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Research Article

Development of an Oxidation Resistance Surface Coating on Niobium Base Metal

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ABSTRACT

Nb (niobium) and Nb-based alloys are promising refractory materials for use at high temperatures. However, due to the weak resistance to high temperature oxidation, a dramatic modification in oxidation resistance is required to use Nb-based refractory materials. Alloying Nb with other elements improves its mechanical properties and oxidation resistance to some extent. An improvement in oxidation resistance by forming Al (aluminum) based coating with dense Al2O3 by utilizing different methods seems a prospective way for developing Nb-based refractory materials.

In the current study, halide activated pack cementation (HAPC) and subsequent plasma electrolytic oxidation (PEO) were combined to form an oxidation-resistant coating on niobium base metal. Prospective Al2O3 phases in amorphous or various kind of crystalline forms at the top were formed by anodic oxidation of cementation layer and modified to oxidation resistant α-Al2O3 by subsequent annealing at 1000oC for 2 hours in argon gas.

Comparing weight changes after oxidation tests shows that formed protective oxide film has a noticeable positive effect on the protection of Nb metal at high temperatures.

Keywords: *High temperature oxidation, refractory metal, niobium, pack cementation, plasma electrolytic oxidatio*

Niyobyum Altlık Metali Üzerinde Oksidasyona Dayanıklı Bir Yüzey Kaplamasının Geliştirilmesi

ÖZET

Nb (niyobyum) ve alaşımları yüksek sıcaklıklardaki kullanım için umut veren refrakter malzemelerdir. Ancak, niyobyumun yüksek sıcaklık oksidasyonuna karşı çok düşük direncinden dolayı, niyobyum bazlı refrakter malzemeleri kullanmak için oksidasyon direncinde önemli bir modifikasyona ihtiyaç duyulmaktadır. Diğer elementlerle alaşımlamak niyobyumun mekanik özelliklerini ve oksidasyon direncini bir dereceye kadar

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iyileştirmektedir. Farklı yöntemlerden yararlanarak, yoğun Al_2O_3'den oluşan Al-bazlı kaplama oluşturarak oksidasyon direncinde yapılacak bir iyileştirme niyobyum bazlı refrakter malzemelerin geliştirilmesinde olası bir yol olarak gözükmektedir. Bu çalışmada, niyobyum altlık metali üzerinde oksidasyona dayanıklı bir kaplama oluşturmak için halid aktivatörlü kutu sementasyonu ve ardından plazma elektrolitik oksidasyon yöntemi kombine edilmiştir. Sementasyon tabakasının anodik oksidasyonuyla oluşan amorf ve değişik kristal formlardaki Al_2O_3 fazları daha sonra argon gazı içerisinde 1000 ^oC'de 2 saat süren bir tavlama işlemiyle oksidasyona dayanıklı α-Al_2O_3'e modifiye edilmiştir.

Oksidasyon testleri sonrasıda ağırlık değişimlerinin karşılaştırılması oluşturulan koruyucu kaplamanın Nb metalinin yüksek sıcaklıklardaki korunmasında farkedilebilir bir koruyucu etkiye sahip olduğunu göstermektedir.

Anahtar Kelimeler: *Yüksek sıcaklık oksidasyonu, refrakter malzeme, niyobyum, kutu sementasyonu, plazma elektrolitik oksidasyon*

I. INTRODUCTION

The materials for high temperature applications have contributed to increase the performance of both jet engines and gas turbines on a large scale. However, for higher efficiency of advanced gas turbines, there is an increasing demand to the materials resistant to temperatures higher than the current application limits. Therefore, new materials of high melting point, low density, high temperature strength, and good oxidation resistant in the temperature range of 1300-1400^oC have been seeking.

Refractory materials have been often applied for the turbine applications for many years. Niobium (Nb) as refractory metal is a promising material with higher ductility at room temperature and lower density from nickel super alloys which are currently used. Nevertheless, use of Nb at high temperatures is limited to its poor oxidation resistance due to non-protective oxides since their volumes are higher than substrate metal [1].

Producing a protective coating on substrate metal is a common method for refractory metals. Pack cementation is one of the most competing technique among them [2,3]. Pack cementation is an in-situ chemical vapor deposition process. The pack consists of substrate to be coated, powders of the elements to be deposited on the surface (master alloy, e.g. Al, Cr, Si), and halide salt. The work piece to be coated is buried in this mixture in a retort and heated to a high temperature (e.g. 700-1100^oC). During process, the masteralloy reacts with the halide activator to yield volatile metal halides, which diffuse through the gas phase of the porous pack, and is deposited on the substrate. Due to the coefficient of thermal expansion mismatch between coating and substrate, coating is brittle.

Combination of different methods could bring out promising solutions for the development of oxidation resistant coatings. Hot dip aluminum coating and subsequent anodic oxidation to generate dense Al_20_3 films were studied by Kumon, Suzuki and Ono [4] to produce an oxidation resistant coating on niobium surface. After dipping Nb into a molten Al bath, an Al coating layer with a granular $NbAl_3$ interphase was produced on the substrate. An amorphous Al_2O_3 layer was produced by anodic oxidation of the Al coating, and crystallized to corrosion resistant α-Al_20_3 by a subsequent heat treatment under vacuum.

In the current study halide activated pack cementation (HAPC) and subsequent plasma electrolytic oxidation (PEO) was combined to form an oxidation-resistant coating on niobium base metal. Prospective Al_2O_3 phases formed by the anodic oxidation of cementation layer were modified to oxidation resistance α-Al_2O3 by subsequent modification treatment (MT) in argon gas.

II. EXPERIMENTAL METHOD

Pure Nb metal (99.99 wt%) were used as substrate in the experiments. After removing sharp corners by grinding, all the samples were pickled to remove hard oxides on the surface.

Halogen activated pack cementation method was chosen to deposit a niobium aluminide on the substrate metal. The pack composed of 5 g. Al, 2.5 g. NaF, and 42.5 g. Al_2O_3 was mixed thoroughly before cementation. The samples to be coated are buried in this mixture in a stainless steel retort, and heated to 950 ^oC for 6 h. After cementation process, all he samples were ultrasonically cleaned, rinsed with alcohol and dried in hot blowing air.

The coating surfaces were oxidised for 10 min. using plasma electrtolytic oxidation at 0.7 A/sample in a solution consisting of 5g/l $Na_3PO_4.12H_2O$ ve 1g/l KOH, and the oxidised surface was modified to stabil α-Al_2O_3 film in argon atmosphere at 1000 ^oC for 2 h.

The coated samples were oxidized in air at 800, 900, 1000, and 1100 ^oC for 4 hours to compare their oxidation performance. Weight changes were recorded after oxidation tests.

Both coated and oxidized samples were embedded in epoxy resin, followed by grinding on 240, 400, 600, and 1000 grit SiC papers, and polishing with 6, 3, and 1 μm diamond slurries for preparation of cross-sections. Stereo and scanning electron microscopes were used to characterize the coatings. Semi-quantitative energy dispersive spectroscopy (EDS) and X-ray diffraction analysis (XRD) were used to identify the phases in the coated and oxidized samples. XRD analysis was conducted in scan modes of $2\theta/\theta$ and 2θ with angular steps of 0.02 and scanning rate of 2^o/min.

III. RESULTS AND DISCUSSION

X-ray analysis of the deposited cementation layer (Fig. 1) indicates that the coating consists of $NbAl_3$ intermetallic (Fig. 2).

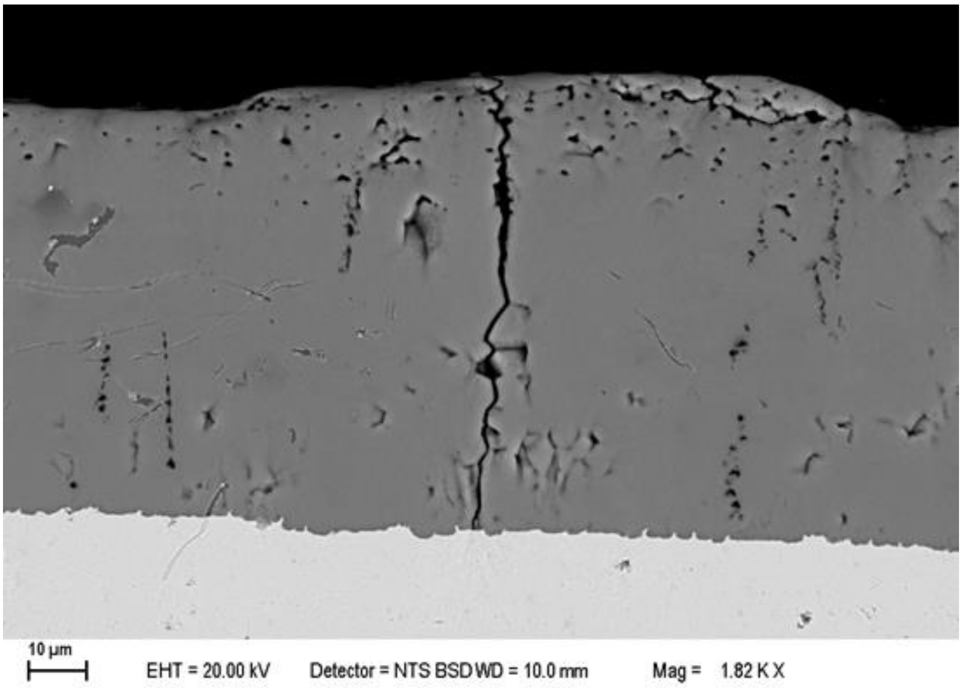


Figure 1. *SEM-BSE image of the cementation layer.*

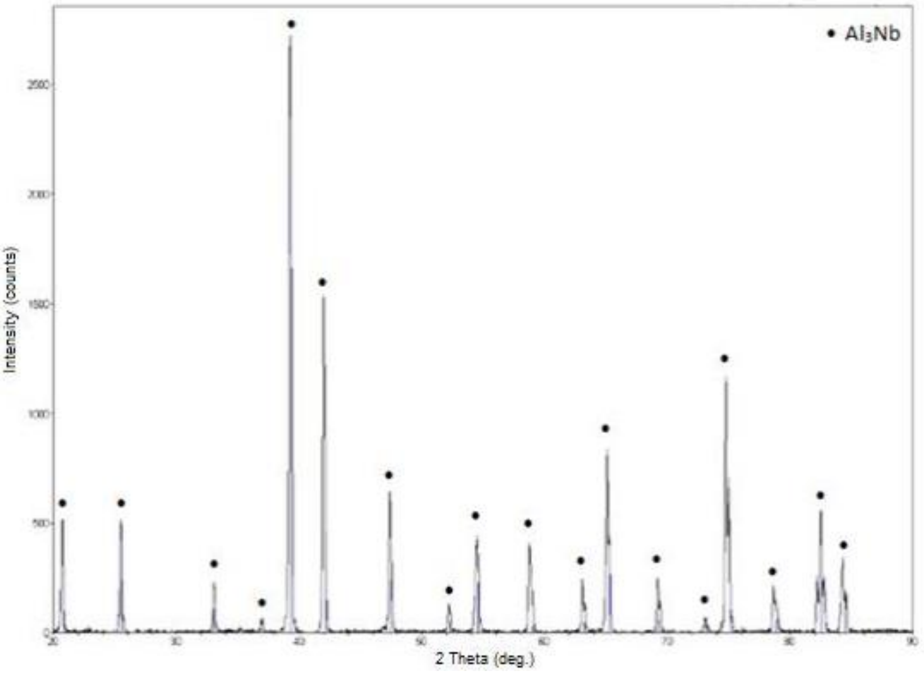


Figure 2. *X-ray analysis of the cementation layer.*

SEM-BSE observations of the PEOed sample reveal the surface morphology of typical micro arc oxidized surface with a fine crack network (Fig. 3). X-ray analysis indicates only $NbAl_3$ phase without Al_2O_3 (Fig. 4) presuming possibility of amorphous and/or too thin Al_2O_3 phases as reported by other researchers [4].

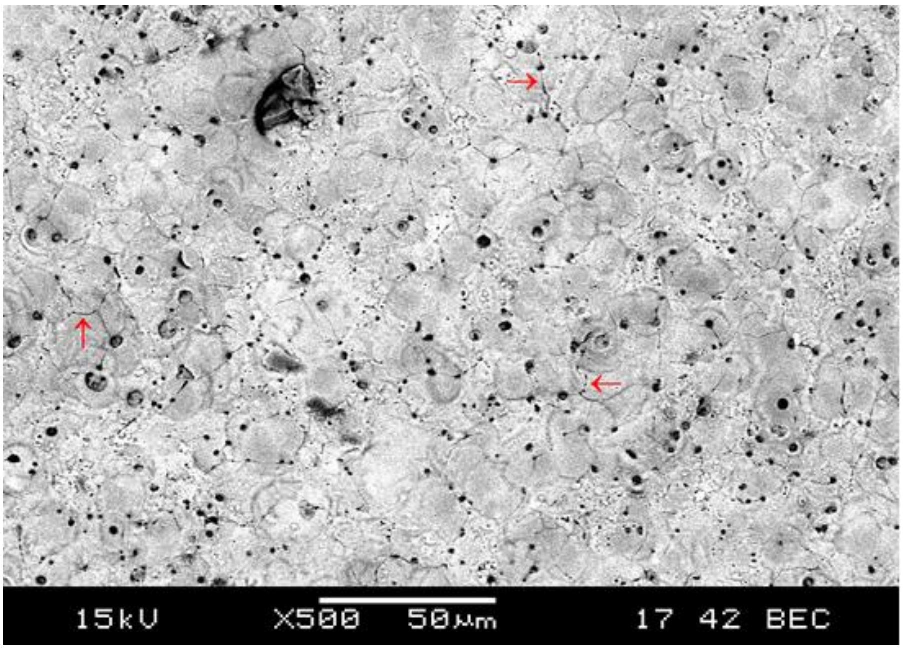


Figure 3. *SEM-BSE image of the PEOed sample*

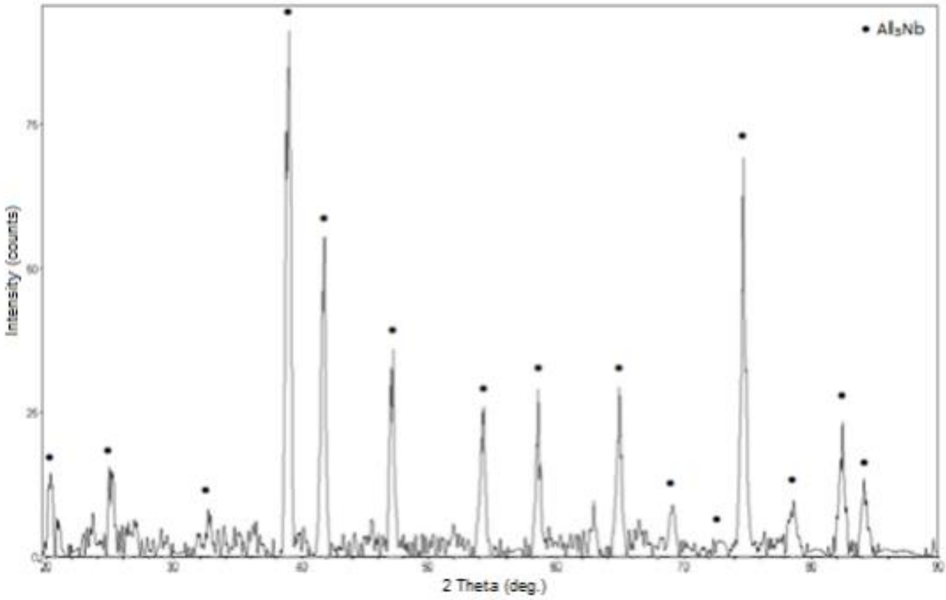


Figure 4. *XRD of the PEOed sample*

No crack was observed on the surface after MT (Fig. 5). Based on the XRD results (Fig.6), the phases on the surface after MT consist of $NbAl_3$ and α-Al_2O_3 (corundum).

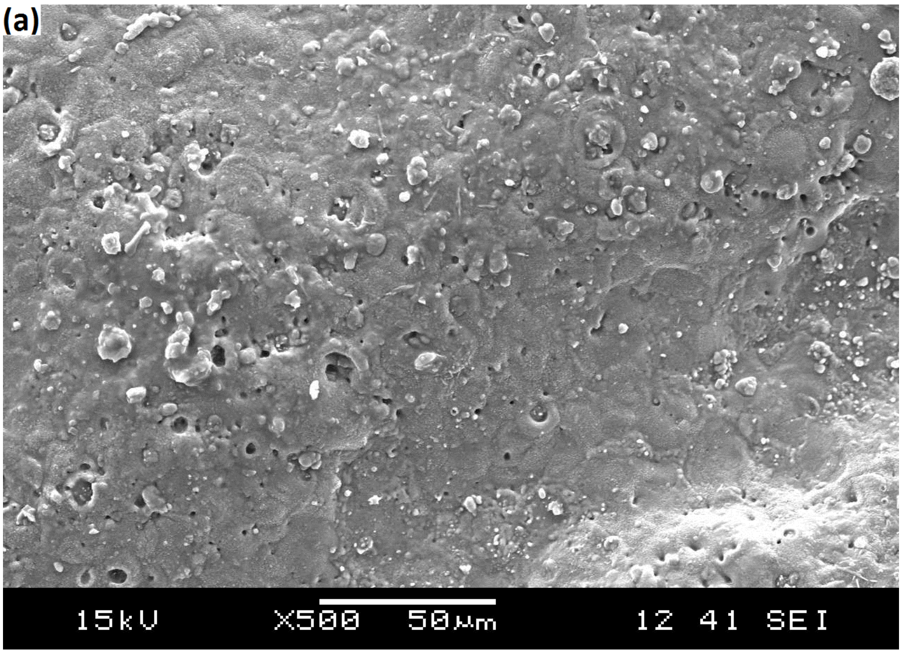


__Figure 5.__ SEM-SE (Seconder Electron) image of the MTed sample

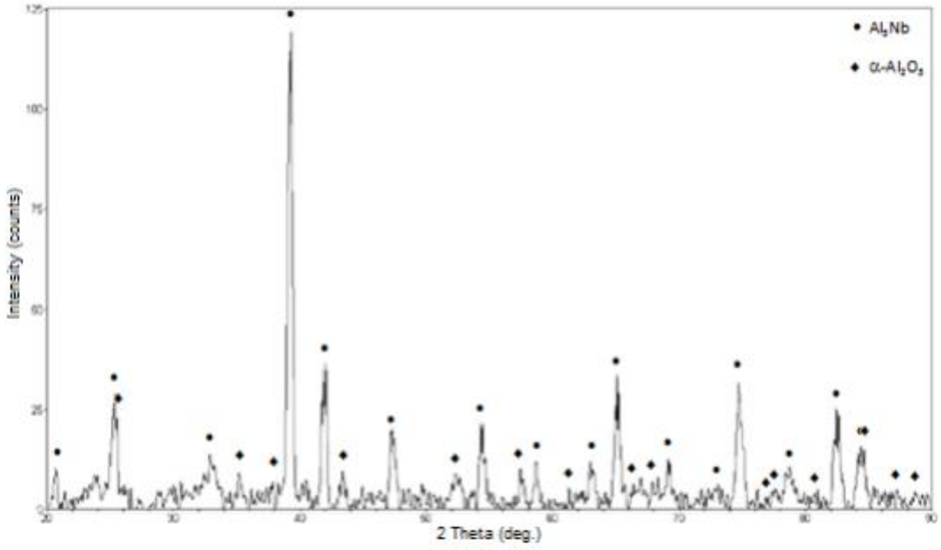
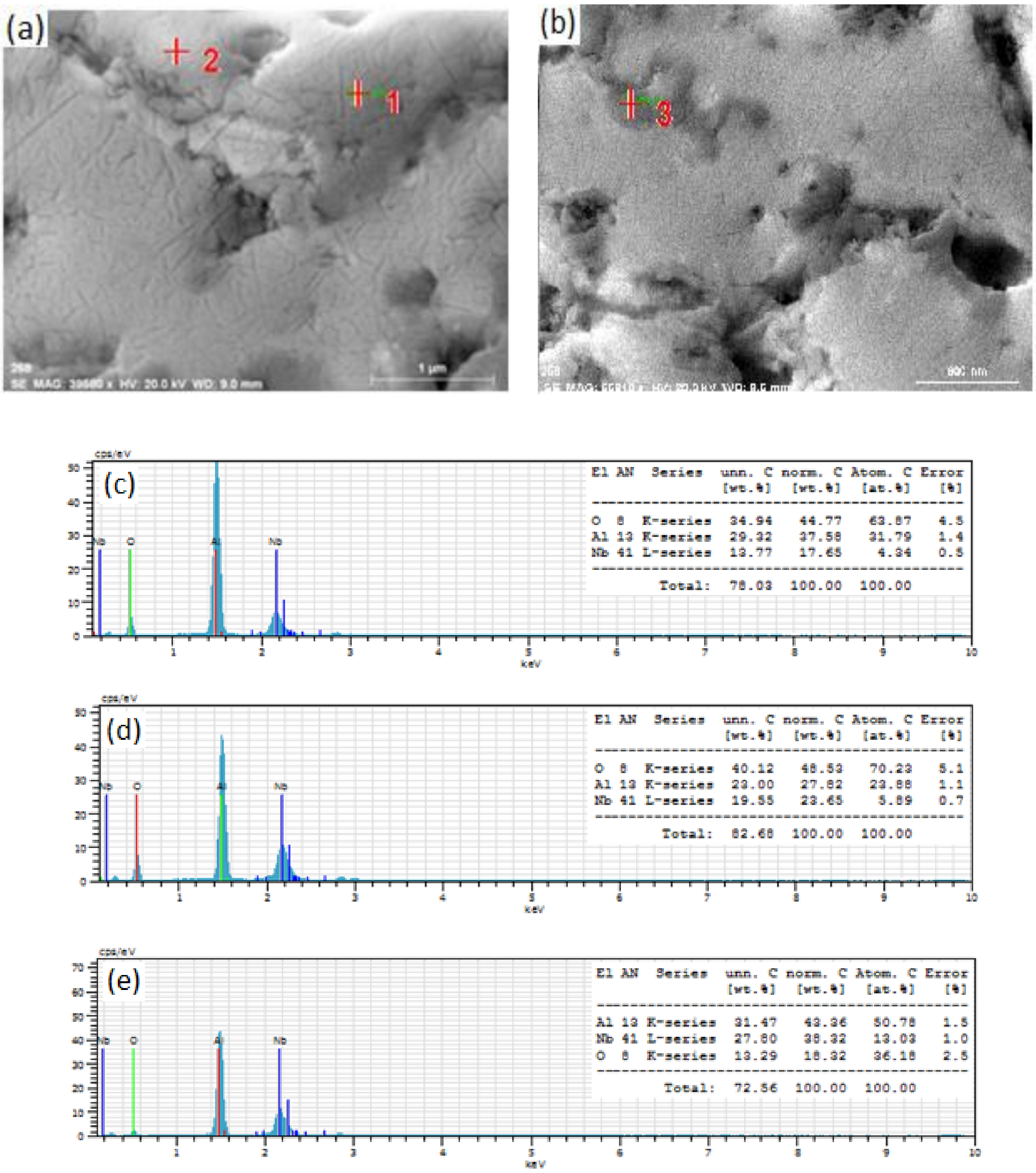


***Figure 6.** XRD of the MTed sample*

In Al-O system, aluminum oxide can be in different crystallinity forms depending on temperature, and however, thermodynamically stable only oxide is α-Al_2O_3. Natesan [5] reported that metastable γ-Al_2O_3, δ-Al_2O_3, and θ-Al_2O_3phases are transformed to α-Al_2O_3 in the following order in long term at high temperatures.

$$\gamma\text{-}Al_2O_3 \xrightarrow{850\ C} \delta\text{-}Al_2O_3 \xrightarrow{900\ C} \theta\text{-}Al_2O_3 \xrightarrow{1100\ C} \alpha\text{-}Al_2O_3 \qquad (1)$$

Oxidation of subsurface regions during oxidation tests is verified by the results of EDS analysis conducted on the regions close to surface (Fig. 7). It is thought that $NbAl_3$ transforms to Nb_2Al by the depletion of Al after anodic oxidation because of high affinity of Al to oxygen. During annealing at 1000°C for 2 h., a Nb_2Al intermetallic phase with less Al content between cementation layer and substrate was produced by diffusion (Fig. 8).

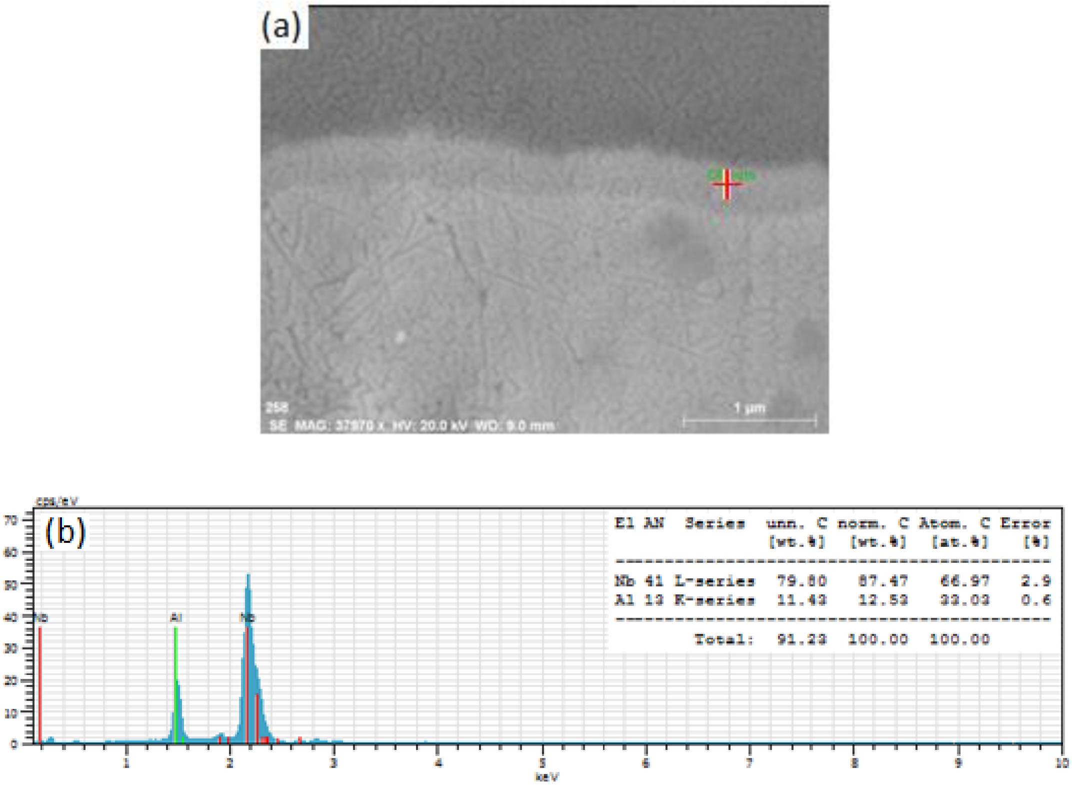


```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
-----------------------------------------------
O   8  K-series  34.94   44.77   63.87   4.5
Al 13  K-series  29.32   37.58   31.79   1.4
Nb 41  L-series  13.77   17.65    4.34   0.5
-----------------------------------------------
          Total:  78.03  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
-----------------------------------------------
O   8  K-series  40.12   48.53   70.23   5.1
Al 13  K-series  23.00   27.82   23.88   1.1
Nb 41  L-series  19.55   23.65    5.89   0.7
-----------------------------------------------
          Total:  82.68  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
-----------------------------------------------
Al 13  K-series  31.47   43.36   50.78   1.5
Nb 41  L-series  27.80   38.32   13.03   1.0
O   8  K-series  13.29   18.32   36.18   2.5
-----------------------------------------------
          Total:  72.56  100.00  100.00
```

Figure 7. *Subsurface regions of the modified sample (a) and (b), and EDS analysis of points “+1” (c), “+2” (d) and “+3” (e) in these regions.*



```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------
Nb 41 L-series   79.80   87.47   66.97   2.9
Al 13 K-series   11.43   12.53   33.03   0.6
--------------------------------------------
        Total:   91.23  100.00  100.00
```

Figure 8. *Interface between cementation layer and substrate after modification treatment (a) and EDS analysis of the point "+".*

Splits and spalls in scale layers were observed on the uncoated samples oxidized between 800-1100°C (Fig. 9). XRD analysis indicates that scale layers consist of Nb_2O_5 (Fig. 10). External niobium pentoxide, Nb_2O_5, which is a non-protective porous scale, continues to grow and thickness of the oxide layer increases with increasing temperature. The oxide layer reaches a limiting thickness at which it can no longer stand the compressive growth stresses due to the high volume ratio of the oxide and eventually fails allowing the penetration of oxygen into the metal surface. This process repeats with the development of a thick outer scale [6].

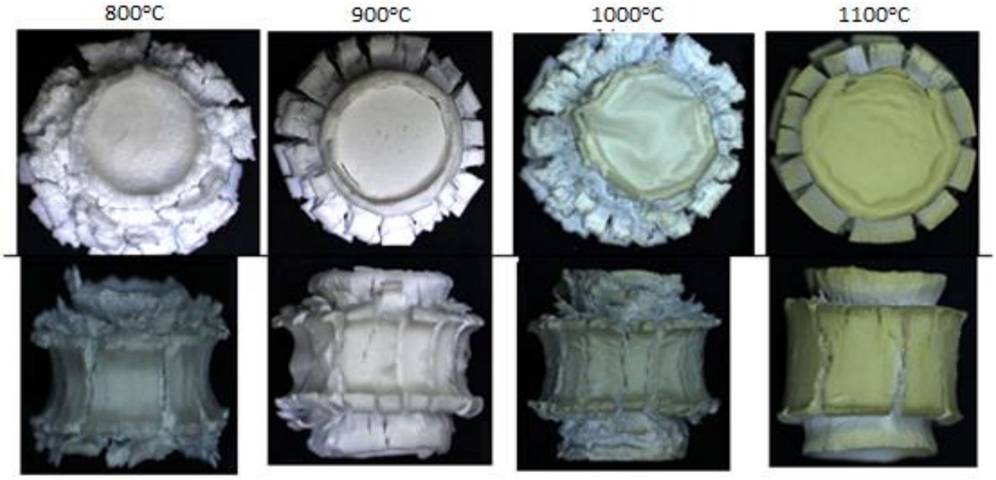


Figure 9. *Images of scale formation on the uncoated samples after oxidation tests: upper row from top (a), lower row from side (b).*

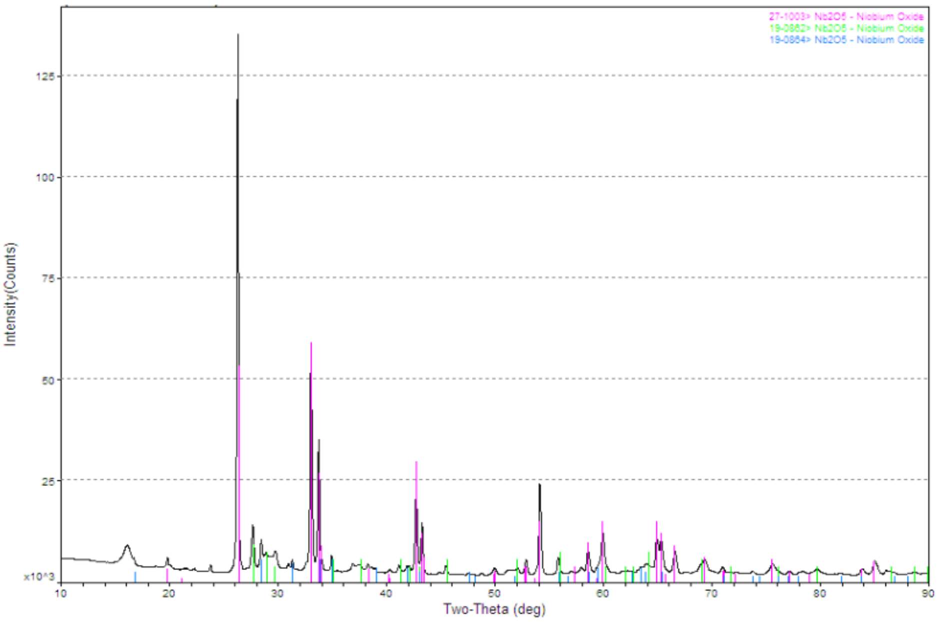
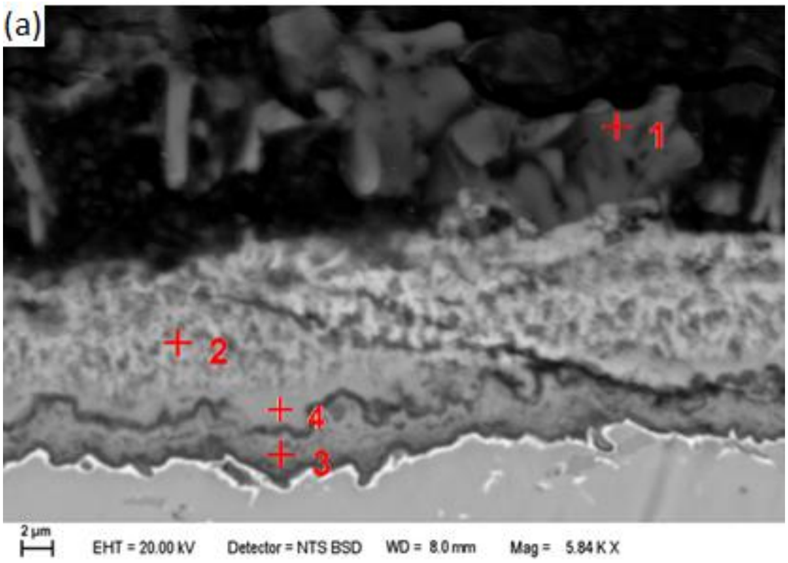
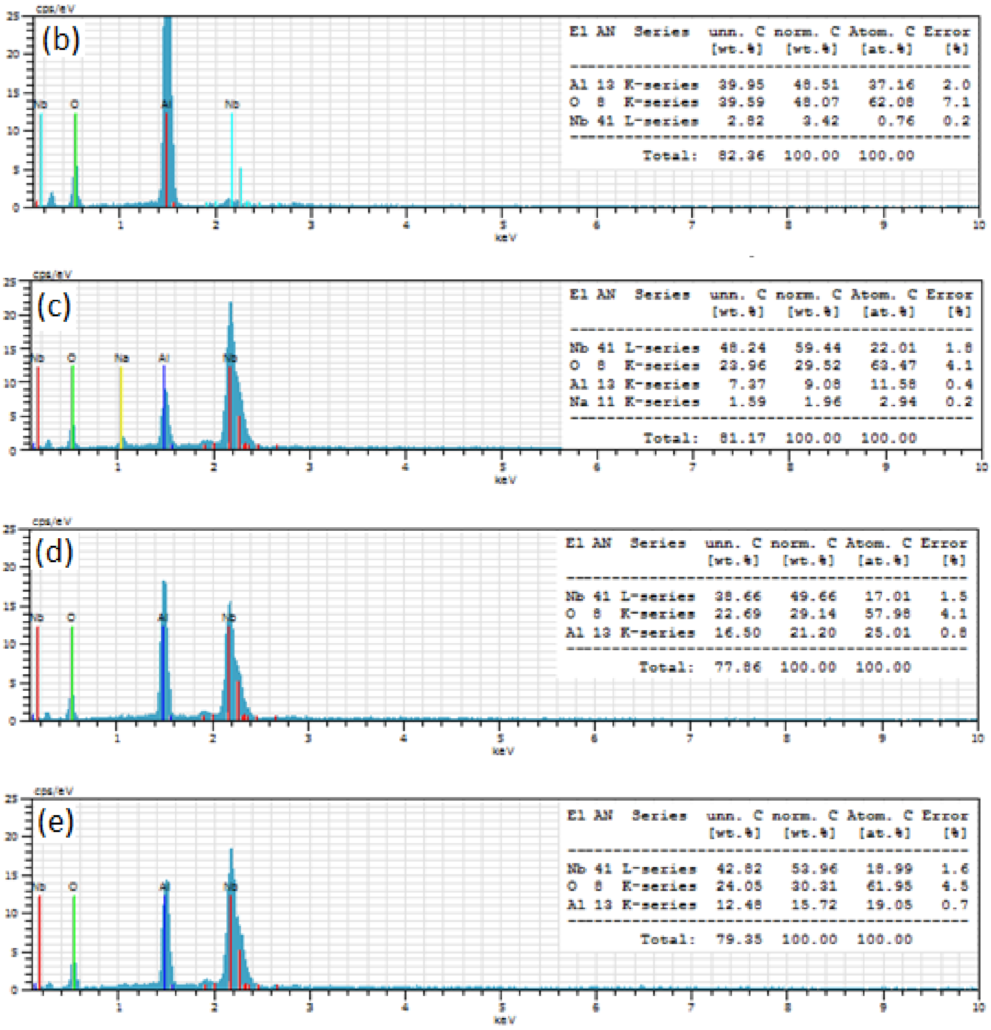


Figure 10. *XRD analysis of the uncoated sample after oxidation at 900ºC*

Splits indicate that a critical thickness has been reached faster than other regions since there are much surface area for oxygen penetration on the corners. Rounding corners could be a remedy for this occurrence.

Cemented samples have a layered scale structure after oxidation (Fig. 11). $NbAl_3$ single phase exhibits a quasi-linear oxidation rate due to the cracking and spallation of protective oxide scale [7]. The Nb_2Al phase is formed at the oxide - scale interface on which the fast-growing oxides $AlNbO_4$ and Nb_2O_5 are formed upon cracking of the oxide scale. The oxidation kinetics of $NbAl_3$ can be explained by α-Al_2O_3 growth according to the parabolic rate law between 1000 °C and 1200 °C. Between 650 °C and 1000 °C, $NbAl_3$ shows the phenomenon of disintegration with no appreciable bulk oxidation, known as "pest". A maximum in the oxidation rate of the $NbAl_3$ single phase is observed at 750 °C [7].





```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Al 13 K-series  39.95   48.51   37.16    2.0
O  8  K-series  39.59   48.07   62.08    7.1
Nb 41 L-series   2.82    3.42    0.76    0.2
---------------------------------------------
        Total:  82.36  100.00  100.00
```

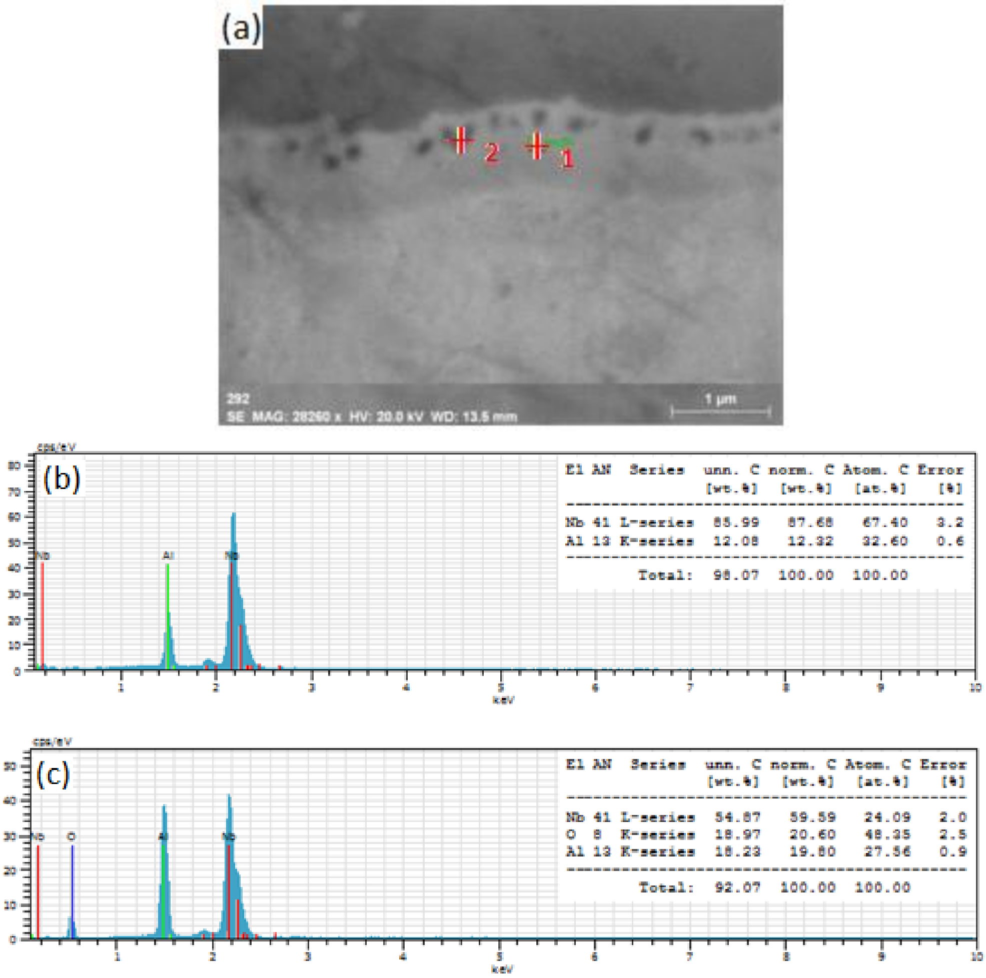
```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Nb 41 L-series  48.24   59.44   22.01    1.8
O  8  K-series  23.96   29.52   63.47    4.1
Al 13 K-series   7.37    9.08   11.58    0.4
Na 11 K-series   1.59    1.96    2.94    0.2
---------------------------------------------
        Total:  81.17  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Nb 41 L-series  38.66   49.66   17.01    1.5
O  8  K-series  22.69   29.14   57.98    4.1
Al 13 K-series  16.50   21.20   25.01    0.8
---------------------------------------------
        Total:  77.86  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Nb 41 L-series  42.82   53.96   18.99    1.6
O  8  K-series  24.05   30.31   61.95    4.5
Al 13 K-series  12.48   15.72   19.05    0.7
---------------------------------------------
        Total:  79.35  100.00  100.00
```

Figure 11. *EDS analysis of different scale layers formed on the cementation layer during oxidation at 1000ºC.*

Similar to the findings of oxide modification at 1000ºC for 2 hours, a Nb_2Al phase with less Al content is seen between cementation layer and substrate after oxidation at 1000ºC for 4 h. (Fig. 12-b). It is thought that diffusion rate is high enough at 1000ºC to create a Nb_2Al phase although it is not observed after cementation at 950ºC for 6 h. Also, based on SEM images and EDS analysis results oxide islands are observed in Nb_2Al phase which indicates high oxidation dissolution in this phase (Fig. 12-c).

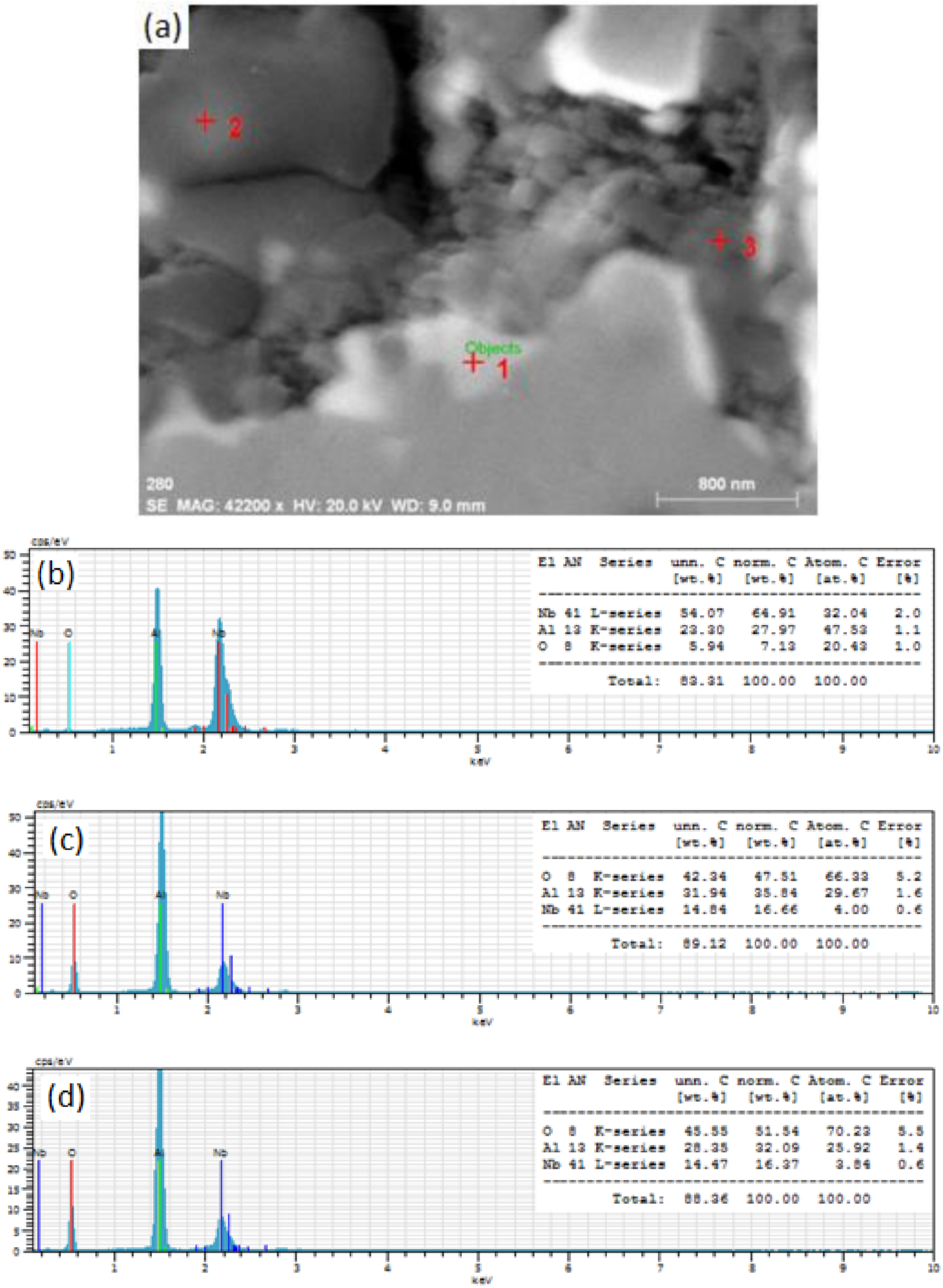


```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Nb 41 L-series  85.99   87.68   67.40    3.2
Al 13 K-series  12.08   12.32   32.60    0.6
---------------------------------------------
        Total:  98.07  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Nb 41 L-series  54.87   59.59   24.09    2.0
O  8  K-series  18.97   20.60   48.35    2.5
Al 13 K-series  18.23   19.80   27.56    0.9
---------------------------------------------
        Total:  92.07  100.00  100.00
```

Figure. 12. *Interphase between cementation layer and Nb substrate after oxidation at 1000°C for 4 h. (a), EDS analysis of this layer (point "+1") (b) and oxide islands in this layer (point "+2") (c).*

Similar to the oxidized cementation layer, a layered scale structure on the top and an interlayer between cementation layer and substrate metal are observed on the cross-section of PEOed sample after oxidation. Based on the EDS analysis of the points "1","2" and "3" points, various phases close to the surface were detected, among them point "1" most likely represent a Nb intermetallic with low Al content (Fig. 13). The points "2" and "3" points outoxide formations enriched with Al and O, most possibly Al_2O_3. These oxide formations can be explained pest-like disintegration of $NbAl_3$ dueto the selective oxidationof Al at grain boundaries, where it leads to Al depletion and Nb_2Al formations [7].



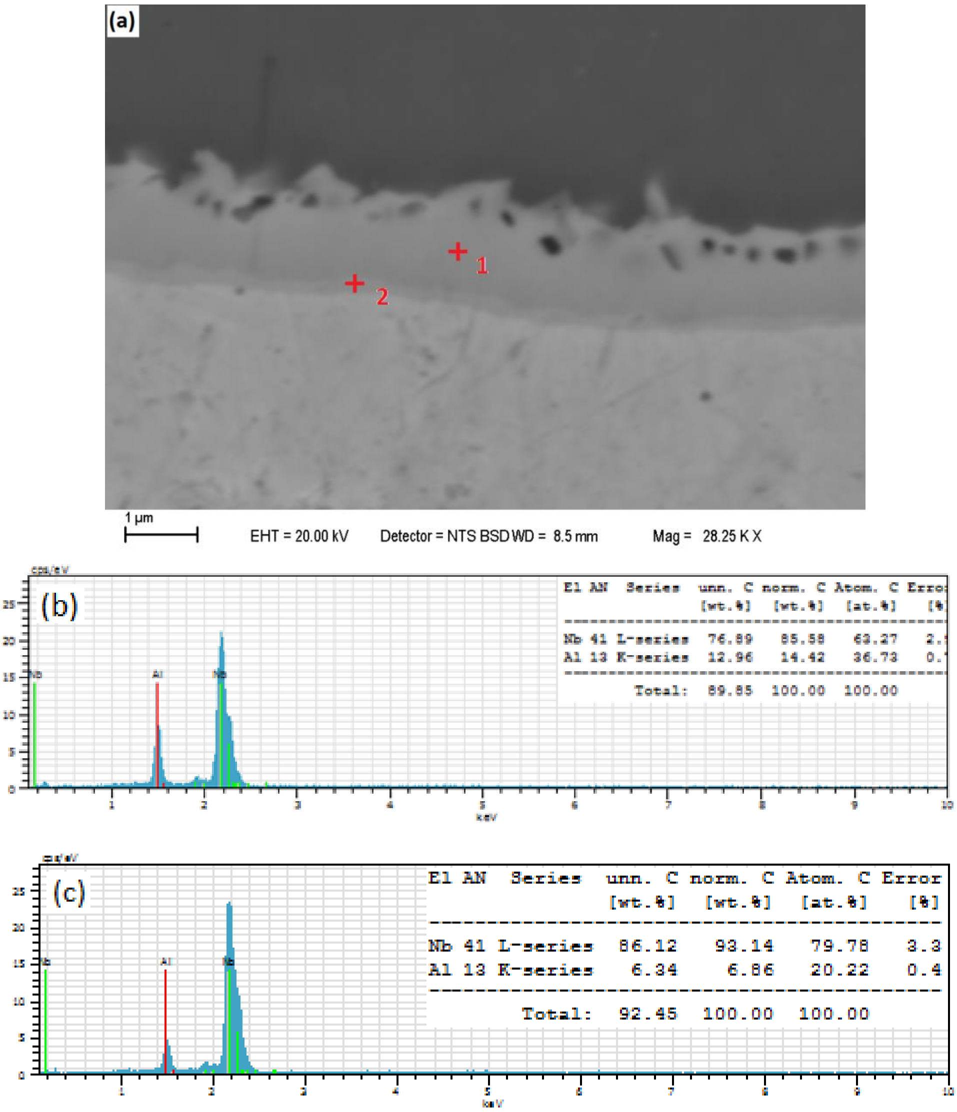
```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------
Nb 41 L-series  54.07   64.91   32.04    2.0
Al 13 K-series  23.30   27.97   47.53    1.1
O  8  K-series   5.94    7.13   20.43    1.0
--------------------------------------------
        Total:  83.31  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------
O  8  K-series  42.34   47.51   66.33    5.2
Al 13 K-series  31.94   35.84   29.67    1.6
Nb 41 L-series  14.84   16.66    4.00    0.6
--------------------------------------------
        Total:  89.12  100.00  100.00
```

```
El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------
O  8  K-series  45.55   51.54   70.23    5.5
Al 13 K-series  28.35   32.09   25.92    1.4
Nb 41 L-series  14.47   16.37    3.84    0.6
--------------------------------------------
        Total:  88.36  100.00  100.00
```

Figure 13. *Different regions close to the oxidized surface of PEOed sample and their EDS analysis.*

As seen in the cemented samples oxidized at 1000ºC, also the PEOed samples oxidized at 1000ºC exhibit Nb_2Al and Nb_3Al phases, additionally oxide particles lined up in Nb_2Al interlayer (Fig. 14).



```
El AN  Series  unn. C norm. C Atom. C Erro
               [wt.%]  [wt.%]  [at.%]    [%
--------------------------------------------
Nb 41 L-series  76.89   85.58   63.27    2.
Al 13 K-series  12.96   14.42   36.73    0.
--------------------------------------------
         Total:  89.85  100.00  100.00
```

```
El AN  Series  unn. C norm. C Atom. C Error
               [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------
Nb 41 L-series  86.12   93.14   79.78   3.3
Al 13 K-series   6.34    6.86   20.22   0.4
--------------------------------------------
         Total:  92.45  100.00  100.00
```

Figure 14. *EDS analysis of the intermetallics in the layer between $NbAl_3$ and metallic Nb.*

SEM-BSE surface image of the oxide layer of the MTed coating after oxiditaion at 1000°C displays the Al rich oxide formations (most probably Al_2O_3) (Fig. 15). It is thought that increased oxidation ratio in the modified samples ispossibly caused by crack formation during transformation of untransformed Al_2O_3 phases.

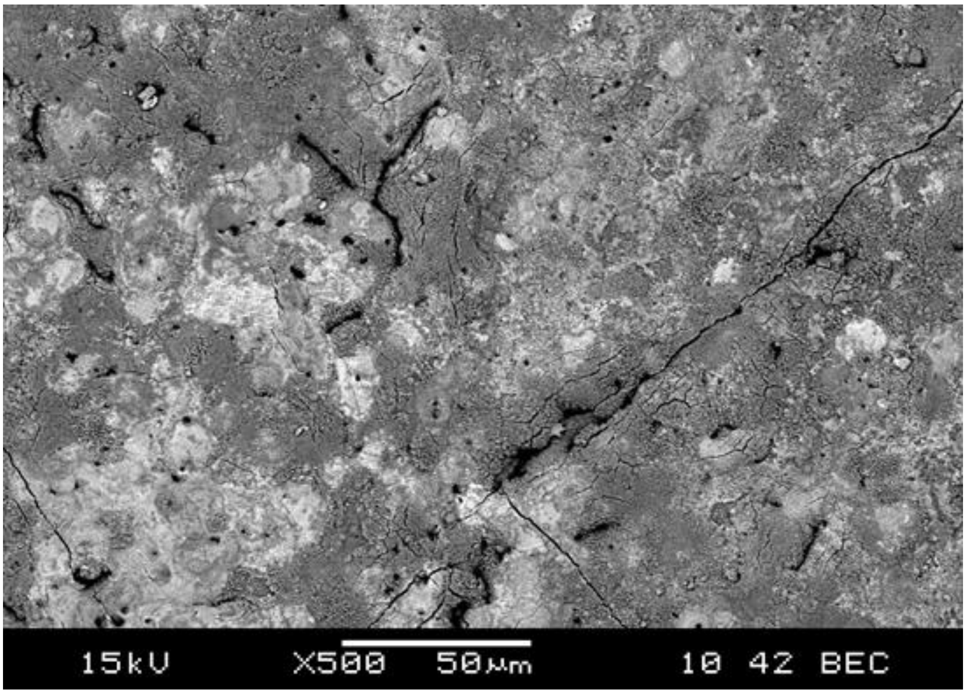


Figure 15. *SEM-BSE surface image of modified samples after oxidation at 1000°C.*

According to weight changes in Fig. 16, oxidation rate of the uncoated Nb metal display a linear increase, whereas it is considerably decreased by cementation and followed by PEO and MT. Compared to the uncoated Nb metal, oxidation trend of $NbAl_3$ over 1000°C is semi-linear even being slow. Weight changes in the PEOed and MTed samples after oxidation tests are very low, however oxidation of these samples can be noticeable after 1000°C. Compared to PEO, the protective effect of MT seems deterrioted at higher temperatures such as 1100°C. This can be explained by accelerated oxidation throughout the cracks generated during phase transformations of untransformed Al_2O_3 produced by PEO.

Although small degradation in protective coatings produced by PEO and oxide modification they prevent oxide diffusion innerward and exhibit a positive effect on oxidation resistance at high temperatures.

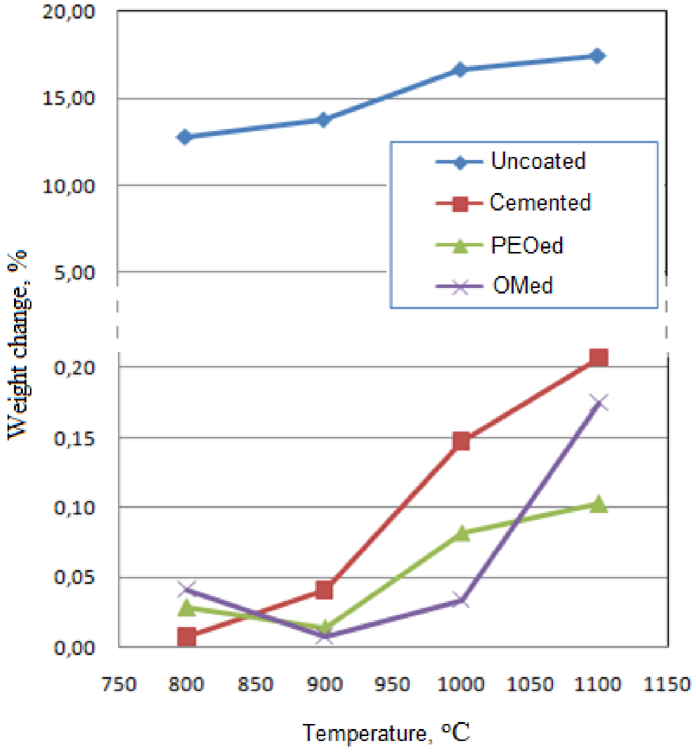


Figure 16. *Weight changes after oxidation tests.*

IV. CONCLUSION

Even though $NbAl_3$ cementation layer is quite effective on the improvement of oxidation resistance of Nb metal, cracks in the coating layer which deteriorate protective properties of the coating can be easily produced due to the mismatch between thermal expansion coefficients of the coating and substrate metal.

PEO and MT form a protective oxide film on the surface of the substrate metal.

Comparing weight changes after oxidation tests points out that formed protective oxide film has a noticeable positive effect on the protection of Nb metal.

By utilizing the positive effect of the PEO and MT, the thickness of the cementation layer can be reduced to avoid crack formations.

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