Characterization of surface oxides on water-atomized steel powder by XPS/AES depth profiling and nano-scale lateral surface analysis

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ABSTRACT

Characterization of oxide products on the surface of water-atomized steel powder is essential in order to determine the reducing conditions required for their removal during the sintering stage which in turn will result in improved mechanical properties. Pre-alloyed powder with 3 wt% Cr and 0.5 wt% Mo was chosen as the model material. Investigation of the powder surface characteristics with regard to composition, morphology, size and distribution of surface oxides was performed using X-ray photoelectron spectroscopy, Auger electron spectroscopy and high resolution scanning electron microscopy combined with X-ray microanalysis. The analysis revealed that the powder is covered by a homogeneous (∼6 nm thick) Fe-oxide layer to ∼94% whereas the rest is covered by fine particulate features with the size below 500 nm. These particulates were further analyzed and were divided into three main categories (i) Cr-based oxides with simultaneous presence of nitrogen, (ii) Si-based oxides of "hemispherical" shape and (iii) agglomerates of the afore mentioned oxides.

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1. Introduction

One of today's challenges for the powder metallurgy (PM) industry is to improve the mechanical properties of the produced parts used in structural applications such as automotive systems, which comprises the largest market for PM structural parts manufactured by means of the press and sinter route. For this reason, significant efforts have been aimed at tailoring the obtained microstructure by carefully incorporating various alloying elements such as Ni, Cu, Cr, Mo, Mn, V, Si, etc., see e.g. Refs. [1–3]. At present, the main alloying elements used for sintered steel besides C are Cu, Ni and Mo [1,4]. On benefit with these elements is the fact that they do not form stable oxides, which means that they do not impose any problem when sintering. However, the large increase as well as the fluctuation in the price for Ni and Mo over the past years along with certain health concerns with Ni and recyclability issues associated with Cu, have led to an increased interest in using cheaper alloying elements such as Cr and Mn as replacement of the afore mentioned elements [5–10].

Chromium and manganese have been extensively used in the steel industry since it increases hardenability in the steel, it is relatively inexpensive and is easily recyclable [11]. However, elements such as Cr and Mn have high affinity to oxygen and will tend to form thermodynamically stable oxides, which in turn could affect the mechanical properties of the final component, if proper attention to the sintering conditions is not given [12–15]. This issue can be dealt with, up to a certain extent, since these elements can be introduced to the powder in the pre-alloyed state during the atomization process which in turn will lower their activity down to their content in solid solution [16]. In pre-alloying, Cr cannot be added in too large amounts as this will lower the compressibility of the powder [17]. Therefore, Cr-levels up to some wt%, necessary to ensure required hardenability, are common [5].

Previous studies [18–22] showed that during the fabrication of the powder, especially by means of the water atomization method, the metal particles produced are oxidised on the surface due to the interaction between the molten metal and the water or steam. Therefore after atomization the powder will undergo subsequent annealing in a suitable atmosphere in order to reduce the surface oxide. Nevertheless, due to the large specific surface area of water atomized steel powder with increased reactivity in comparison with bulk material, the powder is prone to re-oxidation at lower temperatures during handling. Consequently in the end, even after annealing, the powder will be mainly covered by a thin iron oxide layer along with some minor coverage of particulate features rich in strong oxide forming elements such as Cr, Mn and Si, evenly distributed on the surface and the interior of the powder [18,20]. It

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Table 1
Nominal composition of the powder under investigation.

Element (wt%)	Cr	Mo	Mn	O	Fe
Fe–3Cr–0.5Mo powder	3	0.5	0.1	0.14	Bal.

is therefore clear that good understanding concerning the chemical composition of the powder surface is of paramount importance for controlling the final chemical and mechanical properties of the material after consolidation.

Analysis of the powder surface can be performed using a wide variety of surface analytical experimental techniques like X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) as well as secondary ion mass spectroscopy (SIMS) [23]. Even analytical transmission electron microscopy (ATEM) has been employed in some rare cases, following dedicated sample preparation procedures [24]. Still it would be envisaged that the direct characterisation of powder is a preferred way. Also, it is important to be able to depict chemical state globally as well as locally and connect this to the surface morphology observation. In this respect XPS gives information concerning the chemical state of the analyzed elements but offers poor spatial resolution whereas AES offers much higher spatial resolution and dedicated analysis but the identification of the element chemical state is not straightforward. Therefore the aim of this work was to investigate a commercially available material system and to complement previous studies [18,20] by using surface sensitive analytical techniques such as XPS, AES, SEM in combination with EDX at their outermost performance to evaluate the composition, morphology, size and distribution of the surface products. Hence, for the first time it was made possible to take advantage of the high-resolution capabilities of scanning Auger nanoprobe analysis to conduct dedicated analyses on the observed particulate features on the powder surface. Finally, based on the surface analyses, determination of surface oxide coverage and thickness by means of model calculations were performed.

2. Material and experimental procedure

The material used in this investigation was commercially available water atomized Cr–Mo pre-alloyed steel powder, provided by Höganäs AB, Sweden. The production of the final product involves an annealing treatment of the atomized powder in continuous furnaces and using suitable atmosphere in order to reduce the surface oxide formed during the atomization process. The nominal composition of the powder is shown in Table 1.

In order to prepare samples for surface analysis, the powder was mounted onto soft aluminium plates by light pressing (approx. ~1 bar). X-ray photoelectron spectroscopy (XPS) was performed using a PHI5500 instrument in order to obtain overall surface chemical analysis and also identify the chemical states of the elements present. The sample was irradiated with monochromatized Al K_α X-rays and the analyzed area was approximately 0.8 mm in diameter which corresponds to a large number of analyzed metal particles (>100) which in turn gives statistically reliable results representative of the general powder surface composition. For the surface chemical analysis the recorded characteristic signals of the elements were curve fitted into the relevant peaks of the different chemical states present. The peak areas (which will be referred as "intensity" in the rest of the text) of the curve fitted peaks were then converted into apparent surface composition values using standard relative sensitivity factors. These sensitivity factors are derived from calibration measurements on pure elemental standards and pure compounds. The positions of the peaks for the

different chemical states of the elements encountered were determined from the database provided by the instrument manufacturer [25,26]. A surface layer of thickness α and unit area will emit a signal with intensity given by the general formula:

$$I = YD\lambda \cos\theta \left[1 - \exp\left(-\frac{\alpha}{\lambda \cos\theta} \right) \right] \qquad (1)$$

where Y is the relative photoelectron yield, d is the atomic density, λ is the attenuation length and θ is the angle between the normal to the surface and the spectrometer axis. For the specific experimental configuration $\theta = 45°$. If $\alpha > 3\lambda$ then the surface layer can be considered as infinitely thick and consequently Eq. (1) can be simplified to:

$$I = YD\lambda \cos\theta \qquad (2)$$

The ratios of the products Y and λ for different elements in given chemical states basically corresponds to their relative sensitivity factors. The analyzed area was treated as a flat sample which is shown to be a valid approximation for the XPS analysis of metal powder [19,20,22,27,28]. The determination of the surface oxide layer thickness and the compositional depth profiles was done by means of successive ion etchings and subsequent XPS analyses. Here, the influence of powder geometrical characteristics was considered using a model approach derived and validated previously [22,27]. Its application is further addressed in the Results section. The gas used for the ion etching was Ar and the applied accelerating voltage was 4 kV. The Ar ion beam was rastered on a projected area of 4×5 mm to 3×4 mm which then gave an etch rate of 3–4 nm min^{-1} as calibrated on flat oxidized tantalum sample (Ta$_2$O$_5$) with known oxide thickness of 100 nm. The obtained results for the powder are the average of five separate series of experiments.

Information concerning the size, distribution and morphology of the surface compounds were acquired using high resolution scanning electron microscopy (HR-FEG-SEM LEO Gemini 1550). Additional microanalysis was carried out using energy dispersive X-ray spectroscopy with an INCA system attached to the SEM. However the results obtained from the EDX analysis give possibility only to qualitative interpretation due to the large analysis area (μm) of the method and the surface roughness of the powder.

A first effort to obtain detailed information for powder surface features in the nanometer range using Auger electron spectroscopy (AES) was carried out. The high spatial resolution (~20 nm) in comparison with the other experimental techniques and the fact that it provides information only from the outermost atomic layers of the material gives the possibility to investigate accurately individual particulate features on the powder surface for the first time. The instrument used was a Thermo Microlab 350 operated with an electron beam at 10 kV and about 1 nA. Sensitivity factors from the software Thermo Avantage© v. 4.43, provided by Thermos Fisher Scientific, were used for quantification. The results show that the sensitivity factor for O in oxides was not correct for the present analyses. It is known that the sensitivity varies with the oxide composition [29]. In this study the composition changes varied both between and through the profiles. Since anyhow no sensitivity factor would be valid for all profiles the one provided has been used and the focus in the interpretation is on the distribution of cations in the oxides rather than on detailed quantification. For the depth profiling the Ar ion gun used here had an accelerating voltage of 1 kV, rastered 3×3 mm giving an etch rate of 1.8 nm min^{-1} as calibrated on 100 nm Ta$_2$O$_5$.

The shape of both metal powders and particulate features was considered in the depth profiling. The lateral resolution allows for analysis points to be considered as flat even on irregular but smooth particulates with sizes in the range 200–600 nm. The analysis points were then chosen so that they had a local angle of ion incidence