Materials Chemistry and Physics 129 (2011) 862–870

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Mechanical properties of magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and goethite (α-FeO·OH) by instrumented indentation and molecular dynamics analysis

D. Chicot[a,b,*], J. Mendoza[a,b], A. Zaoui[a,c], G. Louis[a,d], V. Lepingle[a,d], F. Roudet[a,b], J. Lesage[a,b]

[a] Univ Lille Nord de France, F-59000 Lille, France
[b] USTL, LML, F-59650 Villeneuve d'Ascq, France
[c] LGCgE – Lille1, Polytech'Lille. F-59650 Villeneuve d'Ascq, France
[d] EMDouai, MPE-GCE, F-59500 Douai, France

ARTICLE INFO

Article history:
Received 7 September 2010
Received in revised form 18 February 2011
Accepted 11 May 2011

Keywords:
Pure and complex oxides
Bulk modulus
Hardness
Instrumented indentation
Molecular dynamic analysis

ABSTRACT

Hardness and elastic properties of pure (crystal) and complex (product of corrosion) iron oxides, magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and goethite (α-FeO·OH), were determined by means of molecular dynamics analysis (MDA) and instrumented indentation. To determine local mechanical properties by indentation, multicyclic loading is performed by using incremental mode. Moreover to study the influence of visco-elastoplastic behaviour of the material, various load-dwell-times were applied at each loading/unloading cycle. To support the indentation results, molecular dynamics analysis based on shell model potential is performed for pure oxides to determine Young's modulus, bulk modulus, Poisson's ratio and shear modulus. The comparison between experimental and theoretical values both with the literature data allows the evaluation of the mechanical properties of the pure oxides. Subsequently, this allows the validation of the mechanical properties of complex oxides which can only be deduced from indentation experiments.

1. Introduction

Finite Element Simulation (FES) of reinforced concrete behaviour requires the mechanical properties of the concrete and of the steel bars. However, the lifetime prediction by FES can differ from the lifetime in service depending on the environmental conditions. Indeed, various complex oxides can be formed at the surface of the steel bars leading to a significant change of the global mechanical behaviour. Then, the introduction of the mechanical properties of these oxides in the FES is required for improving the lifetime prediction. Generally, the mechanical properties of the pure (*crystal*) oxides are taken into account but their values can be quite different than those of the complex oxides produced at the surface of corroded steel. As a result, the aim of this work is to determine the mechanical properties of the most usual iron oxides, under pure and complex forms, by instrumented microindentation supported by molecular dynamic analysis (MDA).

The most conventional instrumented indentation test produces a load-depth curve for a monotonic loading which is used to determine the mechanical properties by studying indentation curves resulting from different levels of loading. By analysing the unloading part of a load-depth curve, Oliver and Pharr [1] provide a methodology to calculate the elastic modulus and the hardness from the indentation contact depth taking into account the sinking-in underneath the indent. Moreover, since the corroded steel surface contains various types of oxide distributed in thin layers, local indentation analysis is required to infer the mechanical properties of individual phases. Then with the objective to obtain reliable indentation data, multicyclic indentation tests were locally performed. A multicyclic indentation curve is produced if the specimen is loaded up to a specific value, unloaded and immediately reloaded. After the reloading, the cycle can reach the same ultimate load-depth values [2,3] or higher values [4,5] than the previous loading cycle. However for these indentation conditions, numerous authors have mentioned anomalous behaviours such as pop-ins, hysteresis loops formation, disparity between two consecutive cycles and depth increasing during the unloading [6]. Additionally, visco-elastoplastic properties of the material may influence the mechanical properties determination by indentation [7]. Indeed, a difference was observed between monocyclic and multicyclic indentation, this difference being mainly related to cumulative plasticity [8]. In any case, such multicyclic indentations were successfully used to study mechanical behaviour of materials if some precautions are taken into account [5,8,9–12]. Thus for determining the elastic properties of the oxides, we applied Oliver and Pharr's methodology by testing various load-dwell-times to study the influence of the visco-elastoplastic behaviour of the different tested oxides. Afterwards the indentation results are compared to

* Corresponding author at: Univ Lille Nord de France, F-59000 Lille, France.
E-mail address: didier.chicot@univ-lille1.fr (D. Chicot).

0254-0584/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2011.05.056

Table 1
Crystallographic parameters of pure oxides: hematite, magnetite and goethite.

Oxide	Structure	Lattice parameters (nm)	Lattice angles
Hematite α-Fe_2O_3	Hexagonal (trigonal)	$a = b = 0.503$ $c = 1.374$	$\alpha = \beta = 90°$ $\gamma = 120°$
Magnetite Fe_3O_4	Cubic	$a = b = c = 0.839$	$\alpha = \beta = \gamma = 90°$
Goethite α-FeO·OH	Orthorhombic	$a = 0.461$, $b = 0.996$ $c = 0.302$	$\alpha = \beta = \gamma = 90°$

the values obtained by MDA applied to the pure oxides to calculate Young's modulus and bulk modulus, Poisson's ratio and the shear modulus since the MDA was previously and successfully used to simulate nanoindentation process of other class of materials [13]. Finally, to study the hardness-load dependence, we calculated the hardness length-scale factor [14] deduced from the strain gradient plasticity (SGP) theory [15].

2. Materials and experimental study

2.1. Materials

From a general point of view, metals form several varieties of oxides. For example, iron forms a wide range of oxides, such as: magnetite, hematite, wüstite, goethite and maghemite, depending on the environmental conditions. In this work, we limited the mechanical study to three of the most common oxides: hematite (α-Fe_2O_3), magnetite (Fe_3O_4) and goethite (α-FeO·OH) which can be found under different forms:

- in a pure form as natural oxides located in particular places (indicated as "*pure oxides*" in the following),
- in multiphase layers as corrosion products on surface of naturally oxidized steels (called "*complex oxides*").

(a) Pure oxides

The so-called pure oxides are the result of a long time natural growth and then polycrystalline without any preferential orientation with crystal size up to 500 μm. The crystallographic characteristics of the pure oxides were determined by X-ray powder diffraction (XRD), using a Brucker D8 diffractometer (θ–2θ) with Co-Kα radiation (λ ~0.179 nm). The crystallographic parameters of these oxides are collected in Table 1. Note that the electronic microstructures defined by the lattice parameters and the crystallographic network given in Table 1 were thereafter considered for molecular dynamic analysis.

(b) Complex oxides

The complex oxides result from a natural steel oxidation. Indeed the sample is drawn from an oxidized steel bar found in a bunker located on the Atlantic Wall. The oxide film is multilayered and mainly composed of successive monolayers of magnetite, goethite and hematite as shown in Fig. 1. For differentiating the complex oxides enclosed into the steel corrosion products as indicated in Fig. 1, the oxide film was analyzed by means of Raman spectroscopy. The Raman spectrum is recorded using a LABRAM Dilor Micro-Raman spectrograph. The excitation source is obtained by a laser providing an emission wavelength at 632.8 nm. An Olympus microscope supplements this analysis. Raman spectra of complex oxides are shown in Fig. 2 where the spectra of pure oxides are also given as a reference. Raman peaks identified in the range of 100–1250 cm^{-1} are collected in Table 2 for complex and pure oxides together with the peak values related to hematite, magnetite and goethite mentioned by de Faria and Lopes [16]. It is noticeable that the values of the Raman peaks observed on the complex and on the pure oxides are very similar and well-supported by the literature data.

(c) Elastic properties of the oxides

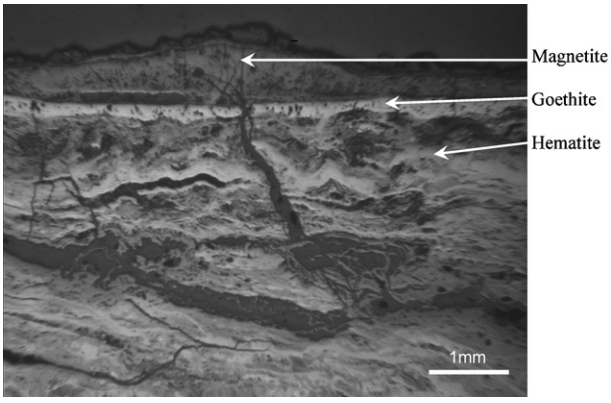

Fig. 1. Morphology of the complex oxides observed in a cross-section of the oxidized steel bar drawn from a bunker of Atlantic's Wall.

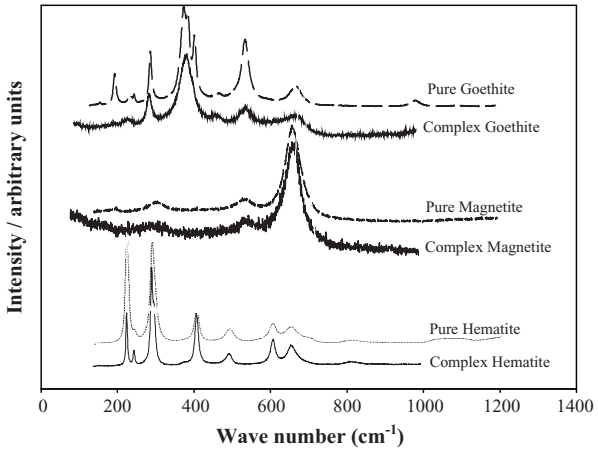

Fig. 2. Raman spectra of the pure and complex oxides.

c1 – Magnetite

Numerous works were devoted to the determination of Poisson's ratio and the elastic modulus of the magnetite. As an example, Poisson's ratio is equal to 0.262 for Gercek [17], this value being calculated using the values of adiabatic bulk

Table 2
Band locations in the Raman spectra obtained for the different pure and complex oxides.

Oxides	Raman band positions (cm^{-1})					
Complex form						
Hematite	227	293	409	498	611	658
Magnetite	300	545	670			
Goethite	245	300	397	480	555	685
Pure form						
Hematite	226	292	409	499	612	660
Magnetite	307	550	670			
Goethite	248	300	388	551	688	
de Faria and Lopes [16]						
Hematite	227	246	293	412	498	610
Magnetite	302	514	534	663		
Goethite	243	299	385	479	550	685