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Electron energy loss spectra near structural defects in TiN and TiC

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Abstract

In this study, we use first principles multiple scattering calculations on atomic clusters to show how the carbon and nitrogen K-edge fine structures are modified in the vicinity of structural defects in TiN and TiC. Changes in the electron energy loss spectra are due to changes in the atomic structure of the first atomic shells around the absorbing atom. Two different kinds of defects, which both modify the structure of these atomic shells, are investigated here. In a first part, we describe a method which correctly takes into account the statistical spatial distribution of nitrogen vacancies in a TiN cluster. We study the influence of vacancy concentration on the shape of the nitrogen K-edge spectra and we find that vacancies mainly affect the height of the second peak of the spectra. This peak decreases when the number of vacancies in the second nitrogen shell increases. In a second part, we study the carbon K-edge spectrum modification near stacking faults in TiC. Two different stacking faults are studied. These two-dimensional defects are responsible for changes in the position of the carbon as well as titanium atoms of the atomic shells centered on the absorbing carbon atom. The shape of the spectra is strongly modified near the stacking faults and several peaks are affected by these modifications. We show that these fine structure modifications only concern the very first carbon atomic layers near the two-dimensional defects.

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1. Introduction

Titanium carbide and nitride are hard refractory materials which are used and intensively studied for their interesting mechanical properties and wear characteristics (Toth, 1971; Holleck, 1986). The remarkable mechanical behaviour of these two compounds is mainly due to the strong covalent bonds between titanium and non-metallic atoms. Several first principles calculations have been done to understand the electronic structure of TiC and TiN and to calculate their bulk modulus and elastic constants (Neckel et al., 1975; Blaha and Schwarz, 1983; Blaha et al., 1985; Schwarz, 1987; Price and Cooper, 1989; Ahuja et al., 1996; Grossman et al., 1999; Mizuno et al., 1999). These studies give insights on the atomic scale processes which govern the macroscopic mechanical behaviour. Occupied electron states of stoichiometric titanium nitride have been studied experimentally by photoemission measurements (Höchst et al., 1982). These experiments are very useful because they give important information—averaged over rather large sample areas—on the states which effectively contribute to the strong chemical bonding. Electron energy loss spectroscopy (EELS) is another important technique for the investigation of the electronic structure. The fine structure of the carbon K-edge in TiC and of the nitrogen K-edge in TiN measured in a transmission electron microscope (TEM) can indeed be used to investigate the density of unoccupied states. These K-edge fine structures have been studied experimentally by EELS (Pflüger et al., 1982; Disko, 1986; Craven, 1995; Craven and Garvie, 1995; Paxton et al., 2000; Scott et al., 2001). They have also been measured by X-ray absorption spectroscopy (Soriano et al., 1993). The corresponding energy loss near edge structures (ELNES) have been calculated by first principles methods, and a very good agreement has been found between calculated and experimental EELS spectra (Paxton et al., 2000; Scott et al., 2001). The aim of the present paper is to show how the EELS spectra of TiN and TiC are changed when the crystal structure of these two compounds is modified. This problem is very important for TEM analysis because the atomic structure of real materials is never perfect, with nanometer size grains, grain boundaries,

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point or extended defects. With subnanometer typical probe sizes (Batson, 1993; Muller et al., 1999), EELS in a TEM is probably the most suitable technique to investigate the local changes in the electronic structure near these atomic structure defects. The results which are presented in this paper mainly show how EELS spectra are modified near nitrogen vacancies in substoichiometric TiN and near stacking faults in TiC.

Substoichiometric TiC_x and TiN_x can exist in the cubic rock salt structure with a wide range of vacancy concentration. Titanium carbide TiC_x, with $0.5<x<1.0$, has been studied by several authors who were interested in the experimental measurement (Dunand et al., 1985; Guemmaz et al., 1997a, 1999) or in the first principles calculation (Zhukov et al., 1988; Guemmaz et al., 1999; Hugosson et al., 2001; Dridi et al., 2002) of the vacancy concentration dependence of the lattice parameter. These authors have shown that the lattice parameter of TiC_x changes by less than 1% when x varies between 0.5 and 1. Relaxations in the vicinity of a carbon vacancy in TiC_x have been calculated by Hugosson et al. (2001). The authors of this publication have shown that the carbon atoms first neighbours of the vacancy move slightly towards the vacancy while the titanium atoms first neighbours of the vacancy tend to be pushed away from it. The small atomic displacement (less than 0.1 Å) of the titanium atoms is due to a reinforcement of the chemical bonding between these titanium atoms and their remaining first neighbour carbon atoms. These local modifications of the electronic structure will induce changes in the mechanical behaviour of TiC_x compounds. The mechanical properties of TiC_x and TiN_x have been investigated in several studies. The shear, Young, and bulk moduli of non-stoichiometric titanium carbide and nitride have been measured (Jiang et al., 1991; Guemmaz et al., 1999) and calculated (Zhukov et al., 1988; Grossman et al., 1999; Jhi et al., 2001; Dridi et al., 2002). The results of these studies show that the bulk modulus changes by about 25% when x varies between 0.5 and 1.0. The electronic structure of TiC_x and TiN_x has been studied experimentally by electron energy loss spectroscopy (Pflüger et al., 1982, 1984; Tsujimoto et al., 2005), by optical experiments (Koide et al., 1990; Schmid et al., 1998) and by photoemission (Höchst et al., 1982; Guemmaz et al., 1997a,b). It has been studied theoretically with the ab initio CPA method based on a disordered distribution of vacancies (Marksteiner et al., 1986) or with methods based on a supercell in which vacancies are periodically distributed (Redinger et al., 1985; Zhukov et al., 1988; Guemmaz et al., 1997a,b; Hugosson et al., 2001; Dridi et al., 2002). These theoretical studies have all the same conclusion: vacancies are responsible for additional peaks in the density of states, just below and just above the Fermi energy. These peaks are the signature of electronic states localised on the vacancy and built from titanium d orbitals. These localised states have been observed in photoemission experiments (Guemmaz et al., 1997b). First principles methods have been used to calculate the carbon K-edge in TiC_x (Scott et al., 2001) and the nitrogen K-edge in TiN_x (Tsujimoto et al., 2005). Vacancies are responsible for changes in the relative intensity of the different peaks in the near edge structures. Scott et al., have shown that these changes are due to the modification of the scattering events which give rise to the peaks in the carbon K-edge spectra. Tsujimoto et al., have shown that the peak modifications are only important when one (or several) of the second neighbour nitrogen atoms are missing near the absorbing nitrogen atom.

The electronic structure and the EELS spectra are also modified near an interface. EELS has for instance been used recently to study changes in the unoccupied electron states near a tunnel junction (Pailloux et al., 2002). Several recent works have investigated the atomic structures of interfaces in which TiC or TiN are involved. The interfaces TiC/TiB_2 (Chien et al., 1993), TiC/Ti_5Sr_3 (Kooi et al., 1999), TiC/Co (Christensen et al., 2002), TiN/GaN (Komninou et al., 2000) and TiN/AlN (Ma et al., 1999) have for instance been studied in details. Some of these interfaces, specially those between TiN and a semiconductor, are very interesting for industrial applications and would deserve to be studied by EELS. Stacking faults are the simplest titanium carbide interfaces which can be investigated in an EELS experiment. The same chemical species are indeed present on both sides of the interface, and changes in the electronic structure result only from local changes in the atomic structure. Harris et al., have studied several stacking faults in TiC and found that some of these two dimensional defects are energetically meta-stable and could be observed experimentally (Harris and Bristowe, 1997). These stacking faults can be considered as very simple model interfaces for which local changes in the electronic structure could be observed in an EELS experiment.

The present paper, which shows from calculations how the electronic structure of TiN and TiC is modified near structural defects, is organized as follows: in Section 2 we present the ab initio method which has been used for the calculations. In Section 3 we explain how we have efficiently distributed the nitrogen vacancies in the TiN cluster and we describe the modification of the spectra with the vacancy concentration. Results for the EELS spectra near two different stacking faults in TiC are presented in Section 4. We finally conclude in Section 5.

2. Computational method

The calculations have been performed with the real space multiple scattering code FEFF8 (Ankudinov et al., 1996, 1998; Rehr and Albers, 2000; Ankudinov and Rehr, 2000; Ankudinov et al., 2002) which is based on the density functional theory. The local density approximation Hedin–Lundqvist exchange correlation potential has been used in the self-consistent calculations. A cluster of atomic spheres describes the material. The cluster is centred on the absorbing nitrogen (or carbon) atom and surrounded by successive atomic shells of nitrogen (or carbon) and titanium atoms. These atomic shells have a spherical shape for the perfect TiN and TiC compounds. As shown by Scott et al., (2001) for the carbon K-edge fine structures in titanium carbide, the cluster size must be increased until convergence is reached. The clusters which have been used to calculate the nitrogen and carbon K-edge