

Initial Stage Oxidation of Cr in Dry and Wet Environment at 1073 K and the Significant Differences of FT – IR Spectra Produced Thereof

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Keywords: High temperature oxidation of Cr, Cr₂O₃, dry and wet environment, surface chemistry of Cr, IR studies.

Abstract. Little information has been known on the initial – stage oxidation if there is water vapor involved. Cr samples of 10 mm × 10 mm × 1 mm were isothermally oxidized in dry and wet environment respectively for 86.4 ks. Compact and even surface of Cr₂O₃ was formed on samples oxidized in dry environment. However, the ability to form compact and even Cr₂O₃ was retarded in wet environment. XRD analysis on all samples shows that Cr₂O₃ can be formed in dry and wet environment. The IR transmission spectra for samples oxidized in dry environment, were consisting of more intense peak while samples oxidized in wet environment has more relaxed peak. Moreover the peak of samples oxidized in dry tends to be narrower, while samples oxidized in wet tend to have broader peak.

Introduction

Studies on high temperature oxidation of metals have always been focusing on the diffusivity of the cation and the oxygen through the oxide scale. There is an important role to look into the surface reaction during the initial-stage oxidation of metals at high temperature. Saunders et al. [1] concluded that the information on high temperature literature pertaining to the first step reaction in any oxidation reaction involving gas adsorption is inadequate. There is a strong correlation between the adsorption and dissociation of water molecule on the catalytic activity of the surfaces. Moreover this can be significantly altered by the oxide defect structure and alloying additions. Majority contemporary studies on water's interaction with oxide's surface were done at room temperatures. Some of these studies were summarised in Table 1.

Table 1: A summary of studies on the interaction of water with oxide surfaces (Fe₃O₄ and α-Cr₂O₃) by various method at room temperature

Oxides	Type of water	Method Employed	Ref.
Fe ₃ O ₄ , and α – Fe ₂ O ₃	D ₂ O	XPS, LEED, TDS, and MSRI	[2]
α – Cr ₂ O ₃ on Cr (110) substrate	H ₂ O	XPS, TDS, LEED, and STM	[3]
α – Cr ₂ O ₃ alternating layer with α-Fe ₂ O ₃ , and α-Cr ₂ O ₃ on α – Al ₂ O ₃	D ₂ O, and H ₂ O	HREELS, TPD and XPS	[4]

Nevertheless, Hultquist et al. [5,6] has contributed to the studies of adsorption and dissociation of various molecules particularly H_2O molecules at high temperatures. They had studied the adsorption of N_2 , H_2 , CO and H_2O on oxidised chromium and zirconium metal in the temperature range 673 – 873 K. H_2O is readily to adsorb at high temperature followed by CO and H_2 . N_2 is least likely to adsorb at high temperature but it is still possible [5]. Another study [6] shows that water dissociation rates decreased with decreasing oxidation rates during the oxidation of Fe-20Cr-10Al at 1193 K.

The objective of this work is to study the initial stage oxidation at high temperature of Cr samples in dry and wet environment. The aim is to explore the possibility of the metal's surface catalytic activity in wet environment at high temperature by employing the FT – IR studies.

Experimental Procedure

Samples. Cr plate was cut into coupons of $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$ dimensions by a precision diamond saw. These coupons were ground with emery paper up to #2000. Then the samples were polished with $3\mu\text{m}$ alumina paste to a mirror-like finish. The samples were cleaned with acetone via ultrasonic agitation.

Oxidation Experiment. The sample was placed at the isothermal zone of the furnace as shown in Fig. 1. At the isothermal zone beside the sample, an R-type thermocouple was placed to monitor the temperature. The distance between the sample and the thermocouple is 5 mm. The isothermal zone is 30 mm in range. For oxidation in dry environment, the sample was heated to 1073 K and held for 86.4 ks. For oxidation in humid environment, a boiler is placed directly below the furnace. The water vapor was channeled into the furnace once the heating process started. The continuous supply of water to the boiler will ensure that the water vapor will be produced continuously throughout the oxidation process. The oxidation process in humid environment was also hold for 86.4 ks. After oxidation, the samples were cooled to room temperature in the furnace.

Analysis. After oxidation, all samples were subjected to analysis by means of XRD and FT – IR. A Perkin Elmer's Spectrum 100 FT – IR Spectrometer was used for FT – IR analysis. Cr_2O_3 's JCPDS pattern no. 00-038-1479 was referred for XRD data analysis.

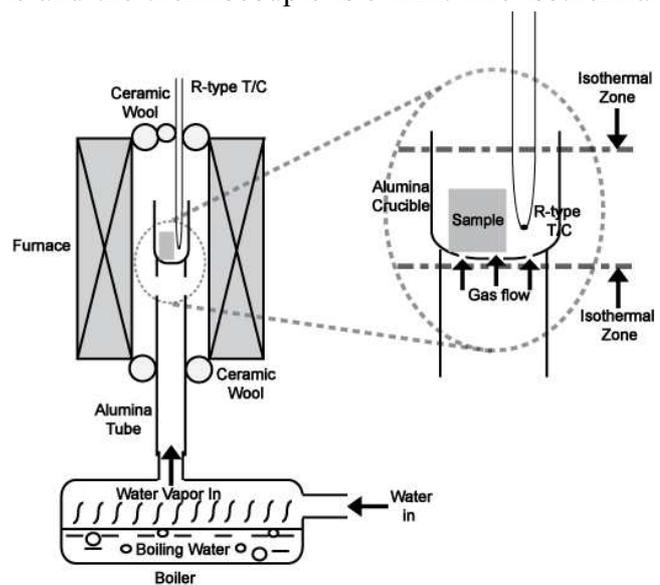


Fig. 1: Experimental setup for oxidation in humid condition at 1073 K

Results and Discussion

Samples Image. Fig. 2 shows the Cr samples after oxidation in dry and wet environment. Fig 2(a) shows a compact and consistent Cr_2O_3 layer after oxidized in dry environment. However for Cr samples exposed in wet environment in Fig 2(b) and 2(c) they are inherently having uneven type of Cr_2O_3 layer.

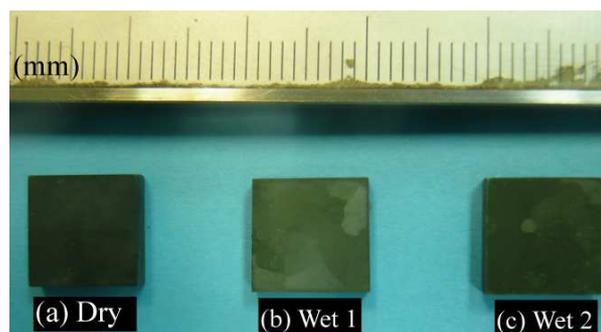


Fig. 2: Cr samples after being oxidized

XRD Analysis. Fig 3 shows the XRD patterns of Cr samples after being oxidized in different environment. The Cr_2O_3 peaks can be observed in all samples. More Cr_2O_3 peaks appeared in dry samples than in wet samples. Cr_2O_3 peaks in wet samples are less intense compared to in dry samples.

IR transmission Spectra. Fig. 4(a) shows the IR transmission spectra of all samples. The differences in IR transmission spectra are apparent by making comparisons between samples that were (i) not oxidized, (ii) oxidized in dry environment, and (iii) oxidized in wet environment. There are 3 prominent peaks that need closer inspection labelled as Peak 1, Peak 2, and Peak 3 respectively.

These 3 peaks show differences in their characteristic depending on whether the samples had been oxidized or not as well as whether it had been oxidized in dry or wet environment. These differences in the characteristic might give the answer on the effect of water vapor oxidation on the surface chemistry of Cr thus promoting the accelerated oxidation of Cr.

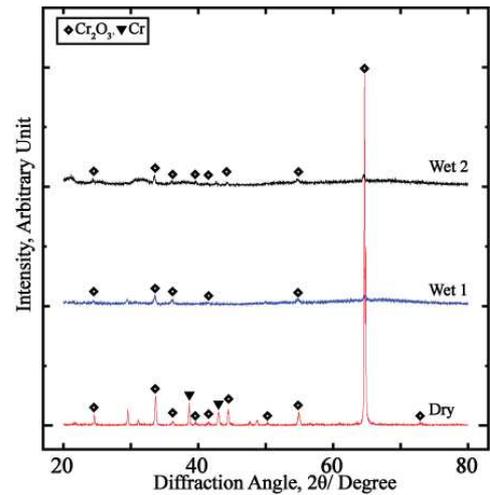


Fig. 3: XRD patterns of oxidized Cr samples

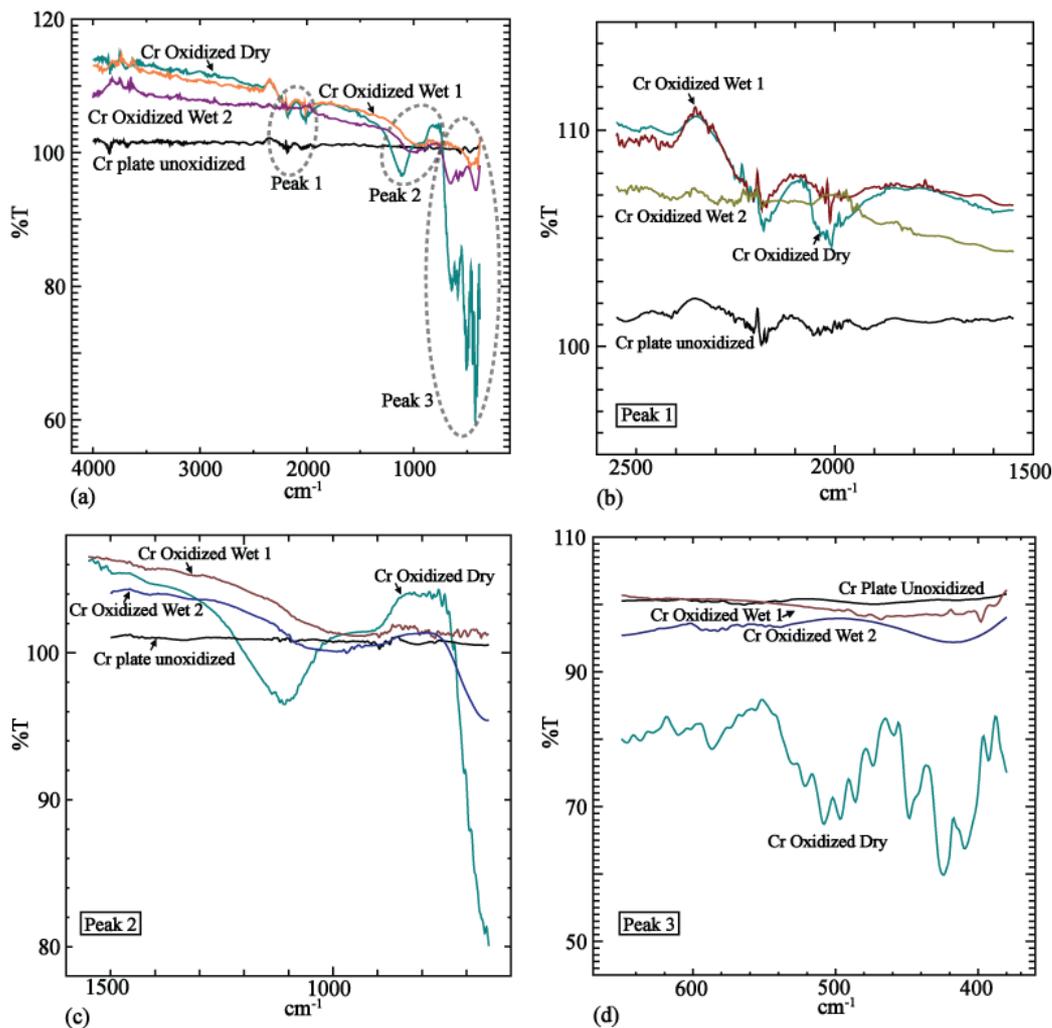


Fig. 4: IR transmission spectra of (a) all samples, close-up of (b) Peak 1 (c) Peak 2, and (d) Peak 3

Fig. 4 (b) is a close-up of Peak 1. There are two peaks appeared for all samples. The dry Cr sample has its peak at 2200 cm^{-1} and 2000 cm^{-1} respectively. The peaks are less intense for wet Cr samples. But peaks are still appeared at 2200 cm^{-1} and 2000 cm^{-1} . The close-up of Peak 2 is shown in Fig. 4 (c). For the dry Cr sample the peak appeared at 1100 cm^{-1} . The wet Cr sample's peak appeared to be broadened and shifted to 1000 cm^{-1} . This effect is due to the water adsorption in the wet environment.

Peak 3 is shown in Fig. 4 (d). The dry Cr sample shows heavy fluctuation in reading and the peaks are hard to be detected in this range. However the wet Cr samples shows the opposite, whereby the peaks can be clearly detected at the range of $400 - 410\text{ cm}^{-1}$. It can be clearly seen that the dry Cr samples often shows a characteristic of intense and fluctuated type of peak while the wet Cr samples shows a more relaxed and usually broaden type of peak. For FT – IR studies by Kuroda et al. [7] the introduction of water vapor (in our case wet environment) to the system has been shown to decrease the intensities of the bands and new broad OH bands appeared.

Conclusion

The initial – stage oxidation of Cr in dry and wet environment at high temperature was investigated. The IR spectra produced by Cr samples oxidized in dry and wet environment are significantly different from one another. The oxidized Cr in dry environment is having intense and fluctuated type of peak, while the oxidized Cr in wet environment has relaxed and broad type of peak. The differences in this peak are due to the water adsorption of oxidized Cr in wet environment.

Acknowledgement

The authors gratefully acknowledged the support for this work by the Malaysian Ministry of Higher Education (MOHE) through its Fundamental Research Grant Scheme: FRGS 0510 – 127, and FRGS 11 – 012 – 0160.

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Advances in Manufacturing and Materials Engineering

10.4028/www.scientific.net/AMR.576

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10.4028/www.scientific.net/AMR.576.619