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ScienceDirect

Mendeleev Commun., 1994, **4(5)**, 176–178

Mendeleev
Communications

Electronic Properties of Solid Solutions in Ti–Al–(N,C) Systems

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The electronic properties and stability of ternary cubic solutions in Ti–Al–(N,C) systems have been investigated using the self-consistent LMTO-ASA method.

Solid solutions (SS) in Ti–Al–(N,C) systems are attracting considerable attention as potential materials for microelectronics, coatings for construction materials and catalysts.[1–3] Questions concerning the structure of their electronic energy spectrum (EES) and their conditions of stability have been poorly studied. Only X-ray photoemission spectra of a number of $Ti_xAl_yN_z$ films have been obtained.[4,5] The KKR-coherent potential method was employed[6] to calculate SS of composition $Ti_{0.75}Al_{0.25}N$. The nature of the chemical bonding of a single Al impurity substituting the central Ti atom in the TiN_6Ti_{12} cluster was described by the discrete variation method.[7]

This paper presents the results of systematic self-consistent band calculations of cubic (B1 type) SS which can be presumably formed in Ti–Al–N and Ti–Al–C systems. Supercells with composition Ti_4X_4 (X = N,C) were used. Substituting some Ti atoms for Al, we simulated the compositions of the SS listed in Table 1. The calculations were carried out making use of the LMTO method in an overlapping spheres approximation.[8] The lattice parameters of the ternary alloys were assumed to be equal to those for the initial binary phases.[9]

The densities of states (DOS) of the calculated crystals are given in Fig. 1. The structure of the valency band (VB) of TiC and TiN has been thoroughly studied.[8] In line with these results it has been determined, for example, that the VB of TiC contains a band of quasi-core states (band A, Fig. 1), a band of bonding Tid–C2p (band B) and antibonding delocalized non-occupied states of the metal (band C). The VB of TiN is similar to that of TiC with allowance for a greater energy distance between the centres of bands A and B and partial occupation of band C in accordance with an increased concentration of valency electrons (CVE) in the primitive cell.

The formation of SS is accompanied by a substantial transformation of the VB structure associated with an increase in the forbidden gap between the C2s- and p-d-bands, a change in the position of the Fermi level (E_F) and a sharp complication of the DOS shape occurring when new substructures are formed, Fig. 1. Among these substructures we shall mark out peaks B′ and B″ whose formation is caused by the introduction of states of Al impurity atoms forming new types of Al–(C,N) interactions in the spectrum of the valency states of TiC and TiN. This is clearly seen in Fig. 1, which depicts the local DOS of Al for the $Ti_{0.5}Al_{0.5}N$ SS.

The nature of the change in occupation of VB is similar for $Ti_{1-x}Al_xC$ and $Ti_{1-x}Al_xN$ SS (with increase in x, *i.e.* with decrease in CVE, E_F shifts towards lower energies), but it has, however, radically different consequences. The band of bonding p-d-states for $Ti_{1-x}Al_xC$ becomes almost unoccupied, while for $Ti_{1-x}Al_xN$ there occurs a decrease in the occupation of the band of delocalized metallic s,p,d-states which is antibonding with respect to Ti–X (X = C, N) bonds.

The above-mentioned effect, together with the energy necessary to break Ti–X bonds (in the process of substitution Ti → Al) can determine the relative stability of cubic titanium aluminocarbides and aluminonitrides. As numerous computations[8] show, the bonding energy (E_b) of Ti–C is much higher than E_b (Ti–N). That is why, taking into account the nature of the change in the bands of different kinds for carbide and nitride phases described above, as well as lower energy losses required for the breakdown of Ti–N bonds, it is possible to assert that the formation of homogeneous cubic alloys will be more probable in the Ti–Al–N systems than in SS based on TiC.

To confirm the aforesaid, the cohesive energy (E_{coh}), the energy of substitution of Ti for Al (E_{sub}) and the partial pressure of the electron-nuclear system to crystals (p_e) have been calculated according to the technique described in ref. 8, Table 1. The latter values can be considered as parameters characterizing the participation of individual states in interatomic interactions determining[8] the contributions from partial pressures of electrons with orbital quantum number l, and are given in the atomic sphere approximation for the q^{th} sphere by

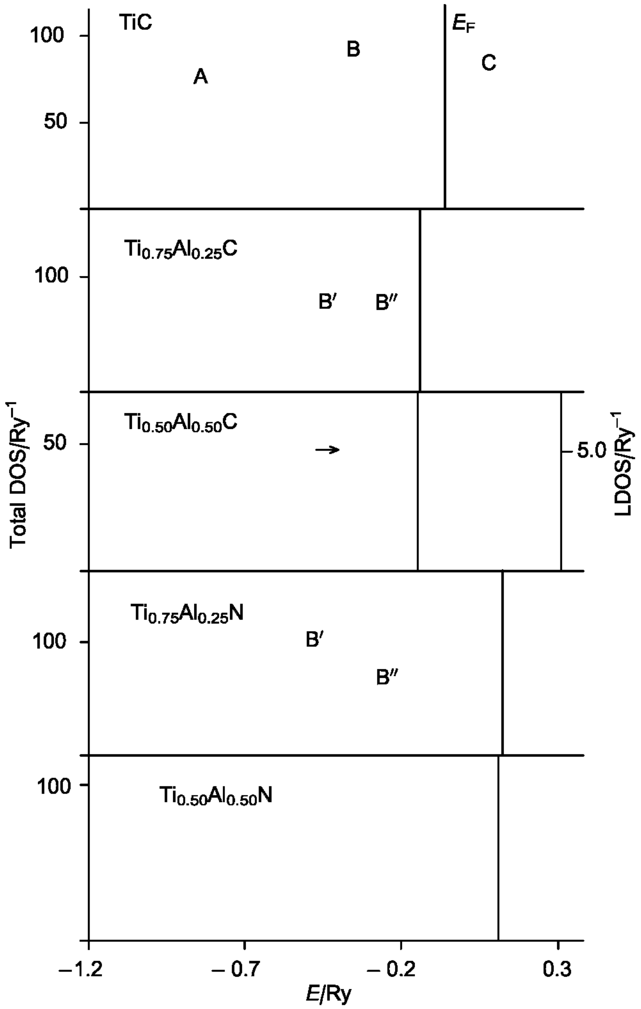

Fig. 1 Total densities of states for cubic ternary phases in the Ti–Al–C and Ti–Al–N systems. The partial DOS of aluminium (dots) is given for $Ti_{0.50}Al_{0.50}C$.

$$3p_l V = \int^{E_F} S N_l(E) R_l^2(E,S) \times ([E - v(S)]S^2 + [D_l(E) + l + 1] \times$$
$$\times [D_l(E) - l] + \rho(r)\frac{\partial \varepsilon}{\partial \rho(r)}|_{r=S} S^2)\mathrm{d}E$$

Here V is the volume of the sphere q, S is the radius of the sphere, $N_l(E)$ is the partial DOS, $R_l(E, S)$ is the volume of the radial part of the atomic orbital at energy E, $v(S)$ is the potential at the sphere (excluding the Madelung term), $D_l(E)$ is the logarithmic derivative for $R_l(E)$ on the sphere, ε is the density of exchange-correlation energy and $\rho(r)$ is the electron density.

For $Ti_xAl_{1-x}N$ SS, $|E_{coh}|$ is observed to decrease with increasing Al content and the sign of E_{sub} becomes opposite, facts which correspond to the actual situation[1–3] for the existence of homogeneous cubic aluminonitrides over a limited range of Al concentrations. In contrast, for all the

Table 1 Cohesive energy (E_{coh}/Ry), substitution energy (E_{sub}/Ry) and partial pressure (P_e/Mbar) in SS of Ti–Al–(N,C) systems.

Compound	Parameter						
	E_{coh}	E_{sub}	p(N(C)2s)	p(N(C)2p)	p(Ti4s)	p(Ti4p)	p(Ti3d)
TiN	−1.327	–	0.207	−0.046	0.027	0.180	−0.540
$Ti_{0.75}Al_{0.25}N$	−1.224	−0.125	0.185	−0.076	−0.024	−0.077	−0.090
$Ti_{0.50}Al_{0.50}N$	−1.062	0.01	0.170	−0.100	−0.051	−0.230	−0.230
TiC	−1.588	–	0.145	−0.177	0.070	0.300	−0.633
$Ti_{0.75}Al_{0.25}C$	−1.452	0.136	0.129	−0.140	−0.020	−0.053	−0.072
$Ti_{0.50}Al_{0.50}C$	−1.316	0.272	0.111	−0.163	−0.049	−0.158	−0.224

compositions $Ti_xAl_{1-x}C$ SS considered, $E_{sub} > 0$, *i.e.* the formation of similar homogeneous cubic SS is hampered. The foregoing is also confirmed by comparing the nature of the decrease in partial pressure (p_e), Table 1. In particular, the binding pressure p_e of the (Ti3d)-type reduces most abruptly for SS based on TiC; in other words, the substitution of some Ti atoms for Al in carbide is less favourable than in nitride and the formation of stable cubic titanium aluminocarbides will be less probable.

This work has been carried out with the financial support of the Russian Foundation for Fundamental Researches (grants no. 93-03-04939 and 94-03-09524).

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Received: Moscow, 6th June 1994
Cambridge, 7th July 1994; Com. 4/03572K