Analytical electron microscopy study of new class material Cr$_2$AlC for coating applications at high temperature environments

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Abstract. The interactions between electron and specimens produce wide range of secondary signals from the specimen that can be used in analytical electron microscopy. These signals will give us chemical information and electronic structure information of specimen atoms. Two techniques which based on these secondary signals, X-rays energy-dispersive spectroscopy (XEDS) and electron energy-loss spectroscopy (EELS), are very powerful to be used for characterization materials. These two techniques are complementary each on the other. The former is very useful to quantify heavy elements and the other is very suitable to identify light elements as oxygen and carbon. In this report, we demonstrated the capability of these techniques to investigate microstructure evolution during the oxidation process of thin film Cr$_2$AlC at 1320 ºC. This thin film belongs to MAX phase, a new class material, and becomes a promising candidate for coating applications since it exhibits a good oxidation resistant.

1. Introduction
Since it has been invented almost 100 years ago, transmission electron microscope becomes a very important instrument for characterizing materials. For imaging, the modern TEM can achieve resolution up to 0.5 pm which is already smaller than atomic neighborhood distance. TEM offers other possibility to characterize materials. The electron specimen interaction produces secondary signals which can be used as addition to imaging techniques. These secondary signals contain chemical information and a lot of details of the specimen. The use of these signals on TEM is known by Analytical Electron Microscopy (AEM). AEM uses X-rays energy dispersive spectroscopy (X-EDS) and electron energy loss spectroscopy (EELS). With the help of better equipment, AEM opens very important possibility to explore the properties of specimen.

As one type of ionizing radiation, electrons capable to remove the tightly bound, inner-shell electrons from the attractive field of the nucleus by transferring some of its energy to individual atoms in the specimen. Secondary signals will be produced during electron-specimen interactions as seen in figure 1(a). One of these signals is produced from generated X-rays photons in beam-specimen interaction. This X-rays have energies characteristic for the different elements in the specimen and can be used in AEM analysis. These X-rays will be captured by energy-dispersive spectrometers (EDS). These spectrometers use lithium-drifted silicon Si(Li) solid state X-ray detectors, intrinsic or high-purity Ge (HPGe) EDS detectors or Si-drift detectors which was
mainly be used in this work. This technique is known as X-rays energy-dispersive spectroscopy (X-EDS). Detail explanation about the principle of EDS can be found in literature [1, 2]. Unlike EDS in SEM system, the condition in TEM is more complicated. The geometry of specimen and also EDS detector requires more depth consideration. For quantitative analysis, the counts that collected by detector need to be statistically significant enough. Due to the geometry setup one needs to find the optimal detector position during the acquisition.

The second type of secondary signals comes from electrons which may have no lost or only small amount energy due to inelastic collisions. The energy distribution of electrons that have come through the specimen is analyzed by the technique called electron energy-loss spectrometry (EELS). These phenomena tell us many specific information of specimen atoms such as chemistry and electronic structure. These information reveal details of these atom’s bonding, nearest-neighbor atomic structure and the free electron density. To get more detail explanation about EELS, reader is strongly suggested to read work from Edgerton [4].

EELS signals can also be used to produce an image from specific electrons. Unlike the conventional TEM, which uses all electrons that pass through the specimen, one technique that allows image formation with electrons that have undergone selected energy losses in the specimen has emerged recently. The technique, energy-filtered TEM (EFTEM), detects chemical contrast in specimens by adjusting an energy filter to accept only electrons that have lost energy in core ionizations of selected elements. Furthermore, the energy filter can also pass the zero-loss electrons, i.e. electrons that do not experience inelastic scattering. As a result, all bright-fields and diffraction patterns taken with energy-filter will only use purely elastically-scattered electrons. As a consequence, the chromatic aberration for thicker specimens and the inelastic background are eliminated. The chemical contrast can be used to map the element distribution in the specimen. There are two methods that are mainly used for elemental mapping, the jump ratio map or two windows technique [5] and the three windows technique [6]. Detailed explanation for these two techniques can be found in the literatures [3, 5–9].

A modern TEM is a mandatory to utilize maximum results of AEM techniques. It must be equipped with analytical equipments such as energy dispersive X-rays and electron energy-loss spectroscopy. Furthermore it should also have scanning capability, known as scanning TEM (STEM), which allows the specimen to be scanned point by point with a small probe. In order to obtain a small probe with a diameter of $\approx 0.25$ nm, a large aperture angle must be used. Two additional pairs of scan coils below the condenser lenses allow the raster process to be performed. Besides producing SE signal as in SEM instruments, the transmitted beam can also produce bright field, dark field and annular dark field (ADF) images. The latter mode is possible because of the presence of an annular detector which is positioned below the specimen that will collect electrons diffracted in large angles.
2. Experiments

A new class material, MAX phase Cr$_2$AlC is known as promising candidate materials for advanced technologies. It displays a unique combination of properties, including low density, high elastic modulus, easy machinability, excellent thermal shock resistance and damage tolerance. Unfortunately, only few descriptions about the oxidation behavior of Cr$_2$AlC are reported in the literature. In bulk systems, Lin et al. [10] have reported that Cr$_2$AlC has a parabolic rate constant $k_p = 6.8 \times 10^{-10}$ kg$^2$m$^{-4}$s$^{-1}$ at 1200 ºC, which is 24 times lower than Ti$_3$SiC$_2$ at 1200 ºC [11–14]. Later on, several extensive investigations on the oxidation resistance of bulk Cr$_2$AlC were reported by Lin et al. [10] and Tian et al. [15] which clearly show that Cr$_2$AlC exhibits an excellent oxidation resistance.

In the selective oxidation of a material containing Cr and Al, both Al$_2$O$_3$ and/or Cr$_2$O$_3$ scales can be formed. Cr$_2$O$_3$ forming alloys generally contain less than 2-3% Al and 15% or more Cr. On the other hand, Al$_2$O$_3$ forming alloys can be found in material with as low as 5% Al. Environments also play an important role. It has been known that at high-temperatures (above 1000 ºC) Al$_2$O$_3$ will be formed more likely than Cr$_2$O$_3$ [16].

In bulk systems, Lee, et al. have showed that only a thin external Al$_2$O$_3$ oxide layer was formed after 336 h of oxidation at 1300 ºC in air [17]. They have also showed the Al-depletion and Cr-enrichment have occurred underneath the Al$_2$O$_3$ layer. Microstructure investigations have revealed that the surface grains of $\alpha$-Al$_2$O$_3$ were fine but the inner grains were coarse and more columnar. The $\alpha$-Al$_2$O$_3$ has grown very slowly and the measured oxide thickness was only $\approx 27$ µm. In this report, microstructure evolution of thin film Cr$_2$AlC oxidized at 1320 ºC will be investigated to understand their oxidation behavior.

Detail for sample fabrication and also other supporting experimental for investigated material can be found in work of Hajas et.al [18].

Prior the AEM investigation were performed, microstructure analysis by means of SEM were done for each selected specimen. A field emission ZEISS DSM 982, equipped with EDS system from Oxford was used. To produce almost homogeneous TEM specimens thicknesses, all specimens are prepared as thin Lamelle by focused ion beam technique on FEI Strata 205. This technique produced lamellae of 12 - 15 µm length and 4-6 µm width with the thickness of less than 100 nm. The AEM investigation was performed on Zeiss Libra 200 FE. It has schotky field-emission source operated at 200 kV. It has also STEM capabilities which as described above are very important for AEM analysis. The microscope is also equipped with in-coloumn corrected omega filter, X-Flash EDS detector from Bruker and HAADF detectors from Fischione. All aquired data were processed using Esprit and DigitalMicrograph™ for EDS and EELS analysis respectively. Typical parameters used in this work are listed in table 1.

| Parameter            | EDS       | EELS | EFTEM |
|----------------------|-----------|------|-------|
| Mode of Operation    | STEM      | STEM | TEM   |
| Type of measurements | spot, line scan, maps | spot | three windows |
| Specimen Tilt        | $5$ ºC    | NC*)  | NC**) |
| Acquisition time     | 180 - 3600 s | 1 - 5 s | 1 - 50 s/image |
| $\alpha / \beta$     | NC*)     | 17.43 / 7.99 m-1 | 17.43 / 18.50 m-1 |
3. Results and discussion

The Cr$_2$AlC thin films were oxidized at 1320 ºC in TGA for three different total times: 4 min, 39 min and 282 min, with the resulting scale thicknesses of approximately 1 µm, 3 µm and 6 µm, respectively. In this report we concentrate our discussion for specimen with the thinnest oxide scale to get the benefit of AEM. Figure 2(a) shows the SEM cross sectional image of the specimen with 1 µm oxide scale which will be noted as Cr-1 specimen. A dense and continuous alumina scale with the thickness approximately 1 µm oxide scale is observed. An additional interlayer, presumably consists of chromium carbide, has formed below the scale interface. Small voids are also found in the Cr$_2$AlC film. In figure 2(b), detail morphology of Cr-1 cross-section can be seen from bright-field (BF) image. A dense and continuous alumina scale with a wavy interface can be seen clearly. SAED analysis identified Cr$_2$AlC as the main phase of the thin film along with Cr$_3$C$_2$ found below the scale interface.

![Figure 2.](image)

**Figure 2.** (a) The SEM cross-section of Cr-1 specimen. Electron beam interaction with the specimen. (b) BF image of the Cr-1 specimen. SAED patterns from region 1 and 2 show that the specimen consists mainly of Cr$_2$C$_3$ and Cr$_2$AlC phases.

More detail investigations were performed by means EDS mapping as shown in figure 3. The STEM-ADF images taken from oxide scale of specimen Cr-1 with corresponding EDS elemental maps for Cr, Al, C, and O, respectively. EDS map revealed that chromium rich area, presumably chromia formed at outer part of the scale and scale-matrix interface respectively. Aluminum depletion can be seen from aluminum map at outer part alumina scale. Higher magnification of EDS maps show chromium oxide rich precipitates distribution on area close to the interface (figures 3(g) and (h)). Chrome-rich interlayer in size of 250 nm is clearly visible at upper part of the alumina scale. Additionally groups of chromium-rich precipitates were also formed at inner part of alumina scale. Unfortunately from EDS map, carbon distribution, especially in alumina scale could not be identified clearly.

Table 2 shows chemical analysis from areas marked in figure 3(a) and 4(a). It can be seen that EDS detected oxygen and include it into the calculation. It is because both C and O peaks locate close to each other at low energy. EFTEM map was used to overcome this problem (figure 4). From EFTEM elemental maps, it is verified that no oxygen was detected on matrix as that has been confirmed by EDS quantification. Moreover slightly carbon enrichment was also detected at the precipitates close to interface. Additionally, the chromium elemental map has also suggested that chromium was dissolved in the alumina scale.
Figure 3. (a) STEM-ADF image of cross-section Cr-1 specimen. (b) STEM-EDS combinational and (c-f) EDS maps of Cr, Al, C and O. EDS map at higher magnification of Cr (g) and C (h) elemental maps.

Table 2. EDS and EELS quantification from selected areas

| Position | EDS wt% Cr | EDS wt% Al | EDS wt% C | EDS wt% O |
|----------|-------------|-------------|-------------|-------------|
| Position 1 | 76.56 | 17.15 | 2.43 | 3.86 |
| Position 2 | 85.20 | 0.26 | 3.00 | 11.54 |

| Position | EELS at% Cr | EELS at% C | EELS at% O | EELS N |
|----------|-------------|-------------|-------------|--------|
| Position A | 59.09 | 40.91 | - | - |
| Position B | 27.09 | 23.06 | 19.46 | 30.40 |
| Position C | 30.02 | - | 69.98 | - |

Figure 4. (a) EFTEM elemental maps of the scale region of the Cr-1 specimen and elemental maps of (b) Cr, (c) C and (d) O. (f) RGB map shows distribution of these elements more clearly (especially for carbon). (f-h) EELS spectra acquired from outer part of alumina, Cr-rich precipitates and film marked by position 1, 2 and 3 respectively.

To strengthen EFTEM elemental map results, STEM-EELS analysis was performed. Figure 4(f-h) show EELS spectra were taken from outer part of alumina, Cr-rich precipitates and film. Once again, on the matrix part, no presence of oxygen can be detected and quantification gives 59.09 wt% Cr and 40.91 wt% C. This results close to EDS-quantification if the concentration of oxygen is excluded. At Cr-rich area at outer scale, where aluminum depletion zone, by combining the aluminum EDS map with EELS
quantification results, probably CrO$_2$ formed in this area. Interestingly, Cr-rich precipitates formed at inner scale, as addition to Cr, C and O, N was also detected by EELS spectra (figure 4.g) EELS quantification results suggested that probably a mixture of CrC and spinnel aluminum nitride.

4. Summary and conclusions
The use of Analytical Electron Microscopy (AEM) to investigate Material for high temperature applications was presented in this work. The STEM capability gives AEM possibility to reveal more information in higher spatial resolution than conventional TEM. The quantitative analysis using EDS is very straight forward and very suitable for elements with atomic number higher than Na (Z >11). Some extra precaution needs to be made such as a very thin specimen, when quantification will be done for light elements. On the other hand, EELS is very useful to identify as well as quantify light elements. But to get better EELS results, a very thin specimen is necessary. The EFTEM method can be used to overcome contamination problem which normally appears in STEM analysis. The acquisition time of EFTEM and the use of parallel beam are advantages for beam sensitive materials especially to reduce contamination problem.

Albeit EDS and EELS techniques have their pros and cons, they complement one another. At the end, it is clear that the AEM is an advanced technique to obtain more information on chemical analysis.

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References
[1] Goldstein J et al 2003 *Scanning Electron Microscopy and X-rays Microanalysis* (New York: Springer US) chapter 4 pp 170-76
[2] Williams D B and Carter C B 1996 *Transmission Electron Microscopy A Textbook for Material Sciences* (New York and London: Plenum Press) chapter 1 p 7
[3] Brydson R D. 2001 *Electron Energy Loss Spectroscopy (Microscopy Handbook)* (London: Taylor & Francis) chapter 5 p 69
[4] Egerton R F 1975 *Philos. Mag.* 31 199-215
[5] Krivanek O L et al 1980 *Proc. 51st Annual Meeting MSA (San Fransisco)* pp 586-87
[6] Jeanguillaume C 1978 *Ultramicroscopy* 3 237-42
[7] Hofer F et al 1995 *Ultramicroscopy* 59 15-31
[8] Jäger W and Mayer J 1995 *Ultramicroscopy* 59 33-45
[9] Schnenner M et al 1996 *Ultramicroscopy* 65 95-9
[10] Lin Z J 2007 *Acta Mater.* 55 6182
[11] Barsoum M W et al 1997 *J. Electrochem. Soc.* 144 2508
[12] Li S et al 2003 *Mat. Sci. Eng. A-Struct.* 341 112
[13] Sun Z et al 2002 *Oxid. Met.* 57 379
[14] Yang S L et al 2003 *Oxid. Met.* 59 155
[15] Tian W 2008 *J. Mater. Sci.* 43 2785-91
[16] Quadakkers W J and Singheiser L 2001 *Mater. Sci. Forum* 369-372 77-92
[17] Lee D B et al 2007 *Corros. Sci.* 49 3926-34
[18] Hajas D E et al 2011 *Surf. Coat. Tech.* 206 591-98
