Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 80 (2014) 421–434
Acta MATERIALIA
www.elsevier.com/locate/actamat

Solid solution effects in the $Ti_2Al(C_xN_y)$ MAX phases: Synthesis, microstructure, electronic structure and transport properties

W. Yu [a], V. Mauchamp [a], T. Cabioc'h [a], D. Magne [a], L. Gence [b], L. Piraux [b], V. Gauthier-Brunet [a], S. Dubois [a,*]

[a] *Institut PPRIME, Département de Physique et Mécanique des Matériaux, CNRS, Université de Poitiers, ENSMA, UPR 3346, SP2MI, Téléport 2, Boulevard Marie et Pierre Curie, BP30179, 86962 FUTUROSCOPE CHASSENEUIL Cédex, France*
[b] *Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium*

Received 31 May 2014; received in revised form 17 July 2014; accepted 29 July 2014

Abstract

$Ti_2AlC_xN_y$ solid solutions are synthesized using hot isostatic pressing. The X site solid solution effects are investigated, focusing on the microstructure, electronic structure and transport properties of the $Ti_2AlC_xN_y$ MAX phases. Combining X-ray diffraction with scanning electron microscopy and wavelength dispersive X-ray spectroscopy measurements, it is shown that solid solutions can be synthesized with well-controlled chemical compositions in the entire composition range ($x = 0$–1). The measured a and c lattice-parameter values are shown to be in good agreement with those calculated using the cluster-expansion formalism. Combining electron energy-loss spectroscopy (EELS) and band structure calculations, it is demonstrated by Arroyave et al. that solid solution effects induce weak perturbations on the electronic structure. The solid solution effect thus results mainly in a rigid shift of the Fermi energy in a flat part of the electron density of states of Ti_2AlC (or Ti_2AlN). From these observations, the variations in two key parameters of the conductivity are rationalized. The relative variations in the residual resistivity in the whole composition range are shown to be small, which agrees well with the weak disorder evidenced by EELS. However, the values of the slope of the variation in resistivity vs. temperature are shown to vary quite significantly, evidencing a deviation from Matthiessen's rule in these systems. By comparing the experimental data with calculations based on the semi-classical Boltzmann equation, it is demonstrated that the observed variations are due to a combination of band structure effects and changes in the scattering mechanisms. Finally, vacancies are also shown to have a prominent effect on the transport properties of $Ti_2AlC_xN_y$ solid solutions. In particular, both residual resistivity and $d\rho(T)/dT$ values are shown to be significantly higher than those of the corresponding stoichiometric compounds.

Keywords: MAX phases; Solid solution; Resistivity; Electron energy-loss spectroscopy; Band structure calculations

1. Introduction

$M_{n+1}AX_n$ phases (with $n = 1$, 2 or 3) form a wide class of nanolaminated ternary carbides or nitrides, with a hexagonal structure, where M stands for an early transition metal, A for an A-group element, and X for either carbon or nitrogen [1–9]. In addition to the considerable possibilities of changing the chemistry of these systems by playing on the M, A or X elements, solid solutions can also be synthesized on every one of these three atomic sites, thereby allowing the tuning of their electronic, mechanical, optical or thermal properties [10–17]. In these so-called MAX phases, the $M_{n+1}X_n$ layers, characterized by mostly strong covalent M–X bonds, are interleaved with A layers through weaker M–A bonds. This inherent nanolayered

---

[*] Corresponding author. Tel.: +33 549496749; fax: +33 549496692.
E-mail address: sylvain.dubois@univ-poitiers.fr (S. Dubois).

http://dx.doi.org/10.1016/j.actamat.2014.07.064
1359-6454/

structure provides a unique combination of metal-like and ceramic-like properties: machinability, good electrical and thermal conductivity, high thermal shock resistance, good oxidation resistance and stiffness at high temperatures [9], which opens the way to diverse potential applications.

Among the most investigated applications to date are: (i) the realization of ohmic contacts on wide-gap semiconductors to achieve high-quality devices using Ti-based MAX phase compounds [18–21]; and (ii) use in future nuclear power plants [22]. Moreover, because of the combination of their nanolaminated structure and versatile chemistry, these materials were also shown to exhibit promising properties as magnetic inherent nanolaminates [23], and are precursors for a new class of two-dimensional materials, the MXenes [24–27]. In this context, solid solution effects play a key role in MAX phase properties: they induce magnetism and the possibility of tuning some properties [17], and allow the stabilization of MXene carbonitrides or of new MAX phases compounds (such as $(Cr_{0.5}V_{0.5})_{n+1}AlC_n$ with $n = 1$, 2 and 3) [28]. A corollary to these effects is a modification of the electronic properties of the materials compared with the reference system. In this context, the present authors' purpose is to systematically investigate these solid solution effects in the $Ti_2Al(C_xN_y)$ ($x,y = 0$–1) system by focusing on the microstructure, electronic structure and related transport properties.

MAX phase carbonitrides, in particular $Ti_2AlC_xN_y$ phases, are one of the most important examples of MAX phase solid solutions on the X site. Since Ti–N and Ti–C have similar chemical bonding characteristics, resembling those of TiC and TiN binary compounds, it is possible to form a wide range of $Ti_2AlC_xN_y$ solid solutions [29,30] with different physical properties. For example, $Ti_2AlC_{0.5}N_{0.5}$ has been reported [29,31,32] to be significantly harder than either of its end-members Ti_2AlC and Ti_2AlN, and there may be other ratios of C and N with even better properties. As a prerequisite to their application for ohmic contacts, MAX phase electronic properties and especially the modifications resulting from solid solution and/or vacancy effects must be properly studied and understood. Scabarozi et al. [33] have shown that the $Ti_2AlC_{0.5}N_{0.5}$ solid solution has a higher residual resistivity (RR) than the Ti_2AlC and Ti_2AlN end-members. This higher RR has been attributed to scattering by impurities, vacancies or other defects. Results also suggest that vacancies are potent electron scatterers, as is well established in binary transition carbides [36,37]. Indeed, it has recently been proposed that $Ti_2AlC_xN_y$ solid solutions can have a significant number of vacancies on the X site [30]. Even if the stoichiometry of the $M_{n+1}AX_n$ compounds is generally assumed to be 2:1:1; 3:1:2 and 4:1:3 for $n = 1$, 2 or 3, respectively, small differences from this "ideal" stoichiometry can exist and can strongly influence the physical properties. In other words, it is of great interest to know not only the microstructure, but also the exact stoichiometry of the MAX phase compounds when comparing properties of MAX phase samples (see Ref. [38] for a recent review).

In order to understand the microstructure/stoichiometry/transport properties relationships, the present paper reports on the synthesis, microstructural and electronic structure characterizations, with special emphasis on the transport properties of Ti_2AlN, Ti_2AlC and a series of $Ti_2AlC_xN_y$ solid solutions. The samples' microstructure was finely characterized combining X-ray diffraction (XRD), scanning electron microscopy (SEM) and wavelength dispersive X-ray spectroscopy (WDS) to accurately determine the samples' composition. The electronic structure and local order induced modifications were investigated using electron energy-loss spectroscopy (EELS) performed in a transmission electron microscopy (TEM) [39]. This technique allows the analysis of core electron excitations (similarly to X-ray absorption spectroscopy) with the spatial resolution inherent in TEM, thereby giving insights into the site-projected unoccupied density of states (DOS) of the excited element at the single grain level. That EELS and, in particular, electron energy-loss near edge structures (ELNES) is sensitive to disorder was demonstrated on various compounds: (i) in yttria stabilized zirconia, $(Y_2O_3)_x(ZrO_2)_{1-x}$, the blurring-out of the O–K edge fine structures was shown to be characteristic of the disorder on the oxygen sublattice [40]; (ii) in $CaTi_{1-x}Zr_xO_3$ solid solutions, the O–K edge fine structures were shown to be sensitive to the x content as well as the pre-edge structures in the Ti–K edge, which was shown to be a semi-quantitative probe for the short-range cation order [41]. The present study focuses mainly on the X element K-edge (i.e. excitation of a carbon or nitrogen 1s electron) of the solid solutions. The X element core loss spectra were recently shown to be a valuable probe for investigating the local disorder induced in Ti_3AlC_2 by light ion irradiation [42], and the carbon and nitrogen K edges have been used to investigate alloying effects in the TiC_xN_y system [43]. The transport properties were investigated using a four-point probe method for a temperature range going from 20 to 300 K. Both EELS and transport properties were analyzed using ab initio calculations performed in the density functional theory framework.

The paper is organized as follows. In Section 2, the experimental methods (synthesis and characterization) are described. Section 3 describes the theoretical methods that are used in order to interpret both the EELS spectra and the transport data. Finally, the results and discussion are presented, which evidence: (i) the possibility of finely controlling the solid solution stoichiometry; (ii) the relatively low disorder induced in the structure when making solid solutions on the X site; (iii) the important role of electron–phonon interactions in the transport properties variations observed for the solid solutions, leading to deviations from Matthiessen's rule in these compounds; and (iv) the major role of vacancies as scattering centres for the electrons.

2. Experimental methods

Powders of Ti (<45 μm, 99.5% purity), Al (<45 μm, 99.5% purity), AlN (<45 μm) and TiC (<45 μm, 99.5%