

# Phase Transformation on Interface between NiCoCrAlY Bond Coat and Substrate and Study of Thermal Barrier Coating as High Temperature Material

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**Abstract**—Thermal Barrier Coating material consists of Yttria stabilized zirconia (YSZ) as a top coat and bond coat NiCoCrAlY. It is used to protect NiCoCrAlY super alloys for high temperature applications due to its corrosion resistant properties and resistance to thermal fatigue. In the present study, top coat and bond coat were deposited on the substrate using plasma spraying process, followed by thermal fatigue treatment, by heating up to 900 °C for 5 hours and cooling down to 25 °C for 15 minutes, this process called one cycle. Thermal fatigue was conducted until the material failure. Electron microscope was used to analysis microstructure of the sample after thermal fatigue and x-ray diffraction to analysis phase changed on the interface between bond coat and substrate. The result showed that the specimens failed at 42 cycles (210 hours). A new phase identified as Ni<sub>3</sub>Al was formed.

**Keywords**—thermal fatigue, phase transformation, bond coat NiCoCrAlY, substrate NiCoCrAlY

## I. INTRODUCTION

The use of super alloys for applications at high temperatures has been long known in the industry and transportation. Especially for nickel-based super alloy, nickel super alloy has high corrosion and oxidation resistance. For the high temperature applications, it has been developed the thermal barrier coating. The coating system consists of ceramic top coat and bond coat. The top layer of ceramic works as heat resistance and bond coat serves as a protective substrate from attacks by oxygen and the decrease in the coefficient of thermal expansion between ceramic and substrate. Previous study suggested that the coating layer were easily to be failure, this failure caused by growth rate, morphology, microstructure and adhesives of aluminum oxide that is formed on the bond coat layer [1].

Thermal barrier coating (TBC) of ceramic top-coats made from Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) have been used successfully in gas-turbine engine applications for more than 30 years. YSZ has its favorable performance from a combination of properties that include low thermal conductivity, high thermal expansion coefficient, and phase stability to relatively high temperatures. With advanced engine requirements for improved performance and increased durability, a new generation of thermal barrier coatings is needed to provide greater insulation

(lower thermal conductivity) and permit higher operating temperatures [2].

Thermal barrier coating system has been widely used to protect the gas turbine engine components and engine power plant against heat and fluctuating environments. This system serves to reduce the temperature of the metal substrate and improve corrosion and oxidation resistance thus enhancing the efficiency of machines and extending the life of the components. Thermal barrier coatings provide an advantage for increasing inlet gas temperature without raising the surface metal temperature. Typical turbine blade coatings comprise a metal surface layer modified to generate a protective layer of aluminum oxide in service and an outer thermal barrier (usually porous yttria stabilized ceramic). They are approximately 150 microns thick. The coatings eventually fail mechanically in thermal cycling due to stresses generated by thermal expansion differences between the layers and growing layer of oxide metal [3].

In the present study, it was focused on analyzing the bond coat materials sprayed on metal base NiCoCrAlY, and followed by thermal fatigue analysis. The objective of the research was to study the microstructure evolution and phase changed on the interface bond coat and substrate NiCoCrAlY alloy.

## II. METHOD

The material studied was NiCoCrAlY alloy substrate taken from gas turbine blade for high temperature operation, while the bond coat layer used Merck NiCoCrAlY powder. For top coat layer yttria stabilized zirconia powder (YSZ) was selected. Flame spraying coating process used Thermo Spray Gun Type 5P-II, where the NiCoCrAlY substrate material was square-shaped, lined with two layers for the outer layer (top coat) of YSZ ceramics, the middle layer was the adhesive bond coat consisting of the powder NiCoCrAlY. Flame spraying was used in this study, where the material selected as coating material coating was in the form of powder, using acetylene gas fuel and oxygen to melt the powder material for covering the base metal.

Thermal fatigue experiment includes high temperature treatment in the furnace at 900 °C for 5 hours and then cooling at room temperature for 15 minutes, this was conducted for one cycle. Material characterization was done including x-ray diffraction (XRD) with Phillips MPD System to identify phase changes that occur during the process of thermal fatigue, while an electron microscope (JEOL SEM / EDX) was used to observe changes in the microstructure and identify the changes in the composition of the elements in the region interface.

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### III. RESULT AND DISCUSSION

#### A. Macrostructure Analysis on Specimen

Macrostructure analysis was performed on specimens without treatment and the specimens heated at 900 °C for 200 hours. Specimen shown in Fig. 1.a is still in good condition, with a ceramic layer covering the surface of a perfect specimen. This condition is obtained after the specimens coated by plasma spraying process. After the cycling thermal treatment process carried out at 900 °C, the specimens experienced physical changes gradually. In the first two cycles (one cycle is 5 hours of heating), the specimens have patches - black spot on its surface, as shown in Fig. 1.b, but it is still not showing defects or cracks. Defect is not found because the oxides on the surface of the top coat protected top coat surface from the burning surface due to heating. After five cycles, it had been shown cracks in the specimen, Fig. 1.c thermal barrier coating starts to fail when cracks occur, for topcoat thickness is less than 250 μm will lead to local separation at the region near the bond coat. This crack started at the corner of the specimen. The phenomenon of breakdown of the corners of the specimen can be explained because the corner is a section with the highest stress concentration. This is because of stress concentration in the specimen as a resulting the existence of residual stress. In TBC of ceramic coating, there are different variations of residual stress in each layer. The source of this residual stress is from the coating process itself, such as rapid cooling, solidification, thermal contraction and recovery of micro cracks due to stress, the differences in thermal coefficient of heat on the ceramic and bond coat.

These cracks occur only locally at first, but with increasing cycles, crack is getting wider and growing to another area of specimen. Because the thickness of the topcoat more than 250 μm, the crack will occur in ceramics, above the interface between the ceramic bond coat, which agrees with research conducted by another researcher [4]. As shown in Fig. 1.d, there are two areas widened cracks in the specimen for 42 cycles. TGO residual stress, surface roughness, decreased concentration and fatigue of aluminum bond coat layer has an important role in the process of TBC failure.

#### B. Electron Microscope Analysis (SEM/EDX)

Based on Scanning Electron Microscope (SEM) analysis as shown in Fig. 2.a, the specimens without treatment have a thickness of 320 μm in top coat and bond coat of 120 μm. While shown in Fig. 2.b, the thickness of the specimen with a top coat is 300 μm and bond coat of 120 μm. At 100x magnification, the changes can be observed that a depletion layer of top coat is 10 μm. This can be explained that when the system TBC (thermal barrier coating) in the heating treatment up to at above 900 °C, then there will be physical changes to each layer. Top layer (top coat) is made by powder 8% yttria stabilized zirconia receiving the greatest heat load from the other layers. Despite having a low thermal conductivity around 2.5 W/mK, but with a continuous and cyclic heating the ceramic surface will experience expansion and contraction during thermal cycle process. This process is caused that surface of the ceramic thickness is reduced from the initial conditions.

In Fig. 3 specimen with a magnification of 500 times, it can be seen some parts which is oxidized, primarily at the interface between the bond coats to the substrate. Bond coat powder is the first superimposed on the substrate before coating top coat, although composition of alloy generally similar to the substrate, but the powders formed allows the trapped air during the coating process. When the plasma spraying done, powder coated surface were melted, effect of high temperature operation of blower.

By this process the bond coat powder can be attached to the substrate. Hot air trapped due to plasma spraying resulted in porosity on interface bond coat-substrate. Oxidation of elements on bond coat and substrate are also important factor to the formation of black points along with the interface between the bond coats to substrate. But in general, viscosity is generated based on the images that are good enough because not all parts of the interface are porosity, some sections showed good adhesiveness.

By performing on specimens' heat treatment, Fig. 4 shows the interface between the bond coat and substrates that have a finer texture. Oxides arising relatively few and showed a good viscosity, and is also seen that there is no porosity on the interface between the bond coat/substrate. Grooves are formed at the interface bond coat/substrate coating process, a little bumpy due to bond coat by plasma spraying. In the plasma spraying process, before the bond coat layer superimposed on the material, it is preceded by the coorving surface with sand blasting to enhance and expand the surface roughness which later formed the bond between the substrate with the bond coat [5], that the surface of the substrate which in smoothening provides a better resistance than the oxide surface that is not given the treatment does., This is because of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxide that is merely produced.

Observations on the interface area showed the elongated bright colors. This is the result of diffusion layer during the oxidation process takes place so that resulted in physical changes such as changing the color becomes lighter. Emergence of a new layer between the substrate with a bond coat layer has a thickness of the linear to the length of time of sintering or heating [6]. The report also explains that the new layer has similar characters with Ni<sub>3</sub>Al phase, in terms of total percent composition of alloying elements and violence Vickers average hardness. When high temperature is applied to the TBC system based on NiCoCrAlY, inter diffusion alloying elements can lead to fail in materials. NiCoCrAlY bond coat layer with high Al content serves as a source of aluminum for the formation of thermally grown oxide (TGO). If there is a depletion of aluminum diffusion to another layer, it is indicating TGO formation by aluminum and oxygen. EDS analysis indicate that the addition of aluminum at the interface is 35.6%, which means a decrease in the same concentration on the formation of TGO.

Shown in Fig. 4 it was found that light and dark phase dominates the overall image. Dark phase has a relatively wide at 11.1% and the oxide area of 2.77%. It is not seen any porosity in the Fig. 4 due to the bond coat layer coating process where very little air can be trapped in the bond coat. Ni has a melting point of 1455 °C, while the melting point of Co, Cr, Al, Y are respectively 1495 °C,

1907 °C, 660 °C and 1526 °C. Aluminum has a melting point below the temperature treatment at 900 °C, which is 600 °C. Aluminum could oxidize at high temperature; therefore the oxidized aluminum has a very high melting point. By heating the specimen to give the energy at each element and react with the surrounding area, Al reacts easily with Ni producing intermetallic phase Ni<sub>3</sub>Al.

SEM/ EDX analysis on some regions (square line) is shown in Fig. 5, and the elements data are tabulated on Table 3.1. It can be seen that major elements observed is Nickel (Ni) with 40.02% percent of the mass. Other elements based on the percent mass include Cr (21.26%); Co (20.04%), Fe (10.62%), Mo (3.67%), Al (3.28%) and Mn (1.11%). But there is an interesting phenomenon in that there is no ZrO<sub>2</sub> in the sample, as it has been confirmed by XRD analysis (Fig. 6). The ZrO<sub>2</sub> may be found in other area. On the other hand, the presence of Fe element is greater than the weight percent of Al, in as-received specimen; however, after oxidize there was not identifying Fe element. Fe cannot be separated from the alloy even though the amount is less than 1% on total elements on super alloys, so it is also identified on interface layer before oxidation treatment is applied. After oxidation it cannot identify clearly appearance of ferrous on interface layer, it is suggested that aluminum is diffused from bond coat to interface layer. Table 1 shows an increasing %W of aluminum and a decreasing of ferrous because of diffusion Al to interface layer.

Based on Table 1 it can be seen the addition of the Al content at the interface bond coat/ substrate up to 1.19%. Increasing of Al correspond to alumina forming, on the oxidation Al react with oxygen to form Al<sub>2</sub>O<sub>3</sub>. This oxide phase has important role as thermally grown oxide layer. Cobalt has decreased significantly by 8.87%, these elements has transported to the other layer correlated to diffusion. Thus the decline of this element on the interface bond coat/substrate results in the diffusion at this interface. Elevated levels of Ni at the interface of 20.74% indicate the movement of these elements into the interface bond coat/substrate. The addition of Ni element at the interface results in suppression of chemical activity of Al at the interface; it induces disturbing movement towards the surface of alumina bond coat/ topcoat to form the TGO, subsequently acts on material failure. All elements had indicated diffusion process from bond coat to the interface layer and had changed the composition both interface layer and bond coat. As shown in Fig. 4, in the interface layer had formed dark area as thermally grown oxide layer and suggested as Al<sub>2</sub>O<sub>3</sub>. Quadackers explained that during the heat treatment process of thermal fatigue on the specimen formed a thermal barrier coating system, causing the emergence of thermally grown oxide in the area of interface between top coat and bond coat [8]. This region is the weakest area and the start of the formation of cracks.

#### A. X-ray Diffraction Analysis

X-ray diffraction analysis on as received specimen

indicated that the dominant phase is ZrO<sub>2</sub> and new phase of NiAl. Previous study reported that the same phase ZrO<sub>2</sub> was found, but by increasing thermal fatigue cycles zirconia became minor phase followed by phase Ni<sub>3</sub>Al and Ni base phase [6]. However, in the present study, specimen was prepared by removing the previous upper layer until the interface between the substrate-bond coats obtained, around 400 μm from the surface above. Hence ZrO<sub>2</sub> remained of the top coat, not present in the interface.

#### IV. CONCLUSION

Thermal cyclic influences on phase transformation in the interface layer. Intermetallic phase is found in the interface bond coat and substrate as result of diffusion during thermal cyclic. On the thermal barrier coating system, it is found failure in the interface layer bond coat NiCoCrAlY and substrate of super alloys. It is found porosity and crack along interface layer. Porosity is induced by unhomogeneity of bond coat powder when it is spraying on substrate. After thermal cyclic treatment it is found crack propagation. This microstructure failure is induced by significantly difference of coefficient thermal expansion of bond coat and substrate. Thermal cyclic treatment would induce crack propagation worst.

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TABLE 1.  
ELEMENTS ANALYSIS ON INTERFACE LAYER USING SEM/EDX

Elements	As-received (%W)	Oxidation (%W)	$\Delta W$
Al	6.74	8.93	+1.19
Cr	22.71	22.70	- 0.01
Mn	1.13	-	- 1.13
Fe	10.56	-	-10.56
Co	18.88	10.26	-8.62
Ni	37.86	56.04	+18.18
Mo	2.12	-	-2.12
Ti	-	2.07	+2.07



Fig. 1. Macrostructure analysis on specimen as received (a) and specimen after thermal fatigue at 900oC (b) 2 cycles, (c) 6 cycles, (d) 42 cycles

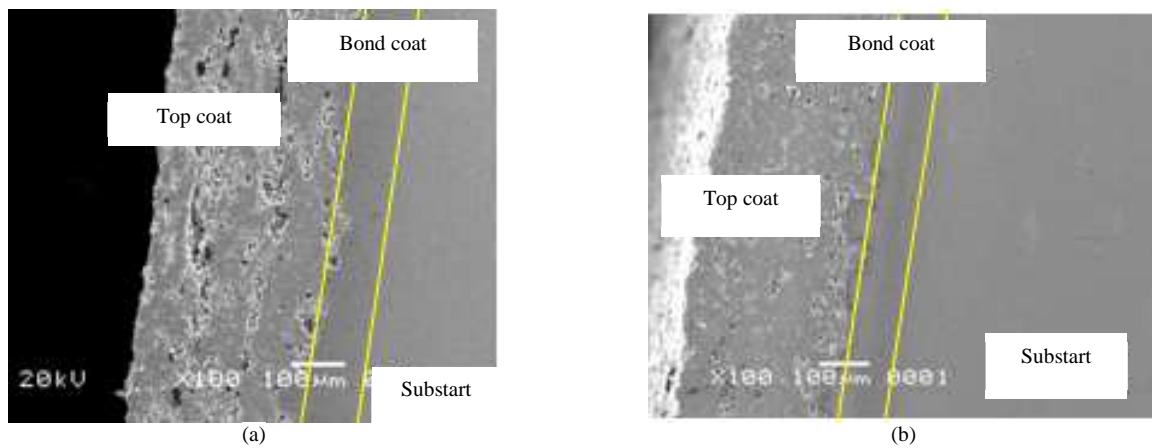


Fig. 2. Electron microscope analysis on specimen (a) as-received; (b) after thermal fatigue 42 cycles

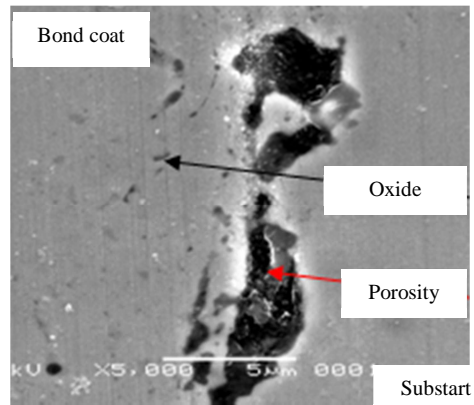


Fig. 3. Electron microscope analysis on as received specimen

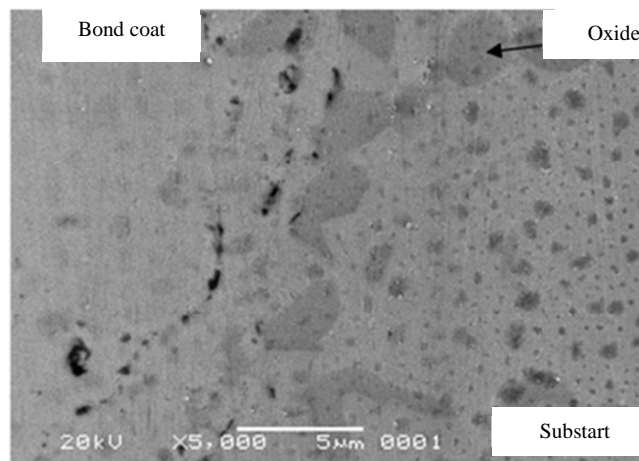


Fig. 4. Electron microscope analysis on specimen after thermal fatigue at 900°C – 42 cycle. It is shown dark area and bright area indicating the difference on morphology

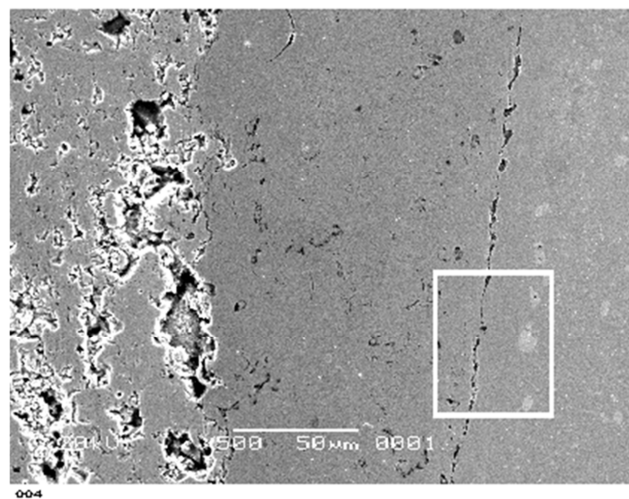
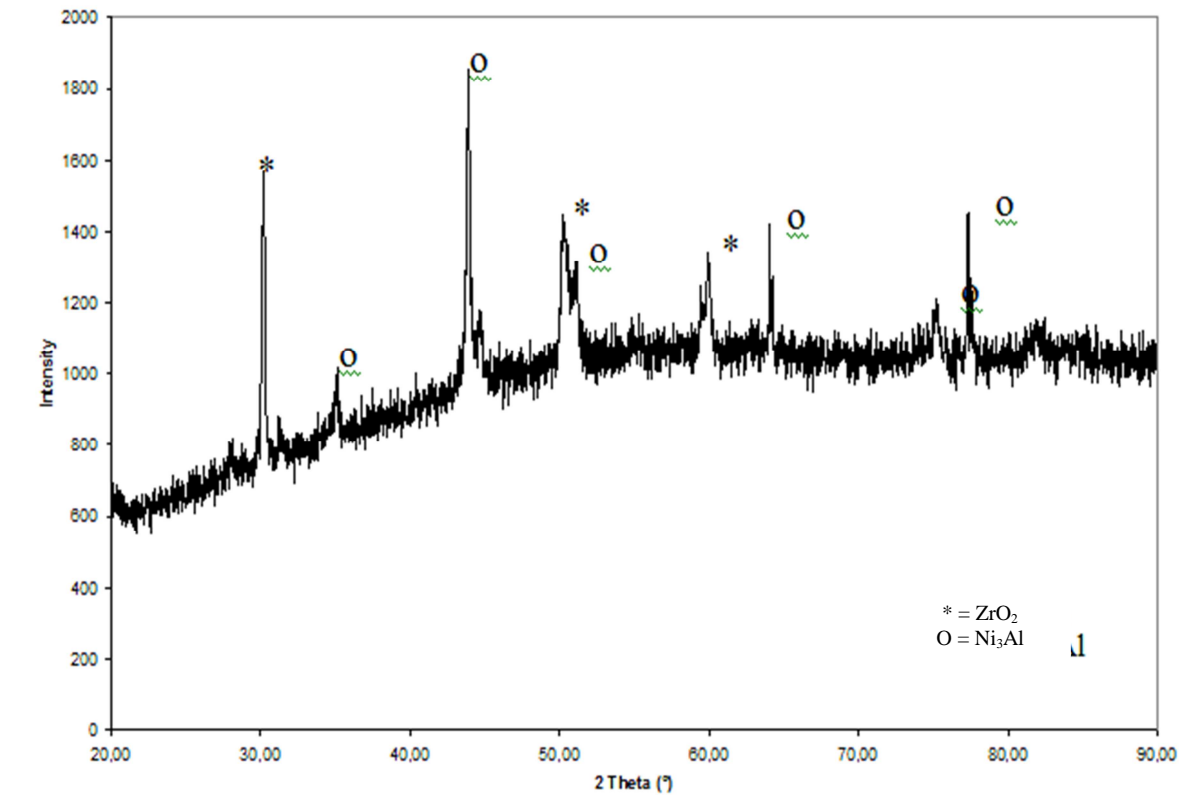
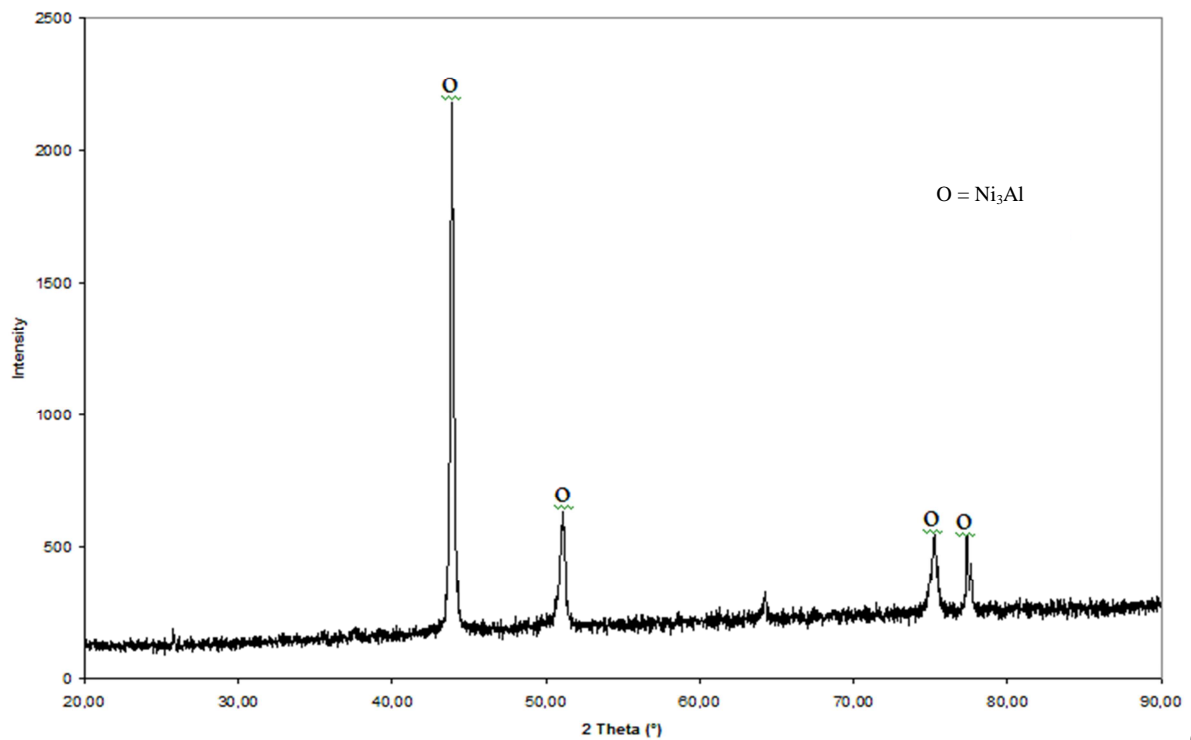


Fig. 5. SEM/EDX analysis on thermal fatigue specimen, this analysis was done to observe element diffusion along the interface



(a)



(b)

Fig. 6. X-ray diffraction analysis on (a) as-received, (b) after thermal fatigue at 900°C-42 cycles. On as-received specimen indicate zirconia and Ni<sub>3</sub>Al phases. Zirconia is remaining phase of top coat layer and Ni<sub>3</sub>Al is new phase that is formed by diffusion of elements bond coat and substrate

