been indicated in fig. 1 by the dotted curve. Note, that due to the neglect of contributions of the cohesive energy the curve shown represents the upper limit of the Pt surface content after a very high temperature equilibration. Clearly, the results of the present calculations are in excellent agreement with experimental data. Finally, we note that the results presented are also in good quantitative agreement with predictions of Miedema for dilute solutions [2], and in qualitative agreement with predictions of Lambin and Gaspard [31] and of Mezey and Giber [32].

4. Conclusions

The surface of atomically clean Pt–Rh alloys, equilibrated at temperatures in the range of 1000–1500 K is significantly enriched in Pt. This surface segregation behaviour can be understood from a fundamental point of view when contributions of vibrational entropy are taken into account.

Acknowledgements

Stimulating discussions with Professor V. Ponec (Gorlaeus Laboratories, State University of Leiden, The Netherlands) are gratefully acknowledged. JWN acknowledges financial support from a Huygens Fellowship granted by the Netherlands Organization for the Advancement of Pure Research (ZWO).

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