Applied Surface Science 379 (2016) 242–248

Contents lists available at ScienceDirect

Applied Surface Science

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

XPS and EELS characterization of Mn_2SiO_4, $MnSiO_3$ and $MnAl_2O_4$

A.P. Grosvenor[a], E.M. Bellhouse[b], A. Korinek[c], M. Bugnet[c], J.R. McDermid[d,*]

[a] Department of Chemistry, University of Saskatchewan, Saskatoon, SK S7N 5C9, Canada
[b] Global R & D—Hamilton, ArcelorMittal Dofasco, 1330 Burlington St. E, Hamilton, ON L8N 3J5, Canada
[c] Canadian Centre for Electron Microscopy, Brockhouse Institute for Materials Research, McMaster University, 1280 Main St. W., Hamilton, ON L8S 4M1, Canada
[d] Steel Research Centre, McMaster University, 1280 Main St. W., Hamilton, ON L8S 4M1, Canada

ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form 15 March 2016
Accepted 31 March 2016
Available online 12 April 2016

Keywords:
X-ray photoelectron spectroscopy
Electron energy loss spectroscopy
Selective oxidation
Manganese silicates
Manganese aluminates

ABSTRACT

X-ray Photoelectron Spectroscopy (XPS) and Electron Energy Loss Spectroscopy (EELS) are strong candidate techniques for characterizing steel surfaces and substrate-coating interfaces when investigating the selective oxidation and reactive wetting of advanced high strength steels (AHSS) during the continuous galvanizing process. However, unambiguous identification of ternary oxides such as Mn_2SiO_4, $MnSiO_3$, and $MnAl_2O_4$ by XPS or EELS, which can play a significant role in substrate reactive wetting, is difficult due to the lack of fully characterized standards in the literature. To resolve this issue, samples of Mn_2SiO_4, $MnSiO_3$ and $MnAl_2O_4$ were synthesized and characterized by XPS and EELS. The unique features of the XPS and EELS spectra for the Mn_2SiO_4, $MnSiO_3$ and $MnAl_2O_4$ standards were successfully derived, thereby allowing investigators to fully differentiate and identify these oxides at the surface and subsurface of Mn, Si and Al alloyed AHSS using these techniques.

1. Introduction

In order to meet Corporate Average Fuel Economy (CAFE) requirements, automobile manufacturers are increasing their use of advanced high strength steels (AHSS) such as dual phase steels (DP) and transformation induced plasticity (TRIP) steels and are demanding third generation AHSS (3G AHSS) steels such as quench and partition (Q&P) and so-called medium manganese 3G AHSS. These steels employ significant alloying levels of manganese and tend to have significant alloying levels of silicon and\or aluminum [1–6]. These alloying elements form selective oxides on the steel surface during annealing prior to continuous galvanizing, which can result in poor reactive wetting during galvanizing and bare spot defects in the zinc coating. Many studies have focused on identifying these selective oxides and relating them to the reactive wetting behaviour in the metallic coating bath [1–3,7–17]. However, accurate identification of these compounds has been challenging due to a lack of high resolution X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) data on the ternary oxides $MnSiO_3$, Mn_2SiO_4 and $MnAl_2O_4$. Both XPS and EELS are well suited to perform these types of analyses as XPS is suitable for chemical analysis of the steel surface after selective oxidation and prior to metallic coating and EELS is suitable for studying the steel-coating interface at the fine length scales available to the transmission electron microscope, where fine oxides can remain after metallic coating or can be found within the bulk steel itself due to selective internal oxidation [1–3,8,9,12,13,15–17]. Furthermore, the use of these surface (XPS) and near-surface sensitive (EELS) techniques is necessary to identify these oxides since neither technique requires that the oxides be highly ordered to study them, as is required when using X-ray diffraction for quantitative phase analysis.

The XPS binding energies for elemental Mn, Si and Al and the binary oxides MnO, SiO_2 and Al_2O_3 are readily available in the literature [18–22]. However, limited XPS binding energy data are available for the ternary oxides Mn_2SiO_4 and $MnAl_2O_4$, as summarized in Table 1. No XPS binding energy data could be found for $MnSiO_3$ when present as a pure species. Limited binding energy data are also available for Mn_2SiO_4 and $MnSiO_3$ when present with other species [23–26]. Thus, the purpose of the present contribution is to provide these spectra using high purity $MnSiO_3$, Mn_2SiO_4 and $MnAl_2O_4$ standards prepared by the ceramic method.

---

* Corresponding author.
E-mail addresses: andrew.grosvenor@usask.ca (A.P. Grosvenor), erika.bellhouse@arcelormittal.com (E.M. Bellhouse), korinek@mcmaster.ca (A. Korinek), bugnetm@mcmaster.ca (M. Bugnet), mcdermid@mcmaster.ca (J.R. McDermid).

http://dx.doi.org/10.1016/j.apsusc.2016.03.235
0169-4332/

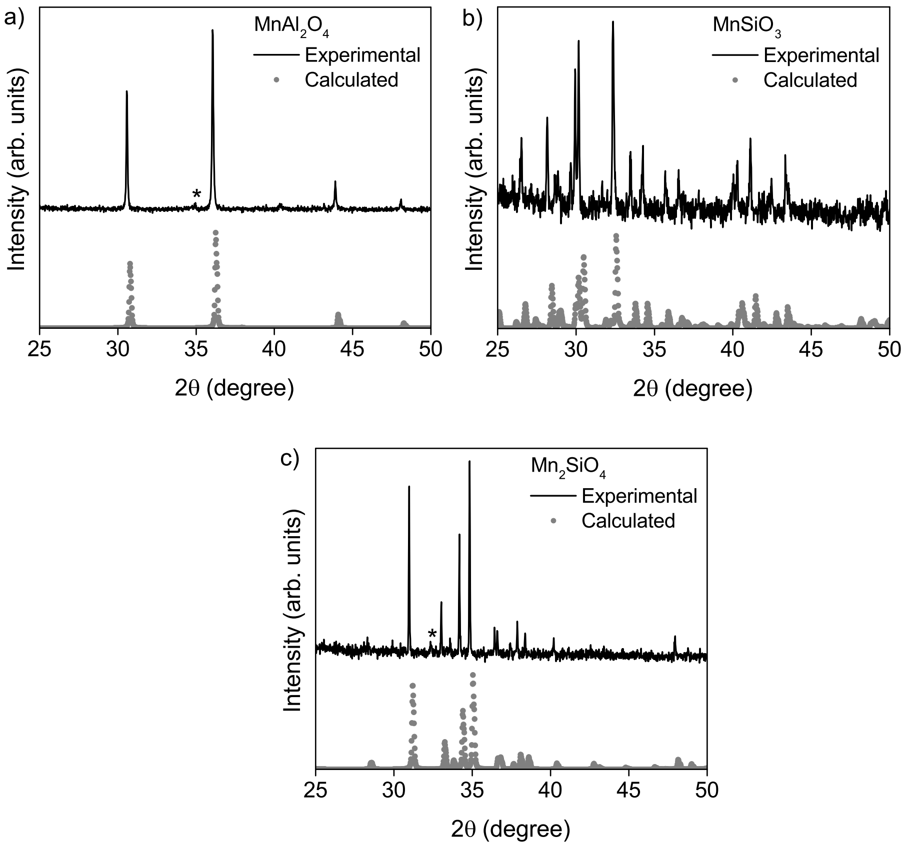

Fig. 1. Powder X-ray diffraction patterns from (a) $MnAl_2O_4$, (b) $MnSiO_3$, and (c) Mn_2SiO_4 collected using a Cu $K_{\alpha 1}$ X-ray source. The collected diffraction patterns are compared to the calculated diffraction patterns determined using the known structures of the materials [29]. Major peaks from impurity phases are marked with an asterisk in the diffraction patterns.

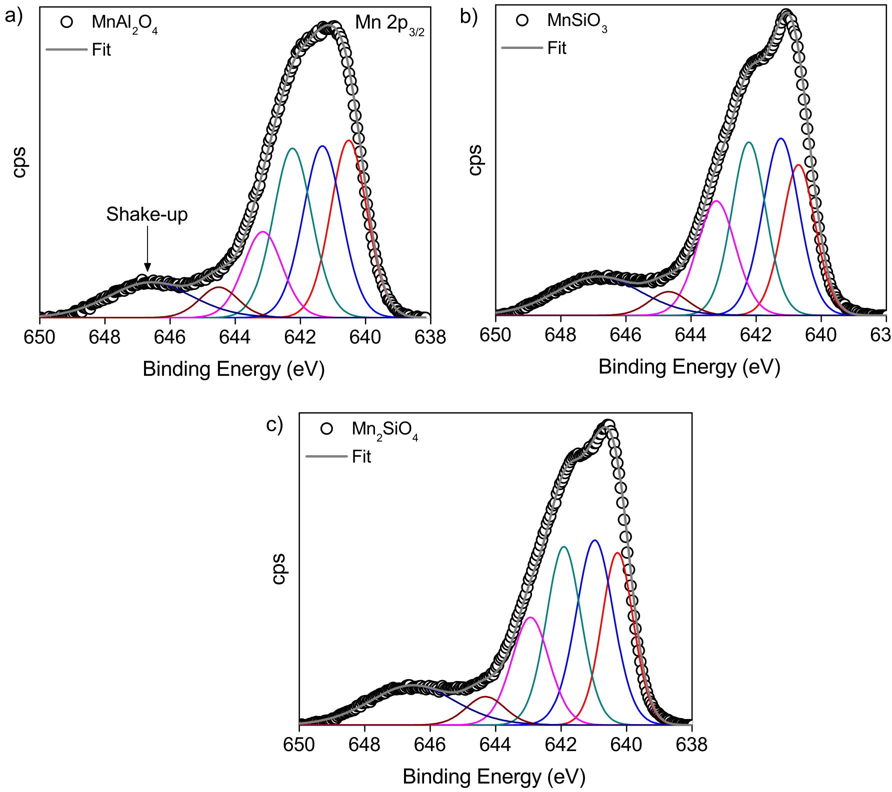

Fig. 2. Background subtracted Mn $2p_{3/2}$ high resolution XPS spectra from (a) $MnAl_2O_4$, (b) $MnSiO_3$ and (c) Mn_2SiO_4. The background was removed using a Shirley-type background and the spectra were fitted using multiplet peaks and a shake-up satellite peak using the method described in [21]. The resulting fit is indicated by a grey line.