

## SURFACE ANALYSIS OF WATER ATOMISED HIGH CHROMIUM ALLOYED STEEL POWDER BY X-RAY PHOTOELECTRON SPECTROSCOPY

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### **Abstract**

*The determination of the surface oxide layer composition is necessary to facilitate the adjustment of the sintering conditions for sufficient removal of the surface oxides for providing strong metal bonding between the metal particles during sintering. Investigation of composition and thickness of the surface oxide was carried out on high Cr-alloyed water atomized steel powder. Analysis of the powder surfaces by X-ray photoelectron spectroscopy showed that powder particles in all cases are covered by a heterogeneous oxide layer, composed of particulate features of thermodynamically stable oxides (Si–Cr–Mn) and homogeneous iron surface oxide layer in between. The thickness of the iron oxide layer is about 4 nm.*

**Keywords:** *high chromium alloyed steel, water atomized powder, surface oxides, X-ray photoelectron spectroscopy.*

### **INTRODUCTION**

Further expansion of the market for powder metallurgy (PM) structural parts requires high mechanical properties that can meet demands of modern industry, in particular automotive applications. To fulfill such requirements improved performance of PM parts is reached by adding expensive alloying elements such as Ni and Mo. However, a strong tendency to price increase during the last decade has led to decreased competitiveness of Ni–Mo alloyed PM parts compared to products of conventional metallurgy. Therefore, cheaper alloying elements like Cr and Mn, commonly used in cast and wrought steels, are of great interest [1]. Elements with high affinity to oxygen like Cr, Mn, Si etc., are selectively oxidized on the powder surface during atomization and further annealing. Hence, composition of the surface oxide is determined by both, alloy composition and processing conditions during powder production and further handling [2–6]. Despite the fact that chromium alloyed PM steels are currently successfully produced by water atomization [7], study of the surface oxide layer is necessary for determining optimal sintering conditions.

In the present contribution, the surface of high Cr-alloyed steel powder was investigated using X-ray photoelectron spectroscopy by which composition and distribution of different oxide phases were obtained.

## EXPERIMENTAL MATERIAL AND METHODS

The material used in XPS investigation was high Cr-alloyed water-atomized steel powder. The powder contains 20 wt.% of chromium and the total amount of other alloying elements (Ni, Mn, Si, C, N, S) is 16.9 wt.%. Powder was obtained by water atomization and subsequent annealing in reducing atmosphere.

Surface chemical analysis of the powder surface was performed at Chalmers University of Technology by means of X-ray photoelectron spectroscopy using a PHI 5500 instrument. X-ray photoelectron spectroscopy was used in order to identify elements, present on the powder surface, together with their chemical state. The analyzed area during XPS analysis was about 0.8 mm in diameter and thus a large number of particles (more than 1000 particles) was analyzed at the same time giving a statistically reliable average result that represents the general powder surface composition. Photoelectrons were excited by monochromatic Al K $\alpha$  source. Recorded signals were de-convoluted into the elemental peaks, the intensity of which is proportional to the concentration of elements. Composition of the surface compounds was estimated by curve fittings of the characteristic peaks, and their intensities were corrected using standard relative sensitivity factors. Quantification of the results was performed by calibration measurements on pure elemental standards.

Determination of the surface oxide layer thickness and compositional profiles was done by altering of ion etching and XPS analysis. The ion etching was performed by Ar<sup>+</sup> gas with an accelerating voltage of 4 kV to the depths of 1, 3, 5, 7.5, 10 and 20 nm. The Ar<sup>+</sup> beam was rastered on the area from 4x5 mm to 2x3 mm giving an etching rate from 3 to 5 nm min<sup>-1</sup>. The etch rate was calibrated on a flat oxidized tantalum foil with the well-known Ta<sub>2</sub>O<sub>5</sub> thickness (100 nm), thus the oxide thickness refer to Ta<sub>2</sub>O<sub>5</sub> units, that is of the same magnitude as in the case of Fe-oxide.

## RESULTS AND DISCUSSION

Survey spectrum recorded from the powder in as-received state shows intensive peaks of O and C and less intensive peaks of Cr, Mn and Si as well as traces of Fe and S, see Fig.1.

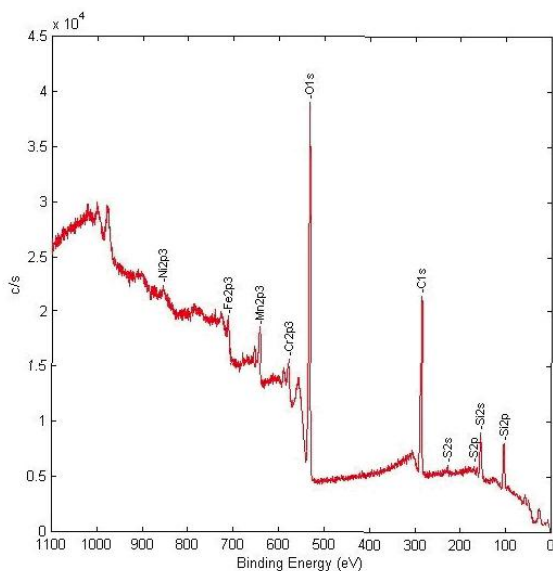


Fig.1 XPS survey spectrum powder in as-received state.

Figure 2 shows detailed XPS spectra of Fe, Cr, Mn, Si and S on the surface of powder in as-received state and after ion etching to 1, 3, 5, 7.5, 10 and 20 nm.

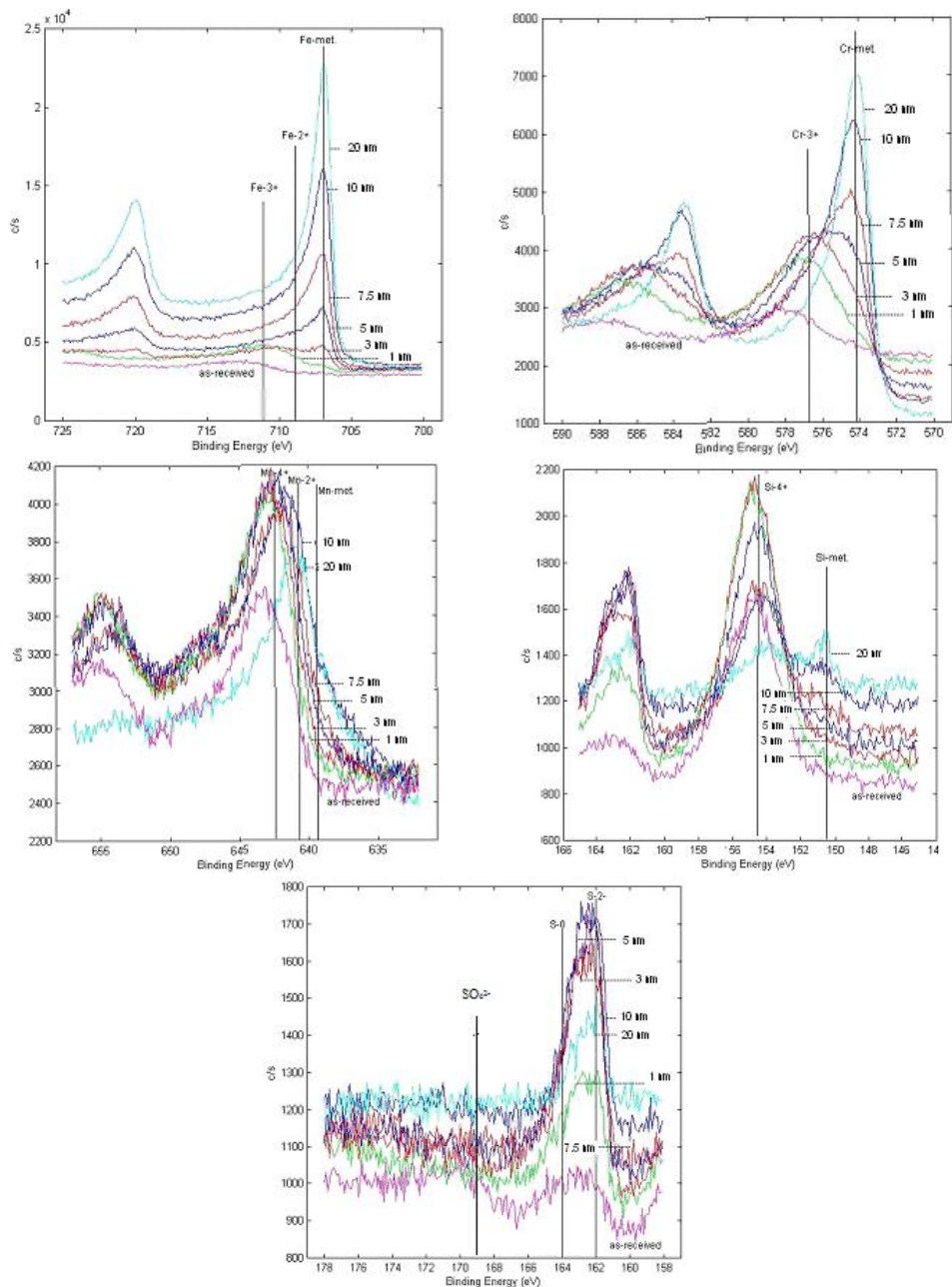


Fig.2 Detailed XPS spectra of Fe, Cr, Mn, Si and S on the surface of the powder in as-received state and after ion etching to 1, 3, 5, 7.5, 10 and 20 nm.

Iron and manganese on the as-received surface of particles are in the form of oxides. An intense iron metallic peak was already observed after an ion etching to 3 nm. And after 5 nm etching the metallic peak become dominant – 70-80%.  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  are very sensitive to the ion etching. This means that after the first steps of etching the photoelectron peaks become shifted to lower binding energies (lower oxidation states) due to the partial reduction of oxides from higher oxidation states to lower oxidation states by an ion beam (etching effect). Silicon on the surface is dominantly in oxide state. Traces of metallic Si (from matrix) appears after 10 nm etch depth. Hence, due to a large affinity to oxygen, Si and Mn create thick oxide islands on the surface of the powder. Chromium is in an oxide state until 7.5 nm etch depth after which the metallic peak of chromium is observed and fraction of the metallic chromium considerably increases with the etching depth.

The peak position of the sulphur on the as-received surface indicates its presence in  $\text{SO}_4^{2-}$  group (~169 eV). Removal of the surface contaminations leads to a shifting in the sulphur peak position to lower binding energy (~162 eV), which indicates the presence of some coarse sulphides.

On the basis of the measured data, the oxide cation concentrations at different etch depths were calculated, see Table 1, by extracting oxide peak areas from superimposed oxide/metal peaks. Figure 3 shows oxide cation concentration in dependence on the etch depth for the powder. Figure 4 represents the relative concentration of metallic iron that allows evaluation of the thickness of the homogeneous iron oxide layer [1].

Tab.1. Concentration of oxide cations vs. etch depth for powder

Etch depth, nm	Fe [at.%]	Cr [at.%]	Mn [at.%]	Si [at.%]
0	8.7	14.8	9.8	66.7
1	11.6	19.2	10.6	58.6
3	7.9	21.8	13.8	56.5
5	2.4	24.3	19.4	53.9
7.5	0.00	23.1	26.6	50.3
10	0.00	20.7	30.9	48.4
20	0.00	19.9	48.8	31.3

Iron oxide was removed after etching to 7.5 nm. At this etch depth only the metallic peak was observed. In as-received state the particle surface is covered mostly by Si, Cr and Mn oxides. During etching the fraction of Si oxides decreases, but their complete removal wasn't obtained even after etching until 20 nm. On the other hand, at 10 nm a strong metallic signal of silicon from matrix was received. The presence of Si, Mn and Cr oxides after removal of the iron oxides indicates that they form 'oxide islands' on the powder surface. However, it has to be emphasized that the increasing tendency of Mn cation concentration is connected with presence of sulphides and thus the estimated amount of Mn oxide cations is overestimated.

Analyzing distribution of oxide cations with the etch depth, it can be concluded [1-4] that the surface of the powder is covered by heterogeneous oxide layer, formed by a thin iron oxide layer with the presence of thick oxide islands, formed by more thermodynamically stable oxides of Cr, Mn and Si. The thickness of the oxide layer can be calculated from the relative intensity of the metallic peak of iron [1, 2] and in the case of the powder studied, is about 4 nm, see Fig.4.

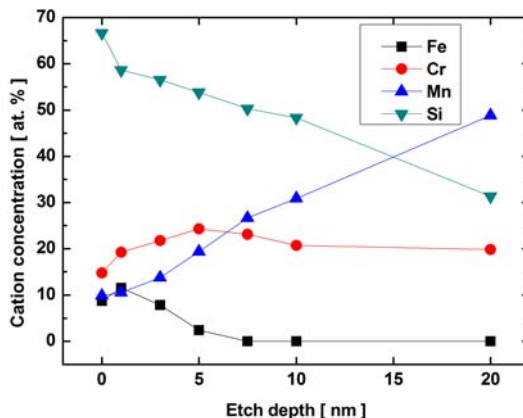


Fig.3 Oxide cation concentration vs. etch depth for analyzed powder.

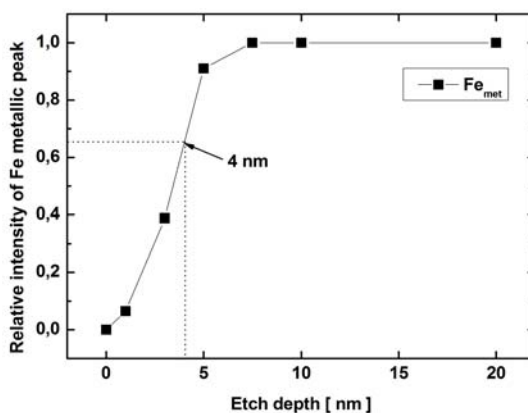


Fig.4 The normalized intensity of Fe-metallic peak (Fe 2p) vs. etch depth, indicating surface iron oxide thickness of ~4 nm.

## CONCLUSIONS

The surface of the investigated powder particles is covered by heterogeneous oxide, formed by a homogeneous iron oxide layer with a thickness of ~4 nm and 'oxide islands' which are formed by thermodynamically stable Cr-Mn-Si mixed oxides where the fraction of the Si is dominant (~70%). Thickness of the oxide islands formed by thermodynamically stable Cr-Mn-Si oxides is rather large as they were not fully removed even after 20 nm ion etching.

## Acknowledgements

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