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Surface Characterization for High Purity Fe-Cr Alloys

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Abstract. Fe-50mass%Cr was prepared in a cold crucible furnace with induction heating, then refined by floating-zone melting (FZM). The chemistries on the surface before and after FZM were compared by XPS measurement. C and O were observed on top surfaces both before and after as a hydrocarbon, carbonyl group and carboxyl group which are adsorbed chemical components. The other impurities were observed on the surface in both cases ; however, the number and level of impurities on the surface after FZM were much larger than those on the surface before FZM ; these adhered to the surface during sample preparation for XPS measurement. It is concluded that sample preparation introduces contamination which affects the detection limit of chemical analytical instruments. Sn was only observed on the top surface after FZM. It was segregated Sn which was contained in chromium as a starting material. It must be eliminated before starting. From XPS depth profiling results, it was concluded that 0.2 nm thickness of carbon such as hydrocarbon and organic components are adsorbed on the 1 nm thickness of oxide layer. Below the oxide layer, a lack of Cr was observed down to a depth of 6 nm.

1. INTRODUCTION

It has been reported that the mechanical and physical properties of high purity metals are different from those of conventional metals and alloys ; these contain many impurities in varied concentrations[1-3]. When the impurities are eliminated from a metal, it may exhibit previously unobserved properties. Fe-Cr alloy as a ferrite stainless steel is an example. Fe-Cr alloys are very resistant to corrosion, acids and high temperatures ; however these materials are severely embrittled by increasing the Cr concentration in the alloys. For example, 475 °C embrittlement and sigma phase embrittlement are well known. Recently, it has been found that Fe-50mass%Cr alloy from high purity metals has good ductility and it has been suggested as a useful material for very harsh environments[4]. Therefore, it is important to re-evaluate the mechanical and physical properties of these materials. It is also important to understand the surface chemical properties relating to corrosion and acid resistance. It has been reported that purified iron has a thinner carbon contamination layer than commercial iron[6]. This contamination may be an effect of the thickness and density of the oxide layer.

Surface analysis techniques such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are widely used today ; they were first used in the late 1960's[7]. Grain boundary and surface segregation are the examples of investigations[8] in which surface analysis techniques are most effectively used. Recently, field emission based AES instruments[9] have become available ; it is possible to measure the chemical information in precipitates of 50 nm in diameter. XPS can be used for studies of surface segregation ; it is possible to measure the average chemical information of the surface segregation in a large area. In addition, XPS is capable of chemical state analysis as well as elementary analysis. A monochromatic X-ray source and high efficiency energy analyzer have been devised ; it is possible to measure the chemical state with high energy resolution. It is important to measure the sample surface

without any X-ray-induced change in composition. A monochromatic X-ray source is suitable for this purpose because Bremsstrahlung X-ray and secondary electrons emitted at the aluminum filter are eliminated. In addition, a monochromatic X-ray source eliminates satellite peaks which are excited by other energy X-rays such as $K\alpha_3$, $K\alpha_4$, $K\alpha_5$, $K\alpha_6$ and $K\beta$ lines. Thus a very low impurity content can be measured without interference from satellite peaks of Fe, Cr., O, and C.

Surface contamination from instruments and sample preparation must also be considered. The impurity levels in high purity metals and their alloys have become very low. Therefore those impurities or adsorbed elements on the surface might effect the measurement limits and repeatability of chemical analysis. Take, for instance, a level of impurity on an Fe surface. The number of atoms on the surface is approximately 10^{12} mm^{-2} . If one monolayer of impurity exists, the total number of impurity atoms is 10^{12} mm^{-2} . If a sample size of Fe is $10 \times 10 \times 0.1 \text{ mm}$, the number of Fe atoms is about 10^{21} and the number of impurity atoms is 10^{15} . Therefore the proportion of impurity is about 1 ppm. This value is close to the detection limit of chemical analysis. The shape of the sample must also be considered. If the area of the surface is increased, the impurity content is also increased.

The high purity Fe-50mass%Cr alloy was made[4] and refined to reduce gaseous impurities by floating-zone melting (FZM)[5]. The gaseous impurity content before and after FZM was measured to investigate the effect of FZM refining[5]. In this paper, we will report the results of elementary analysis, chemical state analysis and depth profiling analysis of the surface of Fe-50mass%Cr alloy before and after FZM ; the surface chemistry and cause of the impurities observed on the surface will be discussed with reference to FZM.

2. EXPERIMENT

2.1 Sample Preparation

The ingot of Fe-50mass%Cr was cast from 99.995 mass % high purity electrolytic iron (Mairon HP™, Toho Zinc Co. Ltd.) and 99.98 mass % high purity chromium (Tosoh Corp.) in a cold crucible furnace in 13 kPa argon gas after evacuation down to 0.7 Pa[4]. Table 1 shows the impurities before melting in a cold crucible furnace. The largest proportion of the impurities consists of iron, which is negligible. The purity of the ingot was 99.99 mass %. First, the ingot was prepared by grinding ; next, it was forged 7 times at 1050°C ; finally, it was subjected to a grinding procedure again. After this process, 20 mm square rod was prepared. This sample was heated to over 900°C and shaped into round rod. The sample was shaved to 9 mm in diameter to remove oxide scale. The rod surface was made as smooth as possible during lathe turning. The rod was refined by 10 passes of FZM with high purity hydrogen gas at 13 kPa after pumping down to $1.3 \times 10^{-7} \text{ Pa}$ [5].

Figure 1 shows a diagram of sample location on the rod after FZM refining. The sample SA was cut for analysis of gaseous impurities. S1 was cut by diamond blade, then cleaned in ethanol. S2 and S3 were cut by tungsten carbide blade. S2 was cleaned in ethanol but S3 was not cleaned. S4 was solidified below the sample rod. S4 was removed easily from the rod, and did not undergo any preparation process such as cutting, grinding or cleaning. sample S0 was prepared by cutting the rod before FZM refining.

Table 1: Impurities of starting materials (mass ppm)

Element	Iron	Chromium
Fe	bal.	1091
Cr	<0.01	bal.
C	1.5	11
N	0.7	23
O	23	34
S	1.5	3
Al	0.3	10
B	0.1	<0.05
Co	<0.1	2
Cu	0.5	4
Ga	—	11
Mn	<0.01	8
Mo	<2	2
Nb	<0.5	0.2
Ni	<0.1	2
P	0.7	3
Si	5	11
Sn	<3	12
Ti	<0.01	7
V	<0.2	3.5
Zn	6.2	—

Figure 1: Diagram showing location of the sample on Fe-50mass%Cr rod. S1 was cut by diamond blade, then cleaned in ethanol. S2 and S3 were cut by tungsten carbide blade. S2 was cleaned in ethanol but S3 was not cleaned.

2.2 XPS Measurements

The surface before and after FZM was measured by XPS. A PHI model-5600ci XPS instrument was used for this study. The elementary analysis and atomic concentration were measured by wide scan spectra. The chemical states were measured by narrow scan spectra with different take-off angles. The depth information was measured by depth profiling with argon ion sputtering at 5×10^{-6} Pa. Photoelectron peaks are generally higher energy than Auger electron peaks. Therefore cross-talk by inelastic mean-free path[10] near the interface between oxide and metal was taken into account by reducing the take-off angle. Table 2 shows measurement conditions. A monochromatic X-ray source was operated at 350 W. The sputtering rate was 22 pm per second which was measured by SiO_2 on Si wafer. To eliminate surface contamination during XPS measurements, the pressure of the analysis chamber was maintained at $3\text{--}8 \times 10^{-8}$ Pa.

Table 2: XPS measurement conditions

Parameter	Wide Spectra	Narrow Spectra	Depth Profiling
Analysis Area (mm in diameter)	0.8	0.8	0.8
Acceptance Angle (°)	7	7	7
Pass Energy (eV)	187.85	23.5	23.5
Energy Steps (eV)	0.8	0.1	0.1
Take-off Angle (°)	44	17, 44, 65, 75	24
Ion Energy (keV)	—	—	3
Ion Current (μA)	—	—	5
Raster Area (mm)	—	—	4×6

3. RESULTS and DISCUSSION

3.1 Elementary Analysis

Table 3 shows the atomic concentration of observed elements on the surface (not the cut face) of the samples S0, S1 and S4. The concentration of Fe and Cr of S0 and S4 were almost the same; however, the Fe and Cr in S1 were lower in concentration than in S0 and S4. C, O and N are observed as usual contaminants from air and environment. The concentration of C in S1, however, was higher than the others. These results show that the top surface of S1 was heavily covered with carbon as a contaminant. Na, Al, Ca were also observed, besides the usual contamination. Samples S0 and S1 were prepared by the cutting process, so the samples would be contaminated by those elements during the cutting process. S was only observed on the surface of S4. S4 would be melted down before being well refined.

On the other hand, Sn was detected from the samples S1 and S4 which were prepared after FZM. However, Sn was not detected from the cut face of S1. This result shows that there are two possible reasons. The first reason is that the sample is contaminated by Sn from the FZM environment. The second one is that Sn is segregated from bulk which contains 12 ppm of Sn in Cr as a starting material (refer Table 1). The parts around the sample in the FZM furnace chamber were measured by XPS, but Sn was not detected. The high purity iron after FZM refining was also measured, but Sn was not detected. This high purity iron was refined in the FZM furnace before the Fe-Cr alloy was introduced. It is known that Sn is segregated on the surface[11] ; it is therefore concluded that observed Sn is surface segregation during FZM refining. This conclusion is reasonable because the Fe-Cr alloy was not refined under the vacuum in the FZM furnace. Most of the Sn might therefore remain in the molten Fe-Cr alloy. Even though Sn evaporated to some degree, that evaporated Sn might adsorb on the rod of the lower temperature area which is near the molten area during FZM refining, and remain as segregation.

Table 4 shows surface concentrations from the samples cut from a rod. Cutting was done repeatedly. As the number of cuts increased, contamination also increased. This is a very important fact and to be considered when preparing samples of high purity materials for the analysis of low content elements. Non-gaseous impurities may be lower than detection limit of the instruments, but gaseous impurities must be considered.

Table 2: Elements observed in S0, S1 and S4 (at.%)

Element	S0	S1	S4
Fe	11.75	6.04	8.6
Cr	15.35	5.03	17.38
C	26.76	42.6	30.25
N	1.94	2.24	1.58
O	43.7	41.62	40.99
S	<0.01	<0.01	0.75
Al	<0.01	1.28	<0.01
Ca	0.26	<0.01	<0.01
Na	0.24	0.75	<0.01
Sn	<0.01	0.43	0.44

Table 3: Change in elements observed by number of cuts (at.%)

Element	S1	S2	S3
Fe	6.04	6.67	6.01
Cr	5.03	11.49	9.77
C	42.6	26.96	28.56
N	2.24	4.9	2.8
O	41.62	44.91	41.02
S	<0.01	<0.01	0.5
Al	1.28	2.45	3.73
Ca	<0.01	0.45	0.68
F	<0.01	<0.01	3.8
K	<0.01	<0.01	1.33
Na	0.75	0.64	1.55
P	<0.01	0.28	0.14
Pb	<0.01	0.06	0.09
Si	<0.01	0.64	1
Sn	0.43	0.55	0.39
Non-gaseous impurities	2.46	5.07	12.71

3.2 Chemical States

Figure 2 shows the angle resolved XPS spectra of Fe, Cr, C and O on the surface of samples S0 and S4 (S1, S2 and S3 were not measured). Fe 2p_{3/2} peaks were observed at 710.9 eV and 707.0 eV. These correspond to Fe₂O₃ and Fe respectively[8]. Cr 2p_{3/2} peaks were observed at 576.7 eV and 574.4 eV. These correspond to Cr₂O₃ and Cr respectively[8]. The angle resolved spectra of S0 and S4 were not the same. From the angle resolved O 1s spectra, it is estimated that S4 has more dense adsorbed oxide.

Figure 3 shows the curve fitting results of O 1s and C 1s photoelectron peaks. Peak positions of O 1s were estimated at 530.25 eV and 531.60 eV which correspond to metal oxide and adsorbed oxygen respectively. At the higher take-off angle measurements, a carbide peak in the C 1s region was observed from the sample S4. The atomic concentrations of O 1s obtained from S0 and S4 are almost same. It is concluded that Fe₂O₃ and Cr₂O₃ are rich at the top surface. Adsorbed oxygen was also observed on each surface, the surface of S1, however, shows higher concentrations than S0 and S4. The adsorption on the surface may be hydrocarbon, carboxyl group, carbonyl group and alcohol.

Figure 2. The angle dependence of Fe 2p, Cr 2p, O 1s and C 1s spectra measured for S1 and S3

Figure 3. The curve fitting of O 1s and C 1s spectra for chemical state analysis

3.3 Depth Profiling

Figure 4 shows the depth profiling results of samples S0, S1 and S4. The results are not much different. However the result of S1 shows that the concentration of carbon is higher than S0 and S4. This result is in a good agreement with the results of Table 2 and the curve-fit results of Figure 3. The thickness of the adsorption layer is approximately 0.2 nm. This corresponds to one atomic monolayer. The thickness of the oxide on S0 and S4 was estimated about 1 nm. The thickness of the oxide on S2, however, was a little thinner : it was estimated at 0.9 nm. Each sample shows that the concentration of Cr is 2.5 times higher than that of Fe in the oxide layer. Below the oxide layer, a lack of Cr was observed down to a depth of 6 nm. It is expected that Cr atoms moved (or segregated) to the surface to create the oxide layer rather than Fe atoms. Therefore, the layer lacking in Cr atoms appeared near the top surface. The concentrations of Fe and Cr in S0 became equal after 10 nm in depth, but the ratio of Fe and Cr of S1 and S4 was not equal after 10 nm in depth ; the layer lacking in Cr still continued. A carbide which was about 3-4 nm thickness was only observed on the surface of S4. A carbide can be formed during FZM refining, because S4 was not well refined area and it was solidified below the sample rod. N was observed only in an oxide layer of S0 and S1. N was not measured on S4.

Figure 4: The XPS depth profiling of S0, S1 and S4

4. CONCLUSIONS

The surface of Fe-50mass%Cr alloy before and after FZM was measured by XPS. The results obtained were almost same ; however, we observed interesting results related to FZM and sample preparation. Finally, our conclusions regarding the surface chemistry are as follows.

(1) Many kinds of impurities were observed on the surface after FZM refining. They are related to sample preparation. As sample preparations multiply, the kinds of impurities increase. The concentration of those impurities excluding C, O, N and Sn before FZM was 0.5% by 2 impurities. However, the sample after FZM is 2%, which contained 5 impurities. The second and third sample preparation contain 5% by 6 impurities and 10% with 9 impurities respectively. As samples are prepared by cutting, this procedure may contaminate them. These results show that sample preparation for chemical analysis of very low contents has to be conducted with care, otherwise the result obtained will be questionable.

(2) Sn was observed in samples after FZM. As the starting material Cr has 12 ppm Sn, observed Sn must be a segregation element. As the floating-zone melting refining work was done in a hydrogen environment, the proportions desorbed from and remaining at the surface must both be taken into consideration. The elimination of Sn should be a priority step in making ultra-high purity Fe-50mass%Cr alloy.

(3) As for the contamination and oxide layer, we conclude that 0.2 nm thickness of hydrocarbon, carbonyl and carboxyl are adsorbed on the 1 nm thickness of oxide layer before and after FZM refining. The thickness of the oxide is very thin, so corrosion and acid resistance might be affected by the segregation elements and contamination elements.

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