

Effects of water vapor on protectiveness of Cr_2O_3 scale at 1073 K

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Abstract. Fe-Cr alloy is commonly being used as boiler tube's material. It is subjected to prolonged exposure to water vapor oxidation. The ability to withstand high temperature corrosion can normally be attributed to the formation of a dense and slow growing Cr-rich-oxide scale known as chromia, Cr_2O_3 scale. However, oxidation may limit the alloy's service lifetime due to decreasing of its protectiveness capability. This paper is to presents an experimental study of thermo gravimetric and Fourier transform infrared analysis of Cr_2O_3 at 1073 K in dry and humid environment. Samples were used from commercially available Cr_2O_3 powder. It was cold-pressed into pellet shape of 12 mm diameter and 3 mm thick with hydraulic press for 40 min at 48 MPa. It then sintered at 1173 K in inert gas environment for 8 h. The samples are cooled and placed in 5 mm diameter platinum pan. It is subjected to reaction in dry and wet environment at 1073 K by applying 100%-Ar and Ar-5% H_2 gas. Each reaction period is 48 h utilizing Thermo Gravimetric Analyzer, TGA to quantify the mass changes. After the reaction, the samples then characterized with Fourier Transform Infrared Spectroscopy, FT-IR and Field Emission Electron Scanning Microscopy, FE-SEM. The TGA result shows mass decreasing ratio of Cr_2O_3 in wet ($P_{\text{H}_2\text{O}} = 9.5 \times 10^5 \text{Pa}$) and dry environment is at a factor of 1.2 while parabolic rate at 1.4. FT-IR results confirmed that water vapor significantly broaden the peaks, thus promotes the volatilization of Cr_2O_3 in wet sample. FESEM shows mostly packed and intact in dry while in wet sample, slightly porous particle arrangement compare to dry. It is concluded that water vapor species decreased Cr_2O_3 protectiveness capability.

1. Introduction

Chromium oxide has variety of applications in various technologies such as catalyst, protective layer (corrosion and wear resistance of stainless steel), adhesion promoter, and magnetic recording media. Typically, the protective passive film on Fe-Cr stainless alloys is composed of an inner Cr_2O_3 film layer and an outer hydroxylated layer [1]. Despite their technological importance, basic understanding of Cr_2O_3 stability in any oxidation reaction involving gas adsorption is inadequate. There is strong correlation between adsorption and dissociation of water molecule on this activity of the surfaces. Thus, it is important to look into the surface reaction of Cr_2O_3 at high temperature [2]. Several studies of water on Cr_2O_3 surface have been done previously. Some were summarized in table 1.



Table 1. A summary of studies on the interaction of water with Cr₂O₃ surfaces by various methods.

Oxide	Gas	Method	Ref.
Cr ₂ O ₃ (0001)	H ₂ O	Density Functional Theory (DFT+U)	[1]
Cr ₂ O ₃	H ₂ O	FT-IR	[2]
Cr ₂ O ₃	H ₂ O	GCMC Simulation	[3]
Cr ₂ O ₃	H ₂ O	FT-IR, QNS, Dielectric Relaxation	[4]
ZnO, SnO ₂ , Cr ₂ O ₃	H ₂ O	Physisorption Apparatus	[5]

Costa et al. [1] has studied water adsorption on (0001)-Cr–Cr₂O₃ surface done by applying the Density Functional Theory, DFT+U method. They conclude that water adsorbs with energies of adsorption between 80 and 115 kJ/mol on the surface. The driving forces for the adsorption are the formation of Cr–O coordination bonds with Cr(t_{2g})–O(2p) hybridization and the stabilization through H-bonds between adsorbate molecules in an ice-like network. They propose a representative model for a hydroxylated Cr₂O₃ surface to be used in further theoretical investigation of modeling passive films formed at the surface of stainless steels.

Kittaka et al. [3] has studied the structure of monolayer water molecules on a hydroxylated Cr₂O₃ surface using Grand Canonical Monte Carlo (GCMC) simulations. The experimental 2D phase diagram was described by the simulation, which gave the 2D critical temperature of T=319 K. They proposed structure of the monolayer of water below the 2D critical temperature is composed of a net of many hexagonal water molecules registered on the hexagonal structure of the hydroxylated surface. An analysis of Cr₂O₃–H₂O system using FT-IR and neutron scattering were done by Kuroda [4] and Morishige et al. [5]. In this system, the relaxation frequency for the dipolar relaxation of adsorbed water was found. The activation energy of this relaxation was also estimated to be 48 kJ/mol. IR spectra at 3656 cm⁻¹, 3616 cm⁻¹, 3606 cm⁻¹, 3529 cm⁻¹, 3490 cm⁻¹ and 3402 cm⁻¹ were found broader by increasing the temperature from 93 K until 298 K. This revealed the presence of strong hydrogen bonding among the water molecules and the restricted motion for the water molecules adsorbed.

Both Kittaka and Kuroda's investigations were done in temperature lower than 320 K. Focus has been given on sub-ambient temperature surface analysis. Meanwhile Costa's study is limited to computational simulation and temperature lower than 800 K. Kaderi et al. [2] has studied the initial stage of Fe–Cr oxidation. At T=1073 K, it was found that formation of metal oxide including Cr₂O₃ is retarded due to water vapor. IR analysis on sample surface was done to explore the possibility of metal's surface catalytic activity. It was observed that dry sample has more intense peak and tends to be narrower, while samples oxidized in wet tend to have relaxed broader peak. However, in case of Fe–Cr alloy oxidations, Fe may also oxidized alongside Cr. Study on high purity Cr₂O₃ shall give better clarity of Kaderi's findings.

The objective of this work is to study the stability of highly pure Cr₂O₃ samples in dry and wet environment at 1073 K by thermo gravimetric and FT-IR analysis.

2. Experimental Procedures

2.1 Materials

Samples were used as it commercially available Cr₂O₃ powder from Sigma-Aldrich®. It weighed at 100 mg then was poured into a 12 mm diameter cylindrical steel die. It was cold-pressed using hydraulic press at 48 MPa of pressure and stay for 40 minutes. The sample then was carefully taken

out from the die and ~3 mm thick pellet was obtained. Sample then subjected to calcination process at 473 K for 2 h in oven for dehydration. Finally, it was sintered at 1173 K for 8 h in argon, Ar gas environment. The sample was let cooled to room temperature in the furnace. Final weight of the sample was measured to be 98.3 mg.

2.2 Thermo gravimetric measurement

Sample was subjected to dry and wet environment in Hitachi® STA7300 TGA. Figure 1 shows the schematic diagram of sample placement in the TGA system. Major parts of this machine are furnace, thermocouples and weighing scale. The weighing scale is an alumina insulated Pt-Rh thermocouple connected to laser weighing device. It has two sides – reference side and sample side. For reference, a blank 5 mm diameter platinum sample pan was placed on reference side and calibrated. Cr₂O₃ sample was cut and placed in another platinum pan. The pan with sample then was placed on sample side and its weight was measured and compared to reference. Sample weight was measured to be 41.87 mg. Specific area of the sample was calculated to be 2.1 mm²/mg. Heating rate was programmed at 5 K/min to heat from 300 K to 1073 K.

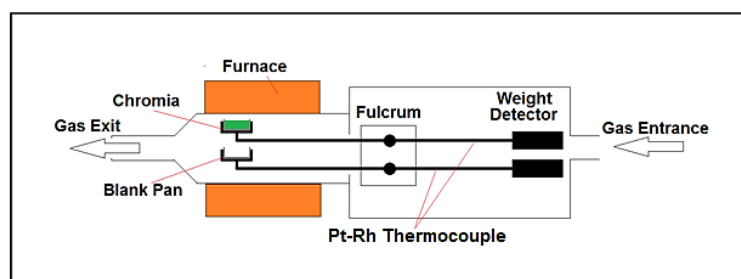


Figure 1. Schematic diagram of sample placement in the TGA system.

Before the reaction started, furnace chamber was evacuated with Ar gas for 30 minutes. After evacuation process was done, the reaction was started and set to hold temperature for 48 h when the temperature reaches 1073 K. For reaction in dry environment, Ar gas was used throughout the reaction at 100 ml/min flow rate. For wet environment, a gas mixture of Ar-5%H₂ was used with the same flow rate. The 5%H₂ is expected to react with impurity O₂ to form water vapor. Below is the possible reaction occurs to form water vapor.



Using Gibbs free energy and thermochemical data collected from Barin [6], water vapor partial pressure, P_{H₂O} is calculated to be 9.5x10⁵ Pa. After 48 h of reaction, gas supply is shut off. Sample then was let cooled to room temperature in the furnace. Both reactions took place in the lab where no human activity within radius of >10 m to avoid vibrations and obtain mass change data within the range of ±1 µg.

2.3 FT-IR measurement

IR spectra measurement was done by using Perkin-Elmer® Spectrum 100 and utilizing the attenuated total reflection, ATR technique. Before measurement, the apparatus was purged with N₂ gas for 25 min to avoid any organic contaminants. Sample from the TGA furnace immediately taken out after being cooled to room temperature. The surface of the sample placed on top of FT-IR window. Eight sheets of tissue papers were placed on top of the sample act as a damper to prevent sample from fractured while applying force on it. Force applied on the sample was at range of 100~110 N. Each sample (control, dry and wet) IR spectra were accumulated 20 times at a resolution of 4 cm⁻¹ and 32 scan time.

3. Results and Discussions

3.1 Mass change analysis.

Figure 2 shows the mass change of Cr_2O_3 after being exposed to dry and wet environment for 48 h at 1073 K. The TGA result shows decreasing of Cr_2O_3 mass in both dry and wet conditions. For dry condition, a mass linearly decreased at $1.10 \times 10^{-5} \text{ mg.cm}^{-2}/\text{s}$ was observed in the first 5.6 h. The decreased rate starts to plateau until the end of reaction time (48 hours). For wet condition, a steep mass decrease at $1.37 \times 10^{-5} \text{ mg.cm}^{-2}/\text{s}$ was observed at the first 3.1 h before its slope changed at rate of $7.36 \times 10^{-7} \text{ mg.cm}^{-2}/\text{s}$. It is interesting to note that the Cr_2O_3 mass is continually decreasing until end of reaction time, in contrast to the observation in dry environment. The overall mass decrease for both conditions is 0.49 % in dry condition and 0.59 % in wet condition.

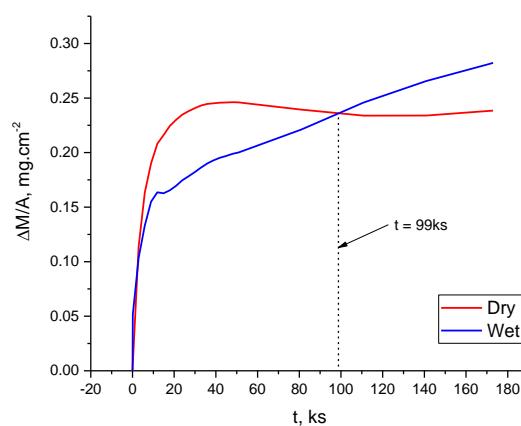


Figure 2. Mass change of Cr_2O_3 (linear plot) being exposed at 1073K for 48 h in dry and wet environment.

By ratio, the mass change different between these conditions is at 1.2. Another important observation is that at 99 ks (27.5 h), the mass change of sample in wet condition surpassed sample in dry condition. This shows that water vapor affect the stability of Cr_2O_3 at exposure time above 27.5 h.

Figure 3 shows the parabolic rate for dry and wet condition. At the end of the reaction time, k_p for dry environment is $3.29 \times 10^{-7} \text{ mg}^2\text{cm}^{-4}/\text{s}$ while for wet environment is $4.61 \times 10^{-7} \text{ mg}^2\text{cm}^{-4}/\text{s}$. From the k_p obtained, the ratio for wet and dry condition, $k_{p,\text{wet}}/k_{p,\text{dry}}$ is calculated at 1.4. It is consistent with the previous study by Graham and Davis [7] which reported the weight loss ratio of Cr_2O_3 when exposed at 1473 K for 72 h in high oxygen partial pressure to be 1.5.

The presence of water vapor in oxidation environment greatly affects the formation of oxide scales especially on Fe-Cr alloys [8], [9]. Its presence is also increases the evaporation loss of Cr_2O_3 [10]. Significant loss of Cr_2O_3 in wet condition is due to several factors. One of the factors is volatilization. Cr_2O_3 scale protectiveness capability can be degraded by the volatilization of Cr_2O_3 [11]. This problem is one of the major limitations on the high temperature use of Cr_2O_3 forming alloys which is more serious in rapidly flowing gases [12]. Asteman's [13] studies showed that H_2O reduced the ability of stainless steel to maintain its protective Cr_2O_3 scale due to volatile species. Below is the possible reaction occurs during volatilization of Cr_2O_3 .

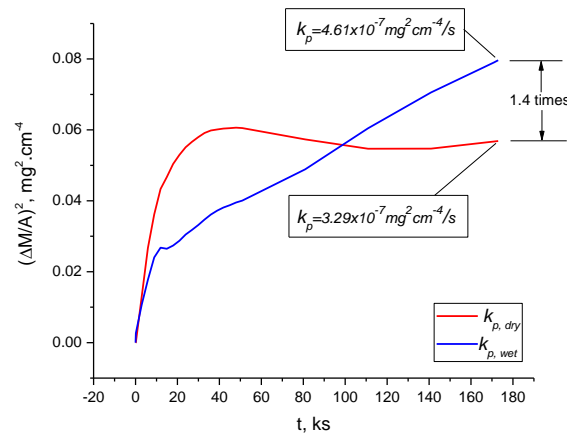
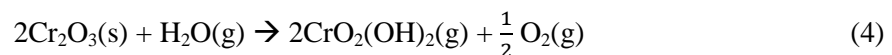
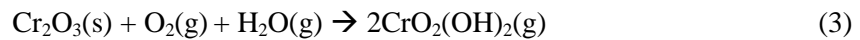
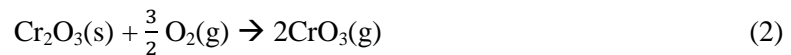


Figure 3. Oxidation kinetics (parabolic plot) k_p of Cr_2O_3 being exposed at 1073K for 48 h in dry and wet environment.

Equation (2) represents reaction that occurs in dry environment while equation (3) and (4) are in wet. In this study, the case is most likely similar to equation (4) where the oxygen partial pressure is low. Michalik et al. [14] stated that at high oxygen potentials, the addition of H_2O to the gas had negligible effect on the scaling behavior. However, at low oxygen potentials when the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio was held constant, the oxidation rate increased with water partial pressure. It is suggested that the evaporation of volatile chromium species $\text{CrO}_2(\text{OH})_2$ primarily occur along the grain boundaries. It accounts for scale cracking and spallation of oxide scales in the presence of water vapor [15].



3.2 IR transmission spectra.

Figure 4 shows the IR transmission spectra of all samples; control, dry and wet. Control sample is which the Cr_2O_3 is not been exposed to high temperature reaction. The differences in IR transmission spectra are apparent by making comparisons between samples control (black), reaction in dry environment (red) and reaction in wet environment (blue).

There are 4 main range of area that needs to be given a specific attention. It is grouped and named Range 1 to 4 to represent IR spectra in the range of $3500\text{--}4000\text{ cm}^{-1}$, $1800\text{--}2500\text{ cm}^{-1}$, $1000\text{--}1200\text{ cm}^{-1}$ and $400\text{--}700\text{ cm}^{-1}$ respectively. Figure 5-8 are the close up view of IR spectra of all group of range.

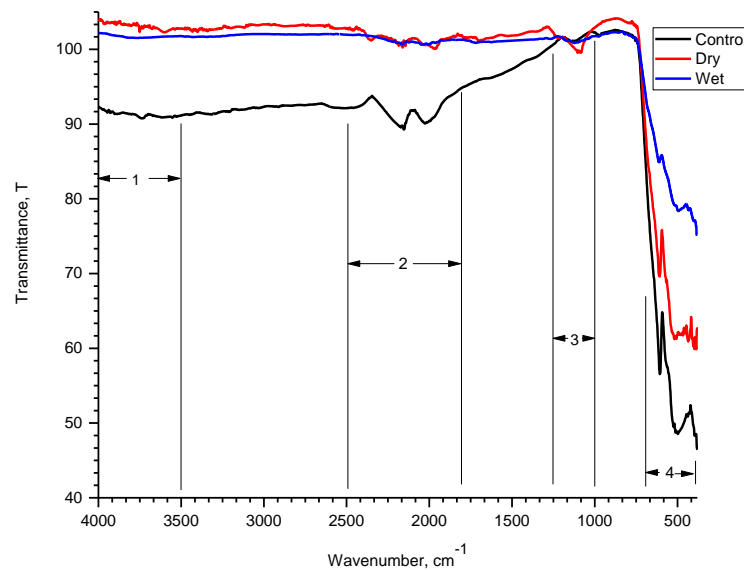


Figure 4. IR spectrum of Cr_2O_3 in dry and wet condition.

Figure 5 shows a close up view for Range 1. Two peaks appeared at 3750 cm^{-1} and 3600 cm^{-1} for control and dry samples while very broad IR spectrum were seen at wet condition sample. This effect is due to the water adsorption in the wet environment. At this region, typical of the stretching vibrations of the hydroxyls of the Cr_2O_3 surface observed at 3714 cm^{-1} , 3656 cm^{-1} , 3614 cm^{-1} , and 3408 cm^{-1} from chemisorbed hydroxyl groups on the Cr_2O_3 surface [4].

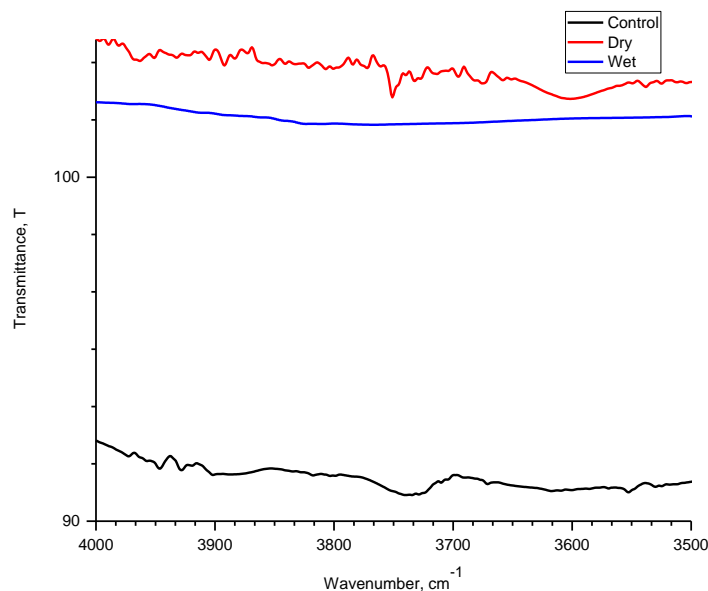


Figure 5. Close up view of IR spectra in the Range 1.

Figure 6 shows a close up view for Range 2. At 2155 cm^{-1} and 2040 cm^{-1} , intense peaks were observed at control sample while it is broader at wet sample. Kuroda [4] has studied, when Cr_2O_3

exposure to higher temperature, the peak would become broader and would disappear upon heating. This is in good agreement with this spectrum where control sample is a sample which not being exposed to high temperature environment.

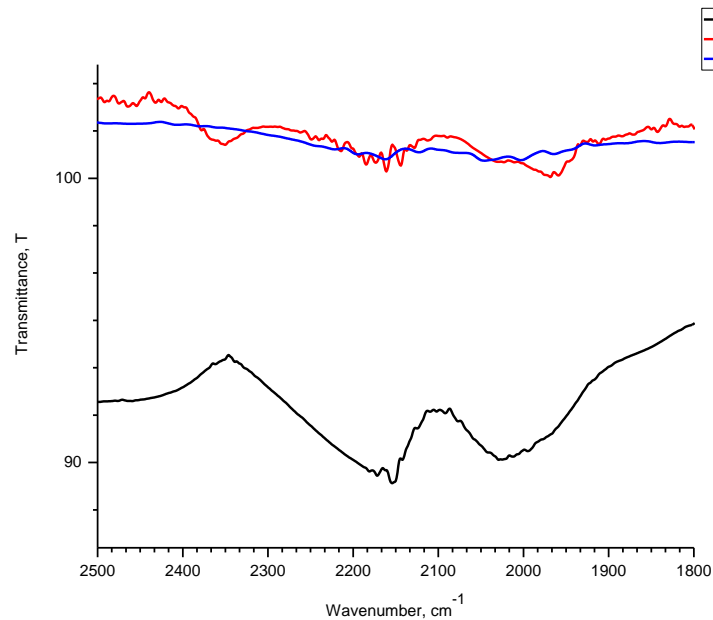


Figure 6. Close up view of IR spectra in the Range 2.

Figure 7 shows a close up view for Range 3. One range of intense peak is seen at 1080-1105 cm^{-1} for control sample and broad spectrum band for wet sample. The peak appeared to be broadened and shifted to 1121 cm^{-1} . This effect is due to the water adsorption in the wet environment.

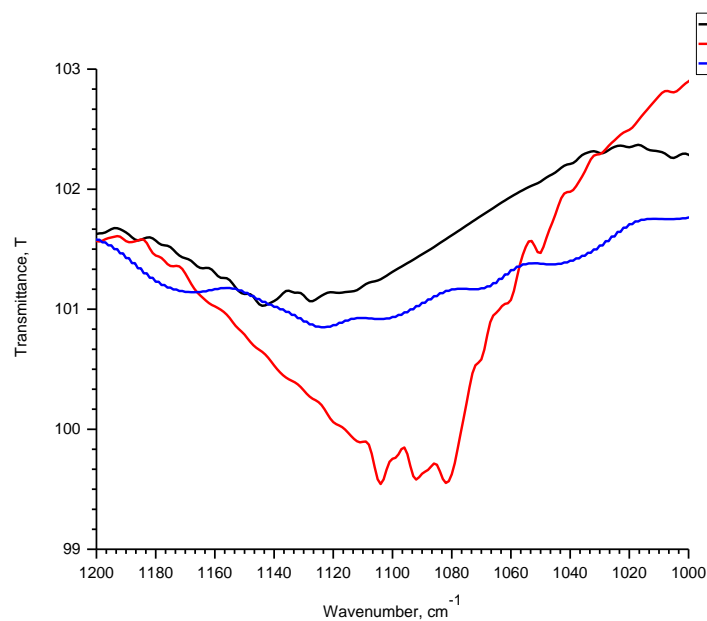


Figure 7. Close up view of IR spectra in the Range 3.

Figure 8 shows a close up view for Range 4. In this region, all three samples have very similar peaks appear at $607\text{--}608\text{ cm}^{-1}$. Dry sample shows heavy fluctuations while no significant peaks at wet sample. The IR spectra is broader in wet compare to both control and dry sample wet This is due to the introduction of wet environment to the system has been shown to decrease the intensities of the bands and new broad OH bands appeared [5].

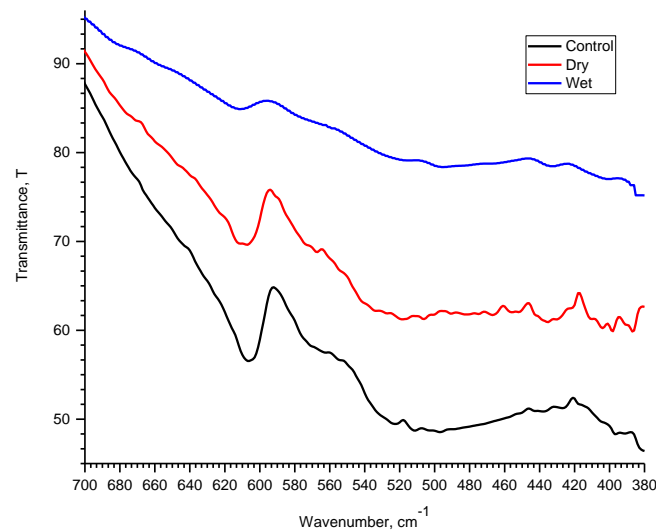


Figure 8. Close up view of IR spectra in the Range 4.

3.3 Surface Morphology

Figure 9 shows images of surface morphology of Cr_2O_3 after 1073 K for 48 h in dry and wet condition respectively. In dry sample, the surface particle arrangement is more compact and intact. Smaller grain size of Cr_2O_3 particles seen to attach with bigger particle. In wet sample, the arrangement of particle is slightly loose compare to dry sample. Smaller particle that attached to bigger particle is also lesser. This is might be due to the introduction of water vapor that increases the volatilization activity.

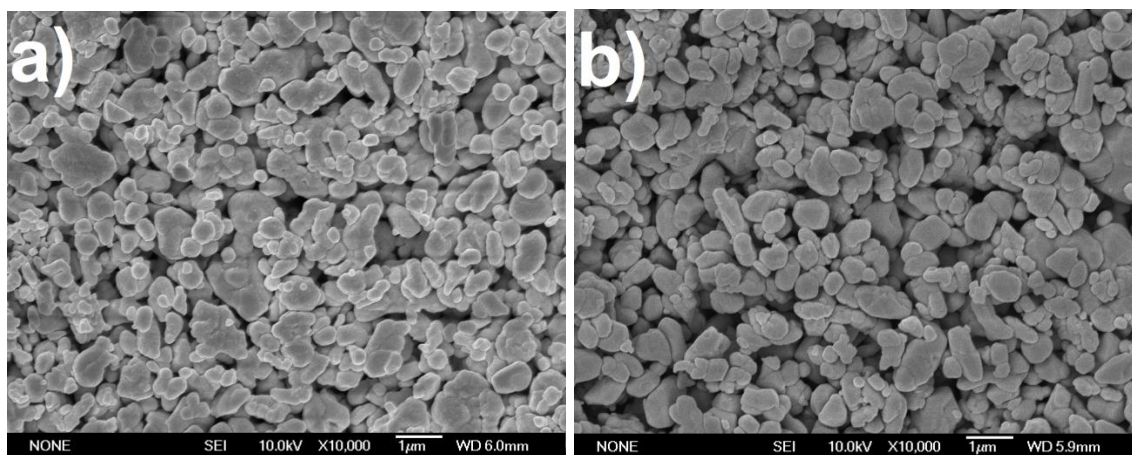


Figure 9. Surface morphology of Cr_2O_3 after 1073K for 48 h in a) dry and b) wet condition.

Hickman and Gulbransen [16] in their study has concluded that the presence of water vapor increase the volatilization of metal oxide by 30 % as compared to dry environment.

Young and Pint [17] studied to predict Cr-evaporation fluxes in the temperature range 923–1073 K. They concluded that a volatilization model, such as that also proposed by Asteman et al. [13], for $\text{CrO}_2(\text{OH})_2$, can account for the losses observed during exposure to air and H_2O .

4. Conclusions

We have shown from thermo gravimetric measurement that initially mass loss in wet and dry environment is almost similar at exposure time <1.4 h. Later, the mass change is separated between these two environments up to 27.5 h. Above 27.5 h, the mass of Cr_2O_3 in dry condition is kept constant, while sample in wet condition increasingly losing its weight. It could be deduced that exposure time of 27.5 h is the critical time where Cr_2O_3 in wet condition loss its protectiveness based on thermodynamic calculation. $\text{CrO}_2(\text{OH})_2$ is susceptible of volatile species. Careful analysis of FT-IR results supported that OH species somehow broaden the peaks significantly, and it is apparent proof of formation of volatile species. This study clearly shows that OH species degrade the protectiveness of Cr_2O_3 scale. Controlling it species is important to maintain protectiveness of Cr_2O_3 species.

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