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FORMATION OF CHROMATE CONVERSION COATINGS ON ALUMINUM AND ITS ALLOYS: AN *IN SITU* XANES STUDY

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We used *in situ* X-ray adsorption near-edge structure (XANES) to investigate the formation of chromate conversion coatings on pure Al, commercial Al alloys (AA 1100, AA2024, and AA7075), and a series of binary Al-Cu alloys. The method employed a new electrochemical cell that can determine the ratio of hexavalent chromium (Cr(VI)) to total chromium (Cr(total)) speciation in conversion coatings as a function of exposure time to a chromate solution. The spectra showed that the initial Cr(VI)/Cr(total) ratios are greater than later ones for pure Al and AA1100, but not for AA2024 and AA7075. Measurements with Al-Cu alloys demonstrated that the difference observed in AA2024 and AA7075 may not be due to Cu alloying. The proportion of Cr(VI) in the coatings becomes approximately constant after 180 s of exposure for all the specimens examined even though the coatings continue to grow.

INTRODUCTION

X-ray adsorption near-edge structure (XANES) offers a powerful method for the *in situ* study of inhibiting species in passive films and in solutions since it reveals the concentration of metals during the processes of dissolution (1). Using this technique, the inhibiting effects of chromate in solutions and the changes in chromate conversion coatings (CCC) films have been examined (2,3). CCCs are used extensively by the automotive and aerospace industries for covering aluminum and its alloys. CCCs are made up of several Cr(III) and Cr(VI) species; the latter is believed to be responsible for CCC's ability to protect scratches on a metal surface from undergoing further electrochemical degradation (4, 5). The more numerous the Cr(VI) ions are in the CCC the better the protection against corrosion. A distinct pre-edge peak at 5993 eV in the XANES spectrum is observed when hexavalent chromium Cr(VI), such as in CrO_4^{2-} is present. The ratio of height above the edge (arising from all chromium species present (Cr(total))) to the pre-edge height (only Cr(VI)) provides a quantitative measure of Cr(VI) concentration in the CCC.

In this paper, we introduce a new design of electrochemical cell that allows a specimen surface to be exposed to a chromate solution for specified periods, including controlled repetitive exposures to the solution. Accordingly, XANES measurements can characterize the formation of CCC with increasing exposure time. We note that the *in situ* XANES measurements with this new cell are unique: all published investigations of CCC were conducted *ex situ*. We present our data on aluminum and its alloys subjected to repeat or continuous exposure to the chromate solution with this new cell. From these findings, we discuss the kinetics of the CCC formation and the effect of the content of Cu alloying element on the ratio of Cr(VI)/Cr(total).

EXPERIMENTAL

The specimens used in this study were rectangular pieces of pure Al, AA 1100, AA 2024, AA 7075, and binary Al-Cu alloys (Cu contents: 0.2, 1, 2, and 4 wt-%), cut to dimensions of *ca* 12 mm × 12 mm × 1 mm. Table 1 lists the specifications of composition for the commercial alloys (6). Their surfaces were wet-ground on 600-grit abrasive paper. The specimens then were immersed in 8 wt-% KOH for 5 min, rinsed in distilled water, immersed in 50 wt-% HNO_3 for 5 min, and finally rinsed thoroughly in distilled water. All specimens were prepared less than 1 hr before the measurements.

Table 1. The composition of the commercial Al Alloys (wt-%) [6].

AA number	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
1100	1.0(Si+Fe)		0.05-0.20	0.05			0.10	
2024	0.50	0.50	3.8-4.9	0.30-0.9	1.2-1.8	0.10	0.25	0.15
7075	0.40	0.50	1.2-2.0	0.30	2.1-2.9	0.18-0.28	5.1-6.1	0.20

We developed a novel electrochemical cell, in which one side of the specimen is covered with a plastic film transparent to X-rays, as schematically shown in Figure 1. The cell is completely sealed except for a tube connected to a reservoir of a chromate solution. By lifting the reservoir, hydrostatic pressure in the cell is increased so the solution flows into the cell and inflates the membrane (Figure 1(a)). Lowering the reservoir causes a fall in pressure in the cell, so that the solution is drained off and the membrane sucked in, thereby suppressing the surface reaction (Figure 1(b)). The specimen surface thus can be repeatedly exposed to the chromate solution. Surface changes can be characterized by repeating this process and making a XANES measurement between immersions. A commercial chromate solution, Alodine 1200 (Parker Amchen, Michigan) was used (7.5g l^{-1}). If the chromate solution is not completely drained from the cell so that a thin film remains on the specimen surfaces, then it is possible to monitor the changes in Cr(VI) ions in this thin layer with increasing exposure time.

The growth of the CCC on the specimen surfaces during continuous exposure to the chromate solution also was monitored in a different cell, the details of which were described previously (7, 8). A cold-rolled thin specimen of the metal or alloy (*ca* 60 μm thick) was mounted on to the exterior of the cell (a small rectangular plastic bottle). The cell had a *ca* 1.5 cm × 0.5 cm window, so that one side of the specimen was exposed to the solution.

The XANES spectra were obtained at Beamline X-10C at the National Synchrotron Light Source (Brookhaven National Laboratory). The specimen surface was oriented at an angle of *ca* 45° to the incident beam which was approximately 5 mm × 0.5 mm. A solid-state detector was held at 90° to the incident beam to collect fluorescence radiation from the sample. The intensity of the fluorescence, I_f, was normalized by that of the incident beam, I_0. Details of the experimental procedure for the XANES studies were given elsewhere (9). Acquiring one XANES spectrum took approximately 250 s.

RESULTS AND DISCUSSION

The cell illustrated in Figure 1, was used to form a CCC film on the metal surface. Figure 2 presents a series of *in situ* XANES spectra of the stepwise growth of the CCC film on AA 2024. The immersion time in the Alodine solution ranged from 2 s to 100 s allowing us to monitor rapid initial changes in the CCC, as well as the relatively slower subsequent ones. After each specified immersion period, the surface reaction was suppressed by draining the solution from the cell, and then a XANES measurement was made. The height of the pre-edge peak seen (at 5993 eV) reflects the amount of Cr(VI) ions present in the CCC, while that above the absorption edge (at 6065 eV) represents the total amount of all Cr species. As Figure 2 shows, the heights of both increase with immersion time (the arrow indicates an increase in immersion time).

Figure 3 illustrates the growth of the CCC on AA 2024 with exposure time. The heights of the pre-edge peak Cr(VI) and above the edge peak Cr(total) are plotted against immersion time. Also shown is the ratio of Cr(VI)/Cr(total) in the CCC. Both the amounts of Cr(VI) and Cr(total) increased with immersion time, indicating that the CCC grew continuously on the specimen surface during the duration of the exposure (530 s). However, the ratio of Cr(VI)/Cr(total) showed a small initial increase from 23 % and then stayed approximately constant at 33 % after 180 s. This result demonstrates that the proportion of Cr(VI) in the CCC becomes constant (at 33 %) after 180 s, even though the CCC continues to grow.

Ex situ XANES measurements revealed that approximately 20 % of Cr(VI) was present in a CCC (2,5), a value lower than that we obtained in the present *in situ* measurements. Possibly, in the *ex situ* measurements the Cr(VI) ions present in the CCC after the coating treatment might be reduced to Cr(III) during exposure to air, thereby leading to the lower Cr(VI) content (2,3,10).

Figure 4 presents the changes in the amounts of Cr(VI) and Cr(total), and the ratio of Cr(VI)/Cr(total) in a CCC formed on AA 1100 with exposure time. The amounts of Cr(VI) and Cr(total) both increase with time in a manner similar to that observed for AA 2024 (Figure 3). However, the concentration of Cr(VI)/Cr(total) for AA 1100 differs from that for AA 2024; the maximum proportion of Cr(VI) (*ca* 67 %) occurred at the beginning of immersion, followed by its rapid decay with time; thereafter, it decreased gradually after 180 s, approaching a value of 35 % at 530 s.

The discrepancy between AA2024 and AA1100 in their initial ratios of Cr(VI)/Cr(total) is significant, although the phenomena after 180 s seem to be similar. We note that initial high proportions of Cr(VI) also were observed for pure Al but not for AA 7075 (3). Therefore, we might expect that the difference in the concentration of Cr(VI) originates from the Cu content in the alloys (Table 1). Copper is the most popular alloying element for Al as the addition of Cu, usually in combination with other elements, improves the mechanical properties of Al alloys after appropriate heat treatment. Thus, we undertook *in situ* XANES measurements on a series of binary Al-Cu alloys (0.2-4 % Cu). Figures 5(a) and 5(b) show the amounts of Cr(VI) and Cr(total), and the ratios of Cr(VI)/Cr(total) in CCCs formed on Al-0.2%Cu and Al-4%Cu alloys, respectively. (The meaning of the black diamond at 583 s in Figure 5(a) will be described later). Both alloys exhibited high concentrations of Cr(VI) in the CCCs at the beginning of immersion (46-48 %), followed by a fast decrease with time, and then gradually approaching relatively steady values at 600 s (36-38 %). In both, the behavior seem similar, implying that the concentration of Cr(VI) in the CCC is independent of its Cu content. Thus, our measurements demonstrated that the variation of the Cr(VI) ratios observed in AA2024 and AA7075 may not be caused by Cu alloying. Their exact origin is being investigated.

Figure 6 shows a series of *in situ* XANES spectra of a continuously growing CCC on Al-0.2%Cu. The cell used was different from that shown in Figure 1. One side of the foil specimen (*ca* 60 μm thick) was continuously exposed to the chromate solution. Monochromatic x-rays were incident on to the other side of the specimen and penetrated through the Al foil to give the spectrum from the CCC growing at the metal/electrolyte interface. The chromium fluorescence signal detected was small compared with that from the background because the metal foil scattered most of the incident radiation. However, as the figure shows, both the Cr(VI) and Cr(total) components increased with immersion time.

Let us assume that the first XANES spectrum in Figure 6 represents only the chromate solution (*i.e.*, only Cr(VI)) since the effect of the CCC is regarded as small at this stage. Thus, subtracting the first spectrum from the others reveals the changes with time only in the CCC film developing at the metal/solution interface. The resultant changes in the ratio of Cr(VI)/ Cr(total) in the CCC film formed on Al-0.2%Cu specimen are depicted against immersion time in Figure 7 (black circles). The portion of Cr(VI) ions is approximately constant around *ca* 32 % within the exposure times we used (from 250 s to 1950 s). We compare with our earlier results in Figure 5(a) where we presented the spectra from specimens of Al-0.2%Cu that were repeatedly exposed. The black diamond in Figure 5(a) indicates the ratio of Cr(VI)/Cr(total) from the surface of the same specimen after it was washed throughly with distilled water, after the measurement. The fraction of Cr(VI) ions decreased from 37 % at the end of the measurement (at 583 s) to 34 % after rinsing (Figure 5(a)). Presumably, the decrease reflects the rinsing away of a very tiny amount of the solution trapped between the surface and the membrane. An interesting feature is that the concentration of Cr(VI) after washing is similar to that obtained from the continuous-exposure measurement. We plot the same data in Figure 5(a) after subtracting this decrease (white squares), together with those data obtained from the continuous exposure in Figure 7. The continuity between the two curves is fairly good. It is clear from the figure that the ratio of Cr(VI)/Cr(total) in the CCC on the Al-0.2%Cu surface becomes constant after *ca* 180 s even though the CCC grows continuously with extended immersion time.

Time-lapse XANES measurements also were made to monitor the changes in both electrolyte and a CCC simultaneously during exposure. The chromate solution was not completely drained off from the cell (depicted in Figure 1) so that a thin film of the solution remained on the specimen surface. Figure 8(a) shows a series of such *in situ* XANES spectra from AA 1100 obtained by taking fast scans (78 s). Two features should be noted. First, the height of the pre-edge peak in the first spectrum is approximately the same as that above the edge, indicating that it represents mostly the chromate solution and the contribution from the CCC is negligible. Second, the last two spectra (6 and 7) show very little change, and the portion of Cr(VI) ions determined from them is *ca* 33 %. This implies that by 470 s the chromate solution remaining on the surface was all expended in forming the CCC. Therefore, the spectra in Figure 8(a) demonstrate the transition from the solution to the CCC with exposure time.

The results can be modeled by plotting the relative proportions of the spectra of the Alodine solution (curve 1 in Figure 8(a)) and the final CCC (curve 6 in Figure 8(a)). Figure 8(b) presents such a plot. The figure caption gives the ratios of those of the solution and the CCC used in the calculation. The portions of the CCC derived from the modeling can be approximated to CCC growth rates since the ratio of Cr(VI)/Cr(total) detected by the measurements after repeated exposures for AA 1100 is 37 % at 78 s (Figure 4), then approaching 35 % for a longer immersion time, which is very similar to that from curve 6 (Figure 8(a)).

Figure 9 shows the estimated CCC growth rate for AA 1100 from the modeling results (black circles). The white squares represent the growth rate of the CCC determined from the Cr(total) absorbance from measurements of repeated exposures (Figure 4). We normalized the latter rate by its absorbance value at 480 s to give the same rate as the former rate (100 %) at this point. For longer immersion times during repeated exposures, the CCC grows more (Figure 4), while the growth of the CCC in the thin layer of solution is suppressed as all the solution has been expended, as described above (Figure 8(a)). Figure 9 clearly shows the very good agreement between the two different experiments, and both results show that the kinetics of the CCC formation are linear up to 320 s for AA 1100.

CONCLUSIONS

We studied the formation of chromate conversion coatings on pure Al, commercial Al alloys (AA2024, AA1100, and AA7075), and a series of binary Al-Cu alloys by *in situ* XANES measurements using a new type of electrochemical cell. The techniques we employed allowed us to determine the ratio of hexavalent chromium (Cr(VI)) to total chromium (Cr(total)) in conversion coatings as a function of exposure time to a chromate solution. The spectra showed that the initial Cr(VI)/Cr(total) ratios are greater than later ones for pure Al and AA1100, but not for AA2024 and AA7075; this difference is not caused by Cu alloying. The proportion of Cr(VI) in the coatings becomes approximately constant after 180 s of exposure time for all the specimens examined, even though the coatings continue to grow. Measurements demonstrated that the kinetics of the formation of the chromate conversion coating for AA 1100 is linear up to 320 s.

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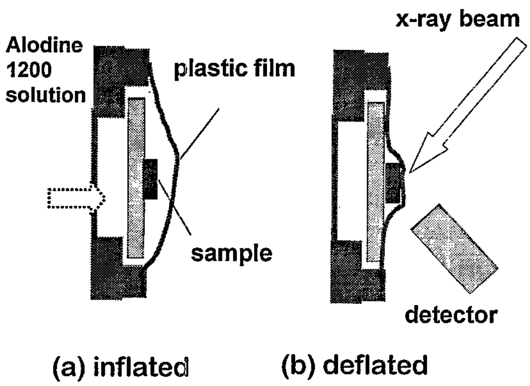


Figure 1. Schematic of the electrochemical cell employed in the present study, showing (a) the inflated position where the chromate solution can react with the sample, and (b) the deflated position where the reaction is paused.

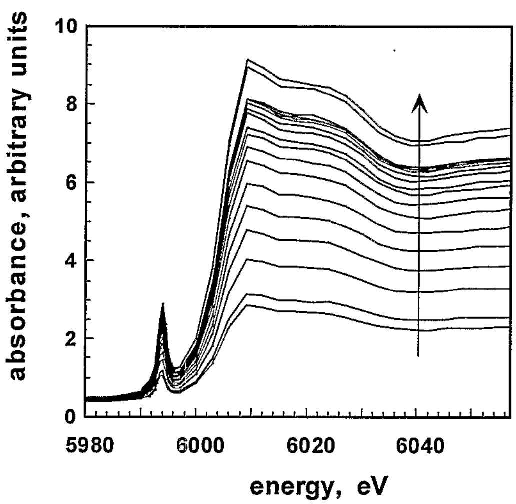


Figure 2. A series of *in situ* XANES spectra of the stepwise growth of the CCC film on AA 2024. The arrow indicates an increase in exposure time.

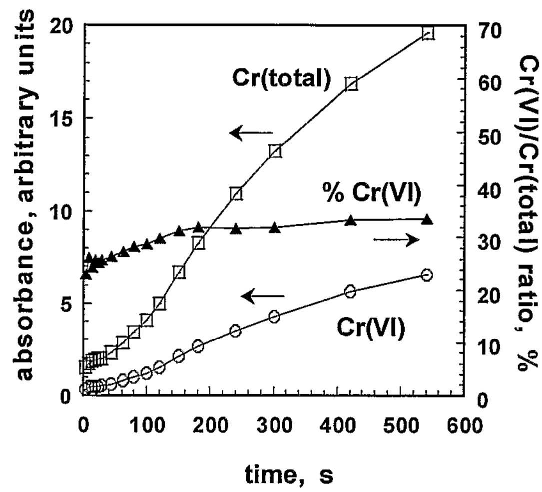


Figure 3. Changes in the amounts of Cr(VI) and Cr(total) and the ratio of Cr(VI)/Cr(total) in a CCC formed on AA 2024. The data are derived from those presented in Figure 2.

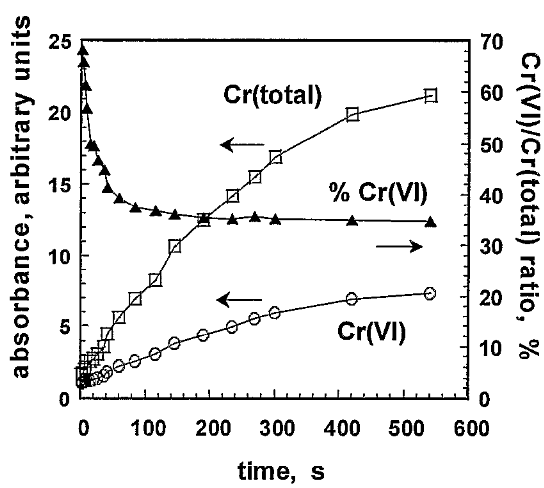
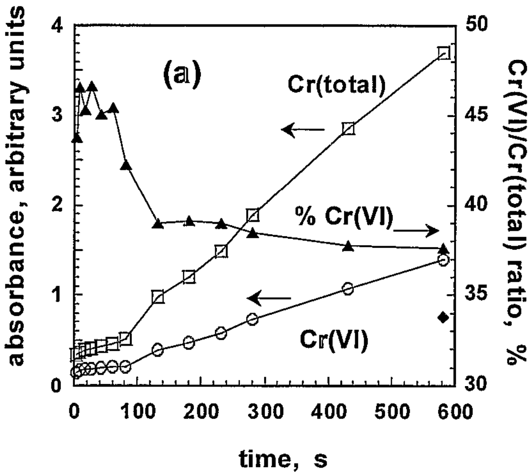


Figure 4. Changes in the amounts of Cr(VI) and Cr(total) and the ratio of Cr(VI)/Cr(total) in a CCC formed on AA 1100.



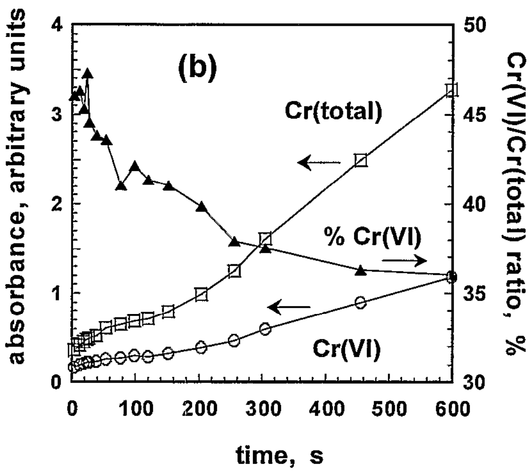


Figure 5. Changes in the amounts of Cr(VI) and Cr(total) and the ratios of Cr(VI)/Cr(total) in CCCs formed on (a) Al-0.2%Cu, and (b) Al-4%Cu. The black diamond in Figure 5(a) indicates the ratio of Cr(VI)/Cr(total) measured after washing out by distilled water, subsequent to the measurement.

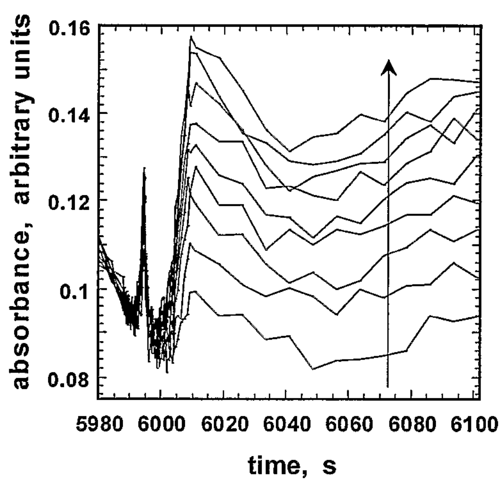


Figure 6. A series of *in situ* XANES spectra of a continuously growing CCC on Al-0.2%Cu. Note that the cell used was different from that shown in Figure 1. The arrow indicates an increase in exposure time.

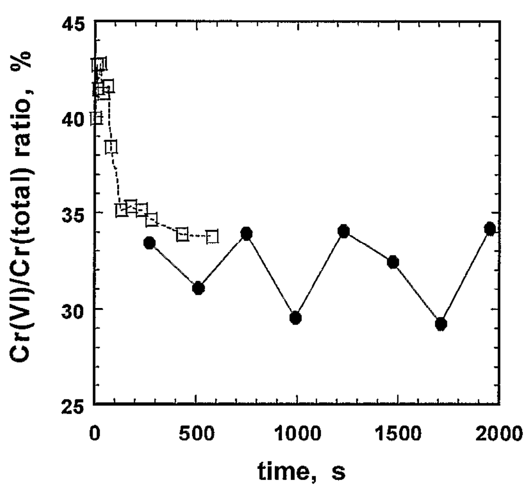


Figure 7. Changes in the ratio of Cr(VI)/ Cr(total) in a CCC film formed on Al-0.2%Cu (black circles). The result from Al-0.2%Cu subjected to the repeated exposure (Figure 5(a)) is also shown (white squares); these have been corrected by the datum measured after washing out (black diamond in Figure 5(a)).

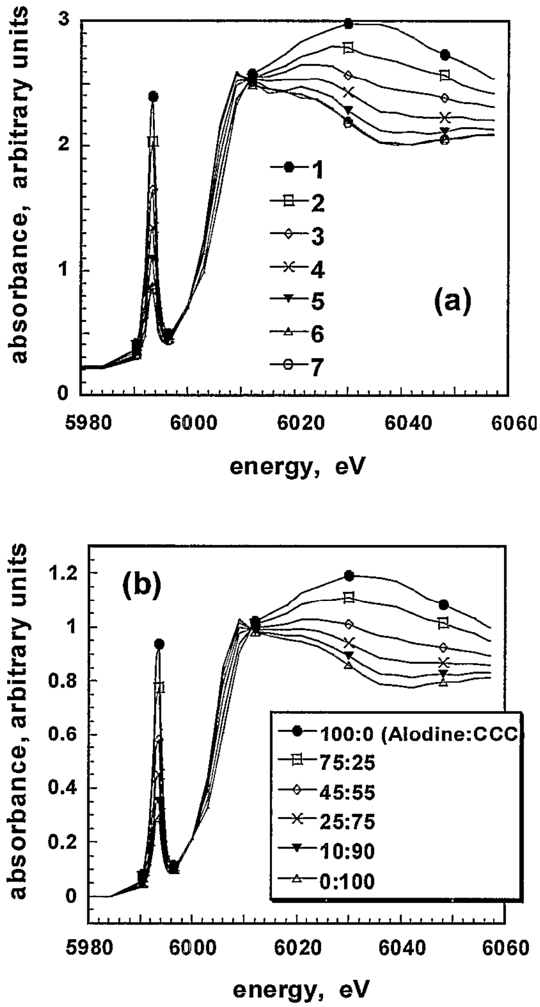


Figure 8. (a) Time-lapse XANES measurements to monitor changes in both electrolyte and a CCC simultaneously during solution exposure for AA 1100. (b) Calculated XANES spectra based on those of the Alodine solution (curve 1 in Figure 8(a)) and of the CCC (curve 6 in Figure 8(a)).

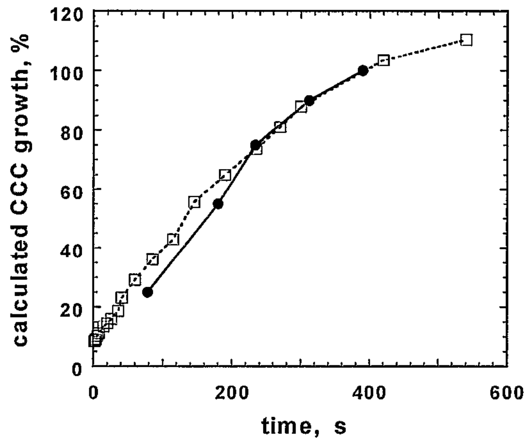


Figure 9. A CCC growth rate for AA 1100 estimated from modeling (black circles). Also shown (white squares) is the growth rate of CCC determined from the Cr(total) absorbance for the repeated exposure measurements (Figure 4).