Modelling of surface segregation for palladium alloys in vacuum and gas environments

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ABSTRACT

Surface segregation of a series of forty Palladium-based binary alloys has been investigated using a thermodynamic model based on an atom exchange approach. Their surface segregation behaviour, both in vacuum and in gas environments, were comprehensively estimated. The calculated results are in good agreement with the available experimental and computational data reported in literatures. Effects of mixing enthalpy, temperature, crystal orientation on the surface, elastic strain energy, adsorption and absorption of gases like H_2, O_2, CO have been discussed in detail. These results can be considered as basic guidelines to design novel Pd alloys for hydrogen separation membranes, sensors or catalysts. The model itself also offers a convenient and accurate routine to predict the surface segregation of other than Pd-based binary alloys in different gas atmospheres.

Introduction

Surface segregation of binary alloys, *i.e.* the surface enrichment by one of the alloy elements, is of great importance as it may enhance or suppress desirable and undesirable chemical reactions at the surface [1]. This phenomenon has been intensively investigated over decades since it became well known that catalytic activity of alloy catalysts is determined almost exclusively by the surface properties [2]. There have been numerous theoretical and experimental efforts made to estimate the surface segregation of various alloys [3,4]. In particular, Palladium binary alloys were studied, because of their application as storage, catalysts and membrane reactor for hydrogen separation, key components towards the hydrogen economy [5—7].

Currently, about 80% of the world energy demand comes from fossil fuels [8]. Use of hydrogen as an alternative energy source could help to address environmental issues [9]. Besides, hydrogen also has many other applications in various industrial aspects, such as petroleum refining, semiconductor manufacturing, pharmaceuticals etc. [10,11]. Therefore, the demand for hydrogen has grown for decades, which has motivated improving production methods. Hydrogen can be produced from water by electrolysis, but the most economical method is steam methane reforming (SMR) [12]. The composition of the SMR product stream is typically 74% H_2, 18% CO_2, 7% CH_4 and 1% CO [13]. However, a majority of hydrogen applications require a minimum purity of 99.99%, while polymer-electrolyte fuel cells (PEFCs) require even ultra-pure hydrogen (99.9995%) [14,15]. Thus, hydrogen separation and purification are essential processes in the hydrogen industry [16,17].

Palladium (Pd) membranes offer an efficient method for separating hydrogen from a hot gas mixture to high purity levels because of their great hydrogen permeability and

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selectivity [6,13,18]. To improve the performance and lifetime of the membrane, Pd is usually alloyed with transition metals [19,20]. Alloying can prevent hydrogen embrittlement of Pd by suppressing hydride formation that is accompanied with a large volume change. Also, alloying may improve the hydrogen permeability and in some cases enhance the resistance to contamination by sulphur containing impurities [21]. At present, most of commercial hydrogen separation membranes are based on Pd–Ag or Pd–Cu alloys [22,23]. However, surface segregation is a major problem that arise when Pd alloy membranes are kept in a hydrogen environment [24,25]. Driving forces for surface segregation may be different depending on the conditions: the gas environment, temperature, enthalpies of mixing, surface energy, size mismatch of the atoms and the entropy contribution are only some of the parameters that influence the segregation process. A comprehensive understanding of surface segregation is of paramount importance for further improvement of Pd alloys for membranes, catalysts or sensors.

Thermodynamic calculation provides a cheap and fast way to predict the surface segregation in vacuum and gas environments without the need of expensive and time-consuming experiments. Models on surface segregation in vacuum have been developed since 1950s. For example, Wynblatt and Ku proposed a thermodynamic model to describe the surface segregation in vacuum, with the surface energy reduction as the major driving force [26]. The enthalpy change was accounted for by an "atom exchange approach": an atom located in the bulk, exchanges position with an atom of the other species located at the surface. As for the influence of adsorption or chemisorption, Tomanek determined the surface segregation for H, O and CO covered surfaces by adding the adsorption enthalpy to the total driving force of segregation, and the effect of absorption (of hydrogen) in the bulk was accounted for by using an empirical parameter [27]. However, this is not a universal method to account for gas absorption (of hydrogen) for various Pd alloys or other alloy systems. There are also some other simulation methods dealing with surface segregation phenomena. For example, Monte Carlo simulations have been applied to predict the surface segregation of binary alloys in vacuum [28]. Density functional theory can also be used to account for the gas adsorption for some specific alloys [29]. However, all these approaches reported do not consider the effect of both gas adsorption and absorption at the same time as would be the case for Pd-based alloys under application conditions.

In the present research, a thermodynamic model also based on the atom exchange approach was developed to describe the surface segregation of a series of forty Pd-based binary alloys. A relation between the surface and bulk compositions upon segregation was obtained for the cases of binary alloys in vacuum, with adsorption on the surface, with absorption in the bulk, and both adsorption and absorption. Effect of hydrogen absorption was considered by the formation enthalpy of metal hydride, which is also feasible for other alloy systems. For a limited set of Pd-binary alloys (Pd–Ag, Pd–Au, Pd–Cu, Pd–Ni and Pd–Pt alloys), experimental and computational results are reported. Those results were compared with our results and a good agreement was obtained.

Method

Surface segregation by atom exchange

Surface segregation refers to the difference in concentration between the surface and the bulk of a material, *i.e.* the surface is enriched with one or several of the constituents. Here surface is defined specifically as the topmost atomic layer only. As mentioned above, surface energy, enthalpy of mixing and elastic strain energy are only some of the aspects contributing to the driving force of the segregation process. Four different cases are considered in the present work, surface segregation (1) in vacuum; (2) with hydrogen adsorption at the surface; (3) with hydrogen absorption in the bulk and (4) with both hydrogen adsorption and absorption, as illustrated in Fig. 1.

In case (1), surface segregation in vacuum will be considered using the basic assumption as Wynblatt and Ku's work [26]. The enthalpy of segregation is then related to the change in the configurational energies of A and B atoms upon their exchange between the bulk and surface, as well as the related elastic strain energy. The segregation enthalpy ΔH_{seg} consist of the change of configurational energy change and the elastic strain energy, $\Delta H_{seg} = \Delta E_{conf} + \Delta E_{elastic}$. ΔE_{conf} can be expressed as [26]:

$$\Delta E_{conf} = (\gamma_A \sigma_A - \gamma_B \sigma_B) + 2\omega Z_l \left(x_A^{bulk} - x_A^{surf} \right) + 2\omega Z_v \left(x_A^{bulk} - \frac{1}{2} \right) \quad (1)$$

where γ_A and γ_B are surface energy of pure A and B metals; σ_A and σ_B are surface area of A and B directly related to the atomic volume; x_A^{bulk} and x_A^{surf} are the solute composition in the bulk material and on the surface. Z_l and Z_v are numbers of nearest lateral and vertical neighbours. For Pd-based alloys with FCC structure, $Z_l = 6$ and $Z_v = 3$ in the (111) plane, while $Z_l = Z_v = 4$ in the (100) plane.

The alloy parameter ω, indicates whether the A–A or B–B bonds are preferred ($\omega > 0$, A–A and B–B bonds preferred, and $\omega < 0$, A–B bonds preferred) [30]:

(a) (b) (c) (d)
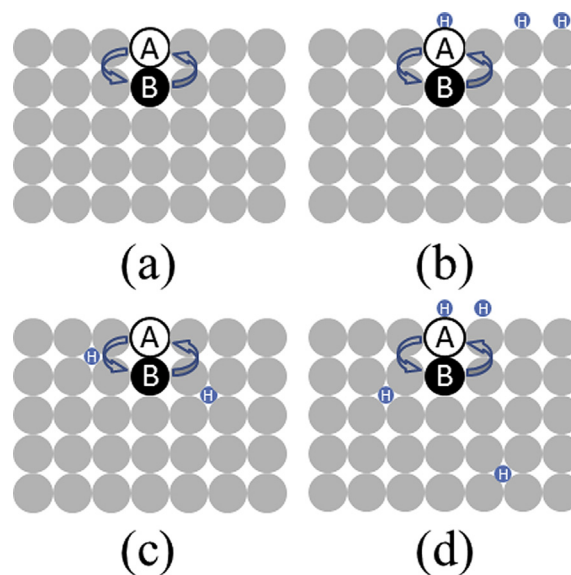
Fig. 1 – **Scheme of surface segregation in terms of the atom exchange model (a) in vacuum; (b) with adsorption; (c) with absorption; (d) with adsorption and absorption.**