HIGH TEMPERATURE CYCLIC OXIDATION BEHAVIOUR TERNARY Ni-Al-Ti ALLOYS DOPED WITH Ge AT 1200°C

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Ni base alloys are widely used for high temperature applications, such as pressure vessel , turbine blade. Ni-base alloys possess oxidation resistance, creep resistance, fatigue resistance, the stability of the microstructure and good mechanical properties at elevated temperatures. The Ni-Al-Ti alloys were melted in a single arc melting furnace under ultra high argon atmosphere. Cyclic oxidation of the alloys was performed in air furnace at 1200 °C temperature for 25 cycles Each cycle consisted of 1 hr heating at 1200°C in an alumina tube furnace followed by 30 min cooling at room temperature. The results show that the higher addition of Ge element content can improve the mechanical properties and oxidation resistance of Ni based alloys. X-ray diffraction examination showed that the compounds were formed on the alloy after smelting Ni$_3$Al, Ni$_3$Ti, Ni$_3$Ge, Ni and Ni$_2$AlTi. While the oxide on the alloy after oxidizing to form a compounds NiO, NiTiO$_3$, GeO$_2$, and TiO$_2$. In the SEM-EDS examination showed that the composition of Ge formed more dominant in the area under the element Ni oxide layer. The higher the Ge element content in the alloy has improved the resistance of the alloy indicated by the thin layer of oxide formed on the surface of the alloy.

Keywords : Ni based superalloy, cyclic oxidation,Ni oxide layer,Gem

1. INTRODUCTION

Superalloys have properties corrosion and oxidation resistance, creep resistance (creep), fatigue resistance (fatigue and thermal fatigue), the stability of the microstructure and mechanical properties of the appropriate use [1]. Super alloys have been developed to achieve maximum oxidation resistance by utilizing the concept of selective oxidation, which is influenced by the composition of the alloy, surface conditions and environment [2]. Ni-based alloys can increase the hardness and improve corrosion resistance [3]. So that the Ni-based alloys much used in nuclear reactors, electrical heaters, gas turbine, aerospace, and industrial high temperature [4]. The addition of alloying elements (Al and Ti) resulting in the emergence of phase γ '[Ni (Al, Ti)] coherent so as to provide reinforcement effect. But the γ-phase and phase γ 'has a different lattice parameter. This difference produces a coherent strain that can hinder the movement of dislocations resulting in precipitates hardening [5]. Elements such as chromium and aluminum are added, aims to improve protection against hot corrosion and high temperature oxidation [6].

Corrosion is a process of material degradation and decrease of quality of a material due to the influence of chemical and electrochemical reaction with its environment. Corrosion (rusting) can also be defined as a chemical phenomenon of metal materials in a wide range of environmental conditions, the chemical reaction between the metal substances in the surrounding areas or with other particles in the metal matrix itself. Corrosion can also cause degradation of the mechanical properties by changing three microstructural features that the grain size, phase composition, and the formation of oxide scale [7]. Factors affecting the corrosion is divided into two, namely, internal factors and external factors. Internal factors include the diversity of structures, heat treatment, cooling and surface treatment. While external factors is the phenomenon of corrosion of metal due to an electrochemical or chemical interaction between the metal with its environment.

High temperature corrosion or dry corrosion is the destruction or deterioration of the material, including the degradation of mechanical properties caused by the influence of the atmosphere at high temperatures. High temperatures have the understanding that water in the gas phase, the atmosphere does not contain water. The temperature at which diffusion of atoms that have a influence considerable and

temperature were estimated by 0.5 Tm (Tm = melting temperature, Kelvin).

Oxide growth begins where oxygen is absorpt to the metal surface, then there reaksi between oxygen to the metal so that oxidation formed on the metal surface which is then the next process are growing oxide scale that has been formed [8]. High temperature double impact against degradation metals caused, which are:

a. The increase in temperature will affect the thermodynamic and kinetic aspects of the reaction, meaning the faster degradation at higher temperatures.
b. The increase in temperature will affect and change the structure and behavior of metals. If the structure changes, the general strength and metallic behavior also changes.

The level of oxidation is determined by a combination of the two processes. One is chemical, which is actually a reaction between oxygen with in the semiconductor at the interface, and the other is the diffusion of oxygen through the oxide film formed previously. The combination of these processes result in linear-parabolic relationship between the oxide thickness and oxidation time [9]. Oxidation kinetics are usually studied through isothermal and cyclic oxidation testing. Usually the oxidation rate measured of several criteria, ie :

a. The amount of metal consumed, ie of the weight lost or the thickness of metal scraps.
b. The amount of oxygen consumed, ie of the weight gain or of the amount of oxygen used.
c. The amount of oxides produced, ie of the based on the weight of oxides formed or of the thickness of the oxide formed.

The most important parameters of the oxidation of metal from the engineering side is the reaction rate. Since the oxide reaction product generally maintained on the surface of the metal, the oxidation rate is usually measured and expressed as the weight gain per unit area. three main laws that explain high-temperature oxidation kinetics of which is a linear rate, the rate parabolic and logarithmic rate [10]. Cyclic oxidation process is carried out by heating in the oxidation temperature and then followed by cooling with air. Changes in mass per unit area as a function of oxidation time. The rise in temperature increase weight gain and change in mass is the amount of the increase in mass by with oxidation of alloying elements. At high temperatures, oxidation is accelerated compared to a lower temperature.

Parabolic oxidation occurs when a metal or oxygen diffusing through the oxide layer continues to grow. Along with the thickness of the oxide layer increases, also increasing the diffusion path. Values parabolic rate constant (Kp) was calculated, based on the level of the parabolic equation for a high temperature oxidation process [11].

$$X^2 = Kpt$$

Where:

X = Weight change per unit surface area.
t = Time.
Kp = Parabolic-growth rate constant.

2. MATERIALS AND METHODS

The chemical composition of the alloy material used in this study is the material of the Ni-Al-Ti with the addition of the germanium element content, the system Ni-Al-Ti-X Ge (X = 0.5% and 1.5%). Where the materials used are nickel, aluminum, titanium and germanium has a purity level of 99,99%. Here is the chemical composition of each material.

Table 1: Chemical composition of alloys (wt%)

Specimens	% weight			
	Ni	Al	Ti	Ge
Alloy-1 (Ni-Al-Ti-0,5% Ge)	82,252	6,617	10,631	0,5
Alloy-2 (Ni-Al-Ti-1,5% Ge)	81.425	6,5	10.525	1,5

The process of making sample is with to smelt the materials alloy using Arc Melting Furnace. Arc Melting Furnace is a furnace used to smelt a metal or alloy into one by using copper crucible hearth furnace by flowing water as coolant, on the *Arc Melting Furnace* (AMF) uses the concept of heating in a vacuum

with using electrodes (In this case tungsten) and protected with argon gas. In the smelting process carried out 4 times to obtain a homogeneous sample. After smelting process , the samples are then solution treatment at a temperature of 1200 °C for 2 hours in tube furnace under argon atmosphere and finally quenching in water media.

Cyclic oxidation were carried out in air furnace at temperature 1200 °C for 25 cycles. Each cycles consisted of 1 hour in air furnace at 1200°C followed by 30 minutes cooling at room temperature. Oxidation behavior of alloys Ni-Al-Ti-Ge measured by examination of the oxide thickness as a function of the thickness vs oxidation time, and analyzed by performing several tests including hardness testing examination of micro structure by an optical microscope, XRD for phase identification and SEM-EDS for cross section examination. In the hardness test specimens were tested using test equipment Krisbow Rockwell Hardness Tester with C-Scale. Analysis of the microstructure of specimens Ni-Al-Ti-Ge tested using test equipment Olympus BX60M optical microscope, which where previously carried out the process of preparation of the surface by means to the conduct of the process of sandpaper 60 to 2000 mesh, then do the polishing process using diamond polishing paste, after the etching process is carried out with a solution of aqua regia (a mixture of 20 ml of HCl and 60 mL HNO_3). Analysis phase compositions and compounds in the samples of Ni-Al-Ti-Ge done with X-Ray Diffraction testing using test equipment X-Ray Diffraction PANalytical X'Pert PRO PW3040 / x0. As well as the surface morphology analysis and analysis of the elements formed on the samples was done by SEM-EDS testing, with the using equipment SEM test namely Hitachi SU3500 and equipment EDS test namely Ametek Apollo XL.

3. RESULTS AND DISCUSSION

Figure 1 shows the hardness of the alloy with different Ge addition. Generally, the higher the curve shows that the addition of germanium element content will increase the hardness of the alloy, because the element of germanium can shrink the size of the grain, resulting in the strengthening of the grain size reduction. Because the smaller the grain size, the more there is a grain boundary area would be dislocation barrier, the more dislocations that occurred then the stronger the metal.

Figure 1 shows the hardness curve of sample after casting, solution treatment and cyclic oxidation process alloy Ni-Al-Ti-Ge at a temperature of 1200 °C. The Figure depicted that the hardness of the sampel will decrease after cyclic oxidation compare with as cast and solution treatment. due to during the process of cyclic oxidation underway cause the grain to coarsening caused by the heating continues, so that resulting in hardness in the specimen decreases. In accordance with the equation Hall-Petch [12] that the larger grain size will decrease the mechanical properties of a material. Figure 2 shows the microstructure results of alloy Ni-Al-Ti-0.5% Ge and Ni-Al-Ti-1.5% Ge the results of the solution treatment process, From these images show relatively similar microstructure results.
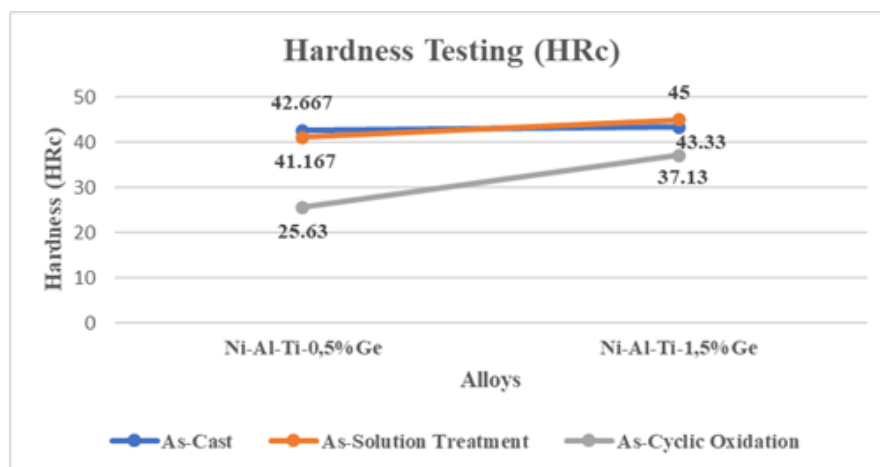

Figure 1: Hardness of alloys Ni-Al-Ti-0,5%Ge and Ni-Al-Ti -1,5%Ge samples results as-cast, as-solution treatment and as-cyclic oxidation

Figure 2 depicted the microstructure of microstructure alloy Ni-Al-Ti-Ge consisting of dendritic shaped microstructure with the formation of ɣ' phase as indicated by the arrow. Ni elements will dissolve and form a precipitate compound Ni3Al, Ni3Ti and Ni3Ge. The compounds that formed it will improve the

mechanical properties of the alloy, due to the precipitation strengthening mechanism [13]. The addition of germanium element will reduce the grainsize, it can be seen in Figure 2, Where the higher the addition of the germanium element content, it will cause grain size gets smaller.
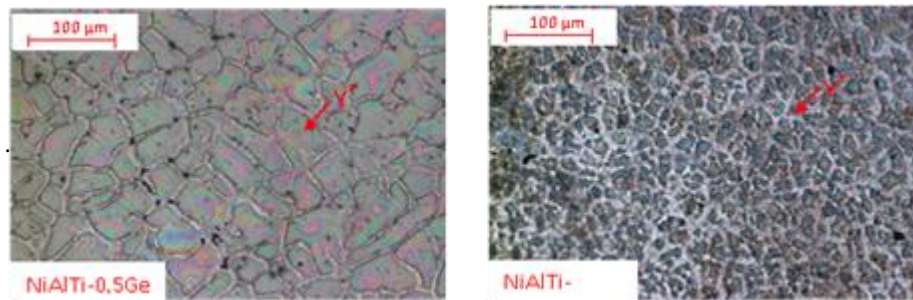

Figure 2: Microstructure of alloys Ni-Al-Ti-0,5%Ge and Ni-Al-Ti -1,5%Ge results as-solution treatment

Figure 3 shows the microstructure of Ni-Al-Ti-0,5%Ge and Ni-Al-Ti -1,5%Ge after cyclic oxidation. The results of alloy Ni-Al-Ti-0.5% Ge and Ni-Al-Ti-1.5% Ge the result of the cyclic oxidation process at temperatures of 1200 ° C for 25 cyclic.
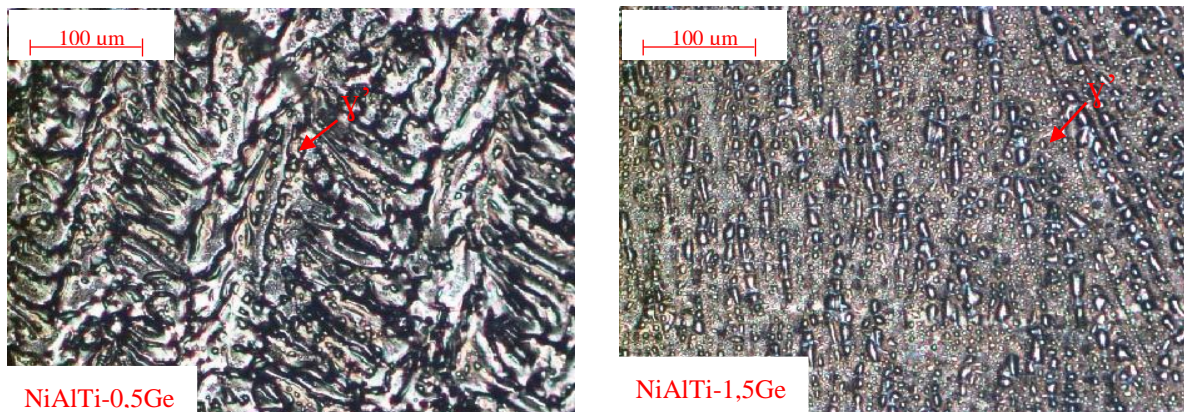

Figure 3. Microstructure of alloys Ni-Al-Ti-0,5%Ge and Ni-Al-Ti -1,5%Ge after cyclic oxidation at temperature 1200 ºc for 25 cyclic

The results from the oxidation process cyclic caused the event coarsening of the heating process results is constantly repeated, causing grains undergo coarsening of this continuing, characterized by grain size small some have disappeared and some others joined together to form clusters, which is characterized by the form of grains big and get bigger, the phenomenon of grain loss is due to the grain matrix dissolves into Ni. However, as a result of the heating process are repeated then some grains will grow back into a new, small-sized grains. This coarsening of events will cause the coarsening phase Ni_3 (Al, Ti). As a result of the process of this coarsening then be decreased mechanical properties.

Figure 4 shows the plot oxidation kinetics of alloy Ni-Al-Ti-0.5% Ge and Ni-Al-Ti-1.5% Ge, between the thickness of the oxide scale against the number of cycles. In Figure 4 indicate that the oxide thickness is directly proportional to the number of cycles of oxidation, so the more the oxidation cycle of oxidation thickness is formed thicker. This is depicted that the oxide growth was dominance compare with the oxide spallation [14]. The higher the addition of the germanium element alloys would increase the oxidation resistance of Ni-Al-Ti indicated by the thin oxide is formed. This is because the elements of Ge is more reactive than the elements Ni, according to the thermodynamics of oxidation, can be proven at Ellingham diagram, the Ge element is the active ingredient compared to the base metal is Ni, so the elements Ge oxidized or reacted first with oxygen to form an oxide layer GeO_2, The addition of Ge in the alloy crease the oxidation resistance of Ni alloy, because it can withstand the elements Ni to oxidized first. The formation of a thicker oxide layer due to the low capacity of the oxide layer to prevent the entry of oxygen which can react with the base metal to form a new oxide layer. In addition, the temperature also affects the rate of oxygen ingress to penetrate the oxide layer.
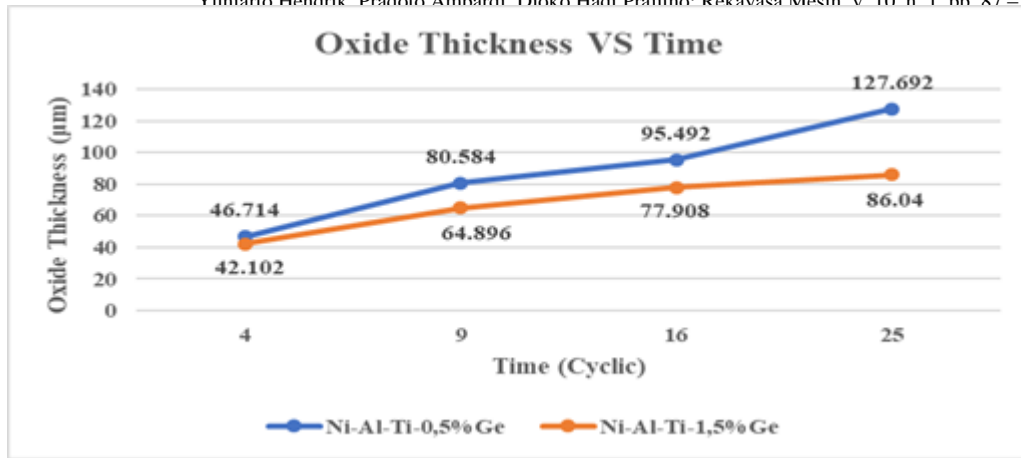
Figure 4: The rate of oxidation of alloys on the thickness of the oxide and cyclic oxidation times

High temperatures will increase the size of the grain so that oxygen more easily fit between the grain boundaries. The thinner the oxide layer formed on a metal alloy that these alloys have excellent oxidation resistance, is due to the oxidation kinetics running slowly, causing the formation of a thin oxide layer. When the thin oxide layer, the potential for degradation of the surface due to the potential difference between the oxide layer and the substrate is getting smaller, so it can be concluded that the thin oxide layer formed on a metal then the better oxidation resistance. Figure 5 shows testing the X-Ray Diffraction samples of Ni-Al-Ti-1.5% Ge before oxidation (a) and samples of Ni-Al-Ti-1.5% Ge after oxidation at temperatures of 1200 °C for 4 cyclic (b).

In Figure 5 (a) indicates that the formation of compounds Ni3Al, Ni3Ti, Ni3Ge, Ni and Ni2AlTi on samples Ni-Al-Ti-1.5% Ge. As well as on Figure 5 (b) shows the formation of oxide compounds are NiTiO3, GeO2, NiO and TiO2 in the samples of Ni-Al-Ti-1.5% Ge after oxidation at temperatures of 1200 °C for 4 cyclic. In specimens NiAlTi-1.5% Ge after cyclic oxidation process by 4 cyclic form NiO primary phase, is due to NiO phase formed due to the enrichment of Ni element is because of the depletion (decreasing concentration) elements Al, Ti and Ge under layers of rutile, nickel titanite and germanium oxide, which causes the phase formation of nickel oxide (NiO) [15]. In this XRD data does not form an oxide layer Al2O3, because Al2O3 phase formed on the part the border with the substrate or not formed on the surface so it does not hit or shot X-rays, so it is not readable on XRD testing. NiTiO3 phase formed a fairly large with a score of 34.3%, NiTiO3 phase itself is a combination of oxide NiO and TiO2 oxide. SEM-EDS testing performed on the part substrate and part cross section alloy Ni-Al-Ti-1.5% Ge has done a cyclic oxidation process at a temperature of 1200 °C for 25 cyclic.
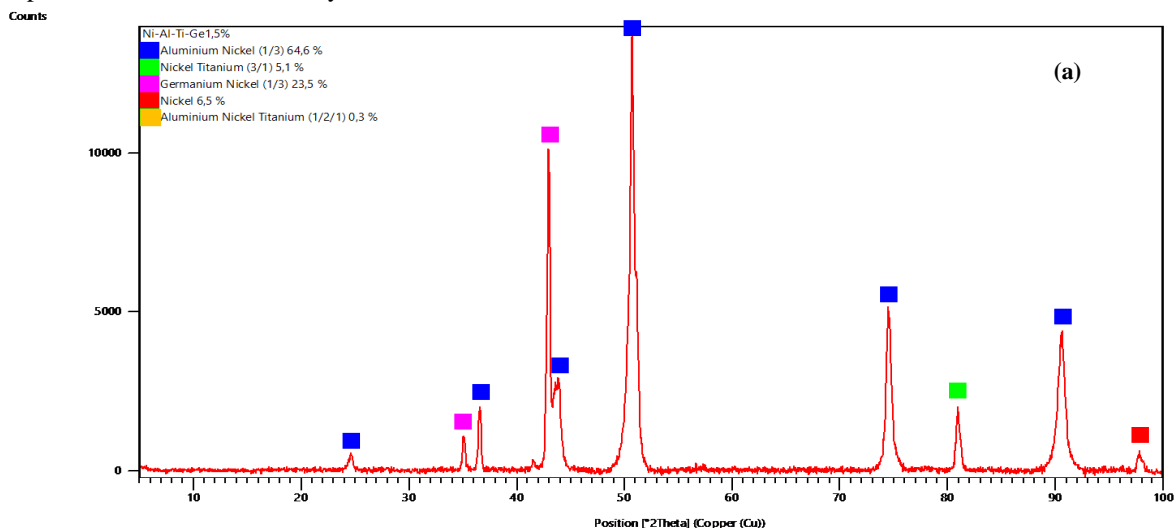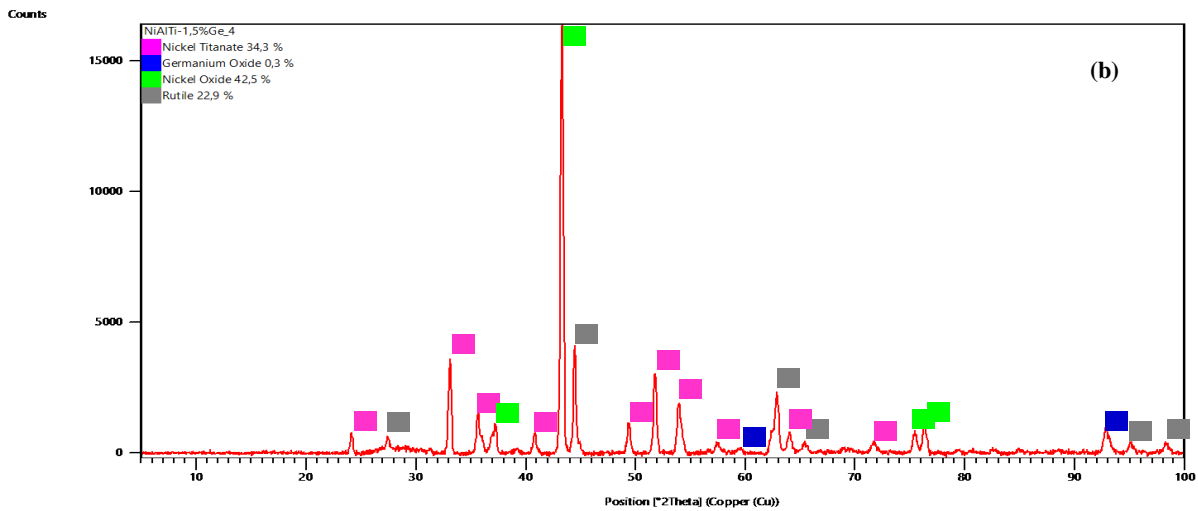
Figure 5: . Results xrd patterns alloys Ni-Al-Ti-1,5%ge (a) before cyclic oxidation, (b) after cyclic oxidation
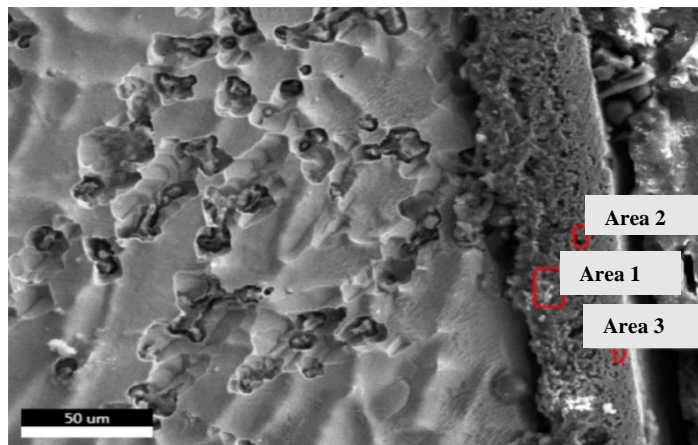

Figure 6: Morphology cross-section Ni-Al-Ti-1,5%ge alloy after cyclic oxidation at temperature 1200 $^{\circ}$c for 25 cyclic

Table 2: Chemical composition of ni-al-ti-1,5%ge (wt) alloy after cyclic oxidation

Elements (Wt%)	1	2	3
Ni	18,61	30,91	72,46
Al	27,87	17,15	-
Ti	11,24	15,25	4,95
Ge	-	0,99	-
O	42,28	35,70	22,59

On Figure 6 indicate that the oxide layer is the formed consisting of several layers of oxide. EDS analysis showed that in Figure 6 ie on area 1 is the area of the oxide layer is rich in Al elements and forming oxides of Al_2O_3. In area 2 show rich in elements Ti forming oxides TiO_2 and Ge element only in area 2 and formed oxides GeO_2. As well, the area 3 in direct contact with the environment shows areas rich in Ni and form the NiO compound.

4. CONSLUSION

The cyclic oxidation process cyclic alloy quaternary Ni-Al-Ti-Ge at a temperature of 1200 °C with a variation of cyclic by 4 cyclic, 9 cyclic, 16 cyclic and 25 cyclic, where the mechanical properties, especially hardness and oxidation resistance will increase with the higher content of elements of Ge on alloy. The results of cyclic oxidation process will reduce the hardness alloys Ni-Al-Ti-Ge as a result of the heating process that is constantly repeated, so that grain experiencing coarsening process continues or called to phenomenon coarsening. Oxides formed on areas of the oxide layer are compounds $NiTiO_3$, GeO_2, NiO and TiO_2.

5. ACKNOWLEDGEMENTS

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