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High Purity Chromium Metal Oxygen Distribution (Determined by XPS and EPMA)

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Abstract. The surface composition of ultra high purity chromium metal and chromium metal produced with conventional Cr^{+3} electrolyte was investigated via XPS. The distribution and formation of oxide in the matrix of chromium metal was also investigated via SEM. The results are discussed in terms of major elemental surface peaks for virgin material and after argon ion etching. It is demonstrated that the oxygen in ultra high purity chromium metal predominantly exists as a surface phenomenon in the form of Cr_2O_3 and the thickness of the oxide layer is a function of the production method.

1. INTRODUCTION

JMC (USA), Inc. produces ultra high purity chromium metal via electrolysis in their Research Triangle Park, North Carolina, USA facility. Product purity, based on metallic elements, ranges from 99.995% to 99.999% chromium providing the highest purity commercial production in the world. The oxygen content of this product ranges from 100 ppm to 300 ppm. Although oxygen is the primary elemental impurity, we have little information about its distribution and structure. The purpose of this study was to investigate the structure and distribution of oxygen in high purity chromium metal products.

The surface composition of JMC's ultra high purity chromium metal and chromium metal produced with conventional Cr^{+3} electrolyte were investigated via XPS (X-ray Photo-electron Spectroscopy) to determine the surface structure. The distribution and formation of oxide in the matrices of these chromium metal products were investigated via SEM (Secondary Electron Microscope). The shape and size of chromium oxide particles were determined by SEM after extracting the chromium metal matrix leaving the chromium oxide particles.

2. ANALYSIS AND OBSERVATION PROCEDURE

2.1 Analysis for Trace Impurities

The metallic impurities were determined by GDMS (Glow Discharge Mass Spectroscopy) and ICP (Inductively Coupled Plasma Atomic Emission Spectroscopy). Oxygen, nitrogen, carbon and sulfur were analyzed by the Leco method (infrared absorption spectroscopy).

2.2 XPS Analysis

High purity chromium metal is harvested from the electrolysis tank in the form of irregular flakes 2 to 3 mm thick. The flake surface was investigated by XPS utilizing a Mg $\text{K}\alpha$ X-ray source. Virgin flake

surfaces were prepared by rinsing with deionized water. The surface of the specimen was argon ion etched (2 kV, 30 mA, 4×10^{-4} Pa) for collecting depth profile data. The specimens of other grades of chromium metal were prepared in the same manner.

2.3 SEM Observation

The chromium oxide particle specimens were prepared for SEM observation by dissolving the chromium metal matrix with hydrochloric acid and extracting the oxide particles by filtering.

The chromium metal flakes were heat treated at 1250 °C for 6 hours in a conventional vacuum furnace to investigate the influence of heat treatment on oxygen distribution and the shape of the oxide particles.

3. RESULT AND DISCUSSION

3.1 Chemical Analysis of the Chromium Metal Samples

The chemical analysis for the chromium metal flake samples investigated in this study is shown in Table 1. In this table, 4N5 Cr is the flake produced in JMC's facility in North Carolina, USA. The metallic elements were determined by GDMS. Other elements including oxygen, nitrogen, hydrogen, carbon and sulfur are determined by the Leco method.

As shown in this table, metallic impurity levels in 4N5 Cr are extremely low. Most of them are less than 1 ppm with a few exceptions. Oxygen, at 180 ppm, is the primary impurity in this material. Carbon and sulfur are extremely low compared to other commercial chromium metals.

2N is a typical commercial grade chromium metal flake. Compared with 4N5 Cr, oxygen and other impurity levels are much higher. The iron level is about 1000 ppm indicating the existence of significant levels of other metallic impurities.

Table 1: Chemical Analysis for Chromium Metal Flakes

Sample Name	4N5 Cr		2N Cr	
	Analytical Data	Analytical Method	Analytical Data	Analytical Method
Cr Purity (%)	99.9995*		99.38**	
Al (ppm)	0.02	GDMS	9	ICP
Si (ppm)	0.06	GDMS	4	ICP
P (ppm)	0.01	GDMS	12	ICP
Fe (ppm)	0.06	GDMS	850	ICP
Cu (ppm)	0.02	GDMS	10	ICP
Pb (ppm)	1.1	GDMS	11	ICP
C (ppm)	10	LECO	60	LECO
S (ppm)	1	LECO	220	LECO
N (ppm)	10	LECO	300	LECO
O (ppm)	180	LECO	4700	LECO

* Based on metallic element

** Total purity

3.2 XPS analysis (Determination of the surface structure)

Figures 1 and 2 show the change in XPS profile for the surfaces of 4N5 Cr and 2N Cr flake, respectively, as a function of argon ion etching time (shown on the vertical axis). In preparation for these analyses, the specimens were only rinsed with deionized water and were not cleaned by any other chemical or physical cleaning method.

Figure 1 depicts the XPS profile for Cr 2p spectra for the 4N5 Cr specimen. The 0 minute spectra shows the virgin surface. A close examination of the spectra shows small Cr_2O_3 peaks and metallic chromium peaks. After two minutes of argon ion etching, the Cr_2O_3 peaks disappear leaving only metallic chromium peaks. No significant change in these spectra is observed after 4 minutes of argon ion etching. This result indicates that the surface oxide layer is extremely thin; we estimate the thickness of the oxide layer to be 10 nm or less.

Although this figure does not show the complete range of binding energy, chromium and oxygen are observed as main peaks and other metallic elements are not evident.

Figure 1: The change in XPS profile for the surfaces of 4N5 Cr flake as a function of argon ion etching time

Figure 2 shows the XPS profile for the surface of 2N Cr flake. In this figure, conspicuous peaks of Cr_2O_3 are found and they remain relatively constant throughout the complete range of argon ion etching time. Please note that the virgin surface data is slightly different indicating surface contamination. Although it is not shown in this figure, the magnitude of the oxygen peak is not changed by extending the argon ion etching time. The oxygen binding energy corresponds to the Cr_2O_3 state which supports the premise that the surface Cr_2O_3 layer is much thicker than that observed in the 4N5 Cr specimen.

Figure 2: The change in XPS profile for the surfaces of 2N Cr flake as a function of argon ion etching time

3.3 SEM Observation (Structure of oxide particle in the flake matrices)

Figure 3 shows results of the SEM observation of extracted Cr_2O_3 particles from 4N5 Cr flake before and after heat treatment. The material was heat treated to determine the influence of heat treatment on oxygen distribution and oxide shape. Figure 3-a shows the specimen without heat treatment. Please note that no extracted Cr_2O_3 particles were found in this specimen; the pattern observed is the shape of the filter

media used for extraction. Figure 3-b shows the specimen after heat treatment. The irregularly shaped particles in this figure are Cr_2O_3 particles. This extracted powder was identified as Cr_2O_3 by X-ray diffractometry. Also, extracted powder exhibited the greenish color characteristic of Cr_2O_3 .

Figure 3: The SEM observation of extracted Cr_2O_3 particles from 4N5 Cr

Figure 4: The SEM observation of extracted Cr_2O_3 particles from 2N Cr

The oxygen in high purity chromium metal flake without heat treatment exists in a form of chromium oxide that may be readily dissolved in hydrochloric acid. After heat treatment, the oxygen is converted to the insoluble Cr_2O_3 oxide as observed in Figure 3-b.

Figure 4 shows the result of the same investigation for the 2N Cr specimen. Extracted chromium oxide particles are observed in this specimen prior to heat treatment, possibly because of the relatively high oxygen content. We assume that the oxide in the flake without heat treatment exists mainly in the grain boundaries of the metallic chromium matrix because the shape of the extracted oxide appears to be the grain boundary structure with the grains removed. After heat treatment, the shape of the extracted oxide particles becomes a rectangular parallelepiped with slightly rounded corners.

4. CONCLUSION AND FUTURE INVESTIGATIONS

4.1 Conclusion

The results of our initial study of the structure and distribution of oxygen in high purity chromium metal may be summarized as follows:

- (1) The surface oxide layer of ultra high purity chromium metal is extremely thin versus conventional grades of chromium metal produced by electrolysis.
- (2) Oxygen in virgin ultra high purity chromium metal flake matrix exists as an oxide which is soluble in hydrochloric acid. After heat treatment, the oxygen is converted to the insoluble Cr_2O_3 oxide.
- (3) The oxide in conventional grades of chromium metal flake without heat treatment predominantly exists in the grain boundaries of the metallic chromium matrix.

4.2 Future Investigations

Data indicates that the corrosion resistance of chromium metal is a function of the purity of the material, i.e. the corrosion resistance increases with increasing purity. These data imply that the integrity of the protective passivation film depends on either the absence or presence of certain impurities. We plan to explore this phenomenon with the following investigations:

- Investigate the structure of potentiostatic passivation films for various grades of chromium metal.
- Investigate the relationship between integrity of protective passivation films and chromium metal impurity levels.
- Investigate purification methods using 4N5 Cr as a starting material.