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ScienceDirect
Thin Solid Films 516 (2008) 1088–1092
www.elsevier.com/locate/tsf

A statistical–thermodynamic model for ordering phenomena in thin film intermetallic structures

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Received 19 November 2006; received in revised form 12 July 2007; accepted 1 August 2007
Available online 15 August 2007

Abstract

Ordering phenomena in bcc (110) binary thin film intermetallics are studied by a statistical–thermodynamic model. The system is modeled by an Ising approach that includes only nearest-neighbor chemical interactions and is solved in a mean-field approximation. Vacancies and anti-structure atoms are considered on both sublattices. The model describes long-range ordering and simultaneously short-range ordering in the thin film. It is applied to NiAl thin films with B2 structure. Vacancy concentrations, thermodynamic activity profiles and the virtual critical temperature of order–disorder as a function of film composition and thickness are presented. The results point to an important role of vacancies in near-stoichiometric and Ni-rich NiAl thin films.

Keywords: NiAl thin films; Order–disorder transition; Point defects

1. Introduction

An attractive class of "advanced materials" are the intermetallic compounds and systems produced on their base as thin layer structures. Nanostructured materials take on an enormously rich variety of properties and promise exciting new advances in micromechanical, electronic, and magnetic devices. Obviously, many of exceptional outstanding properties can be related to both the ordering phenomena in the structure and the type and amount of defects present in thermodynamic equilibrium state, and to the variation of different defect concentrations with composition and temperature [1]. One of the problems encountered in design and fabrication of new technological materials is to control the processes occurring in the structure under different treatment conditions. The modelling and prediction of the behavior of intermetallic compounds under various technological states is therefore of paramount importance.

In this respect, the main goal of the present work is to develop a quantitative, predictive and verifiable model for description of ordering phenomena in nonstoichiometric binary alloy thin film materials with bcc structure.

The theory is based on an Ising approach consisting of pair wise interactions between neighboring atoms belonging to the sublattices in the form of monoatomic layers parallel to the (110) orientated surface. Above the critical temperature of the order–disorder transition, a complex distribution of atoms and vacancies shows various short-range order phenomena, whereas, below the critical temperature, long-range order is established and one observes the lower symmetry of the B2-(CsCl−) structure. In many cases, however, the ordered structure seems to be stable up to the melting point, and the model is then describing a virtual order–disorder transition. In the ordered state, the disorder concerns the occupation of regular lattice sites by anti-structure atoms and vacancies. At low temperatures and near-stoichiometric compositions, the point defects show random distribution. With increasing temperature, short-range order of point defects becomes more and more important, i.e. the crystal in thermodynamic equilibrium is characterized by short-living clusters of two or more neighboring point defects.

The present study uses a theoretical model that has earlier been developed for 3 dimensional nonstoichiometric intermetallic

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doi:10.1016/j.tsf.2007.08.032

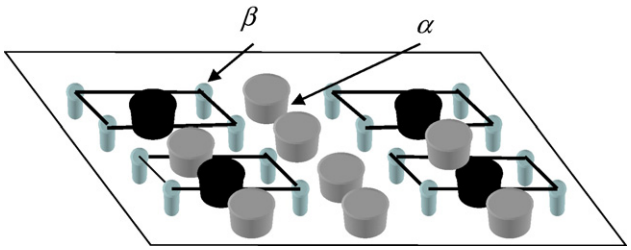

Fig. 1. Two dimensional square lattice divided into α- and β-sublattices. Non-overlapping clusters (β-squares) are depicted.

compounds with non-frustrated lattices [2–4]. We take non-overlapping clusters as the basic units and deal with the atomic sites in between the clusters utilizing the relations arising from the equivalence of those sites with the sites within the clusters. Vacancies and anti-structure atoms are considered on both sublattices.

The challenge was to describe a decreasing dimensionality on the way from the true 3 dimensional crystal to the near 2 dimensional, where surface effects come into focus.

Small particles of long-range ordered alloys have recently been modelled by Fukami and Tanaka [5], and by Numakura and Ichitsubo [6], who used a Bragg–Williams-model, assuming pair-wise interaction energies and random distribution of point defects. (110) NiAl thin films with different thicknesses have been studied by Brown and Mishin by a Monte Carlo method [7], utilizing a concept of mechanical surface stress on individual atoms. Sosa-Hernandez et al. [8] modelled phase transitions in bcc binary alloy thin films by an Ising Hamiltonian, using pair-wise interaction energies and additional parameters for surface interactions, however, vacancies where not considered in the system. In fact, very little is known about the behavior of vacancies in thin alloy films.

In this paper, we present a simple picture of how the vacancy concentrations are affected by the restricted dimensionality.

2. Derivation of the model equations

For the derivation of the model equations, we start from the 2 dimensional case, i.e. we study a monoatomic layer parallel to the (110) orientated surface. In order to transform the 2 dimensional lattice to a 3 dimensional structure, we stack a number of parallel layers in a way resulting in a progressive built-up of the 3 dimensional B2 (CsCl) structure.

To describe the chemical ordering, we consider a 2 dimensional square lattice divided into two interpenetrating simple square sublattices of equal size referred to as α- and β-sublattices. Each of the two sublattices consists of N lattice sites. Coordination number is 4. To accommodate all possible combinations of point defects, we assume that both anti-structure atoms as well as vacancies are allowed on both sublattices.

It is supposed that not only long-range order (LRO) of the A and B atoms on the two sublattices may be established, but also short-range order (SRO) of the various species, whereby the interacting atoms or vacancies occupy nearest neighbor positions in the crystal lattice. The pair-wise interaction energies are regarded as to be constant and independent of the occupancy of any other nearest-neighbor positions, and to be independent of the atom's position in the crystal lattice.

To simplify the description of the degree of SRO, the β-sublattice is divided into non-overlapping clusters (β-squares) [2–4]. Each of these β-squares consists of four β-sublattice sites with a single α-sublattice site in the central position of the β-square, as shown in Fig. 1. The β-squares form a simple square lattice with a total number of $N/4$ lattice sites. A mean-field approximation is introduced by assuming that the state of thermodynamic equilibrium is characterized by a set of equilibrium numbers of the different β-square types which are defined in Table 1: each series of $81=3^4$ different types of β-squares contains either an A-atom, a B-atom, or a vacancy in the central α-sublattice position. The number n_i of β-squares with given numbers of A-atoms (a_i), B-atoms (b_i), and vacancies (c_i) on their four β-sublattice sites is

$$n_i = n_{i\mathrm{A}} + n_{i\mathrm{B}} + n_{i\mathrm{V}} \quad (i = 0, 1, \ldots, 15) \tag{1}$$

z_i in Table 1 is the number of possible arrangements of given numbers of A atoms, B atoms and vacancies on the four β-sublattice sites of a β-square.

Each arrangement of the atoms on the lattice sites, corresponding to a given set of 243 numbers of the 243 different β-squares (i.e., corresponding to a given configuration) is assumed to be associated with the same total configurational energy value E, the same total number of A atoms N_A, and the same total number of B atoms N_B.

The grand potential Ω is a function which depends on

$$\Omega = \Omega(N, T, \mu_\mathrm{A}, \mu_\mathrm{B}, \varepsilon_{\mathrm{AA}}, \varepsilon_{\mathrm{BB}}, \varepsilon_{\mathrm{AB}}, \varepsilon_{\mathrm{AV}}, \varepsilon_{\mathrm{BV}}, n_{i\mathrm{V}}, n_{i\mathrm{B}}, x, y, A), \quad i = 1, \ldots 15 \tag{2}$$

where: N is the total number of α and β sites; A is the number of monoatomic layers; T is the temperature; μ_A and μ_B are the

Table 1
Properties of the different types of non-overlapping clusters (β-squares)

Numbering of squares (i)	Number of A-atoms on β sites of square (a_i)	Number of B-atoms on β sites of square (b_i)	Number of vacancies on β sites of square (c_i)	Number of square types (z_i)
1	0	4	0	1
2	0	3	1	4
3	0	2	2	6
4	0	1	3	4
5	0	0	4	1
6	1	3	0	4
7	1	2	1	12
8	1	1	2	12
9	1	0	3	4
10	2	2	0	6
11	2	1	1	12
12	2	0	2	6
13	3	1	0	4
14	3	0	1	4
15	4	0	0	1