Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 585 (2005) 101–107
SURFACE SCIENCE
www.elsevier.com/locate/susc

Surface segregation of transition metal impurities on the TiC(1 0 0) surface

H.W. Hugosson [a,b,*], O. Eriksson [a], U. Jansson [c], I.A. Abrikosov [d]

[a] *Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden*
[b] *Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[c] *Department of Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, S-751 21 Uppsala, Sweden*
[d] *Department of Physics and Measurement Technology, Linköping University, SE-581 83 Linköping, Sweden*

Received 23 September 2004; accepted for publication 10 April 2005
Available online 26 April 2005

Abstract

The segregation energies of 3d (Sc–Cu), 4d (Y–Ag) and 5d (La–Au) transition metal impurities on the (1 0 0) surface of TiC have been obtained using first-principles electronic structure calculations. The results are in agreement with available experimental data and show that the difference in atomic size between the impurity and host species, as well as the difference in surface energies determines if the impurity will segregate towards the surface or not. The results indicate that the difference in size is the dominant factor for the trends in segregation of transition metal impurities towards the (1 0 0) surface of TiC.

Keywords: Surface segregation; Density functional theory; Electronic structure; Transition metal carbides; Transition metals

1. Introduction

Surface segregation of impurities is one of the most fundamental processes that take place in alloys. Segregation of impurities from the bulk towards the surface layers of a material involves a complicated interplay of the electronic properties of the surface and bulk, via several dynamic steps including diffusion. Understanding this segregation is also important in experimental physics and materials science where the growth of thin films is largely influenced by the presence or absence of impurities on the grown surfaces. Few experimental studies exist for segregation profiles of metal impurities on transition metal carbide surfaces. A study by Souda and coworkers of dilute (0.6 wt.%) transition metal impurities (W, Ta, Zr, Nb and Mo) on TiC(1 0 0) and (1 1 1) surfaces have shown a marked

* Corresponding author. Tel.: +46 855378420; fax: +46 855378590.
E-mail address: hakan@theochem.kth.se (H.W. Hugosson).

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.04.010

enrichment of segregants in the topmost layer of the (1 0 0) and also in the deeper layers of the (1 1 1) surface [1]. A second study by the same team investigating W impurities at the TiC(1 0 0) surface, showed an enrichment of both W impurities and carbon vacancies at the surface [2].

Transition metal carbides have a unique combination of properties (chemical stability, high hardness, high melting point, excellent electrical and thermal conductivity) making them highly suitable for many technological applications [3]. Accordingly, large experimental work and many theoretical calculations have been devoted to these systems. Early work in this field is summarized in two review articles by Calais [4] and Neckel [5] and examples of later comprehensive experimental and theoretical reviews are those due to Schwarz [6], Johansson [7] and Williams [8]. Cubic TiC, which is the subject of study here, is an important thin film material used in coating layers and in binderless cemented carbides together with WC, and as a component material in high speed steels. The cubic NaCl phase of TiC displays deviations in stoichiometry over a wide range of homogeneity, from $TiC_{0.50}$ to $TiC_{0.97}$, this being caused by vacancies in the carbon sublattice [9]. TiC has been studied in several earlier theoretical works. Redinger and coworkers studied substoichiometric $TiC_{0.75}$ using a self-consistent APW method and a model structure with ordered vacancies not allowing for local relaxations around the vacancies [10]. More recently the relaxation of the atoms around the vacancies in substoichiometric TiC_{1-x} has been investigated by first Tan et al. [11], using a tight-binding model, and by Hugosson and coworkers using an all-electron full-potential method [12]. The phase equilibria in TiC_{1-x} was studied using a combination of electronic structure and statistical methods by Pourovski and coworkers [13]. An investigation of $TiC_{1-x}N_x$ by Jhi and coworkers also reported on a mechanism coupling the shear modulus of TiC with the valence electron concentration [14]. Surface properties of TiC (and TaC) were investigated by Price et al. [15,16]. The surface energies of transition metal carbides has been studied systematically by Hugosson et al. using LMTO-ASA method [17]. The surface energy of TiC were also calculated using plane wave pseudopotential methods by several groups [18–20].

The objective of the present work is to study the thermodynamic limit of the dynamic segregation process by calculating the theoretical segregation energies for impurities of all the 3d, 4d and 5d transition metals on the TiC(1 0 0) surface.

2. Method and set-up

Titanium carbide was treated in the B1 (or NaCl) crystal structure, and calculations were done for the (1 0 0) surface. The equilibrium volume for bulk titanium carbide was calculated theoretically, and this volume was used in the surface calculations. No surface relaxation effects were taken into account.[1] The cubic transition metal carbides (TMCs), and titanium carbide among them, are known to be substoichiometric due to vacancies on the carbon sublattice. In this study we have, however, considered both the bulk and surfaces of the TMC without vacancies.

It is important to point out that recent calculations of the surface energy for TiC have shown that it is very sensitive to the choice of the approximation for the exchange-correlation contribution to the total energy and one-electron potential within the density functional theory. Indeed, the generalized gradient approximation (GGA) leads to the calculated energy for the ideal (1 0 0) surface of the order of 1.8–1.9 J/m^2 [19,20], while the local density approximation (LDA) predicts much higher surface energies, 2.5–2.7 J/m^2 [19,17]. The GGA is known to improve calculated lattice parameters for solids as compared to the LDA, and because of this it generally gives better description of the bulk properties of materials, e.g. for Ti, TiC and TiN [19,20]. It is somewhat less known that the reliability of the GGA for the estimation of the surface properties is still under

[1] As has been shown by Price et al. [15,16], the rippling and the energy associated with rippled relaxation in the cases of TiC (and TaC) is quite small. This conclusion is confirmed by more recent pseudopotential calculations [19,20]. Thus, the neglect of the surface relaxation effects in our study should not substantially influence the segregation trends reported here.