Transactions of the Korean Nuclear Society Spring Meeting
Taebaek, Korea, May 26-27, 2011

Application of Electron Beams for Surface Modification of Nickel-base Superalloys

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1. Introduction

Wrought Ni-base superalloy, Alloy 617, is considered as candidate metallic materials for intermediate heat exchanger (IHX) of very high temperature gas-cooled reactors (VHTR) [1-3]. IHX will be exposed to the highest temperature over 900 ^{o}C for the various applications including hydrogen production. Chromium is essentially added to make Cr-rich oxide layers on the surface. However, it is reported that Cr_2O_3 reduction phenomena happens under helium coolant with certain amounts of impurities [4-5]. Protective oxide layer is necessary for long-term stability of the components, and an excessive supply of resources to make that kind of stable oxide is required near the surface when it is destroyed at operating temperature. In this study, proper depth of Al-rich zone is developed using PVD (Physical Vapor Deposition) and EB (Electron Beam) surface alloying methods. The effects of surface modification on high temperature oxidation and self-healing capability are demonstrated.

2. Experimental Procedure

After pure Al is sputtered on the Alloy 617, high energy density electron beam is irradiated on the surface. SEM (Scanning Electron Microscope), EDS (Energy Dispersive Spectroscopy), and EPMA (Electron Probe Micro Analyzer) analysis are conducted to investigate the Al alloying region. Small size tensile test specimens are also prepared to evaluate the mechanical properties at room temperature.

Coupon types specimens of 12 mm in diameter and 1 mm in thickness is used for isothermal oxidation test at 900 ^{o}C up to 1000 hours. As the main purpose of the surface treatment is to lengthen the creep life time by utilizing the self-healing capability, stress is applied to break the oxides and observed the formation of protective oxides on the crack surface.

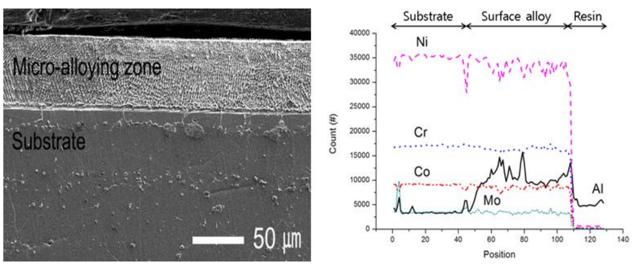

Fig. 1. SEM image of surface treated specimen and EPMA line scanning result.

Table I: Chemical composition of Alloy 617 (in wt%)

Ni	Cr	Co	Mo	Fe	Al
52.7	22.1	11.6	9.57	1.58	1.41
Ti	Si	Mn	W	C	
0.35	0.42	0.12	0.07	0.09	

3. Results

3.1 Electron Beam Induced Surface Microalloying

Thickness of 5 ㎛ of pure Al is coated on the surface of Alloy 617 using PVD method before EB surface treatment. As it is reported that 4-5% in weight percent of Al is enough to make stable Al_2O_3 oxide on the surface [6], following EB irradiation conditions are applied to make 50 ㎛ of surface Al-rich region: accelerating voltage of 60 kV, current of 14 mA, working distance of 200 mm, working pressure of $1.0x10^{-4}$, and scanning velocity of 560 mm/min. Figure 1 shows the depth of the microalloying zone. Compared to the chemical composition of Alloy 617 (Table I), three times more counts were detected from EDS analysis. EPMA line scanning result also verified that rather uniform distribution of Al in the alloying region. Hardness in the surface alloy region is higher. Fig. 2 shows the tensile test result of both surface untreated and treated specimens. Both of yield strength and ultimate tensile strength are equal, but elongation of surface modified specimen is better. Lots of micro cracks are observed in SEM analysis, and it has an effect of increasing elongation. To assess the behaviors in VHTR relevant conditions, high temperature tensile and creep tests are in progress.

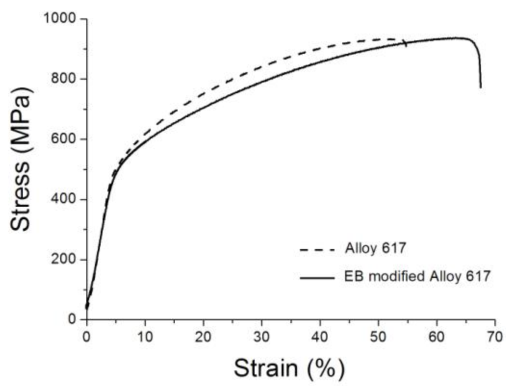

Fig. 2. Tensile test results at room temperature.

3.2 Oxidation Behaviors

Weight gain vs. oxidation time is shown in Fig. 3. For EB treated specimens, weight gains are higher than untreated one up to 24 hours, but it rarely changed after 100 hours. It is known that surface oxides of Alloy 617 are NiO, $NiCr_2O_4$, and Cr_2O_3, and Al_2O_3 exists as an internal oxide [7-8]. To identify the oxide layers of EB treated specimens, XRD (X-ray Diffraction) analysis is carried out, and it was confirmed that they consists of double layers: $Ni(Cr,Al)_2O_4$ and Al_2O_3. However, peak counts of substrate (Ni-Cr-Co-Mo) were much higher than those oxides. In other words, it implies that very thin, or less than 1 ㎛ of oxides are formed even the specimen is exposed to 900 °C up to 1000 hours.

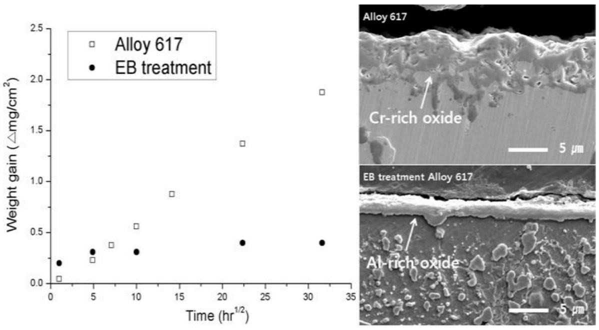

Fig. 3. Weight gain curve and SEM images.

To identify the nature of the thin protective oxides, TEM (Transmission Electron Microscope) analysis was performed (Fig. 4). Though it was not clear on the SEM image, TEM BSE (Back Scattered Electron) image clearly showed that the surface oxide consists of two layers. Chemical composition was analyzed using energy spectrum for eleven points. Surface oxides consists of outer $Ni(Cr,Al)_2O_4$ (Point 1-3) and inner Al_2O_3 (Point 6-8). As the Gibb's free energy of Al_2O_3 is less than other kinds of oxides [6], it may quickly develop at an early stage. This mechanism explains the weight gain curve up to 24 hours. About 500 nm of thickness, dense and continuous Al_2O_3 efficiently prevents the diffusion of Ni, Cr, and O. However, it is not clear whether the outer oxide is formed before or after the formation of the inner oxide layer. In addition, transient oxide (Point 4-5) which is rich in Cr, Al, and O exists between outer and inner one. Small amount of Al_2O_3 exists as an internal oxide (Point 9-10), but its shape and length is different from that of Alloy 617. Further analysis is in progress to clarify these.

3.3 Self-healing Effects

For Alloy 617, Cr-rich oxide is developed at the crack tip and elongated internal oxides are formed around the crack. Such internal oxides could be the crack initiation site and preferred path for the crack growth [9]. On the other hand, high contents of Al for EB treated specimen promoted protective Al_2O_3 oxide on the crack tip in a short time and slowed down the crack growth (Fig. 5). In such case, creep resistance would be improved significantly. To verify this, creep tests are in progress.

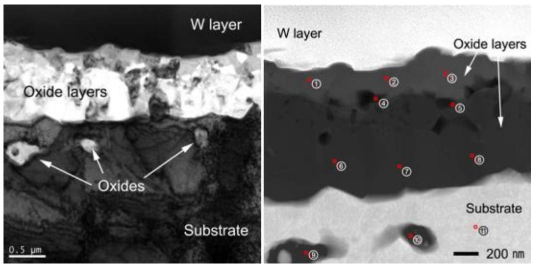

Fig. 4. TEM oxide images of EB treatment specimen.

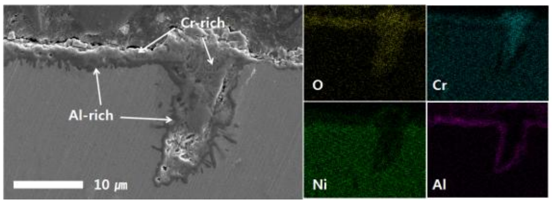

Fig. 5. Self-healing effects of EB treatment specimen when the surface oxide is destroyed.

4. Conclusions

Surface modification technique using PVD and EB treatment is developed. During high temperature oxidation, Al_2O_3 oxide on the surface formed in an early stage, which increases the oxidation resistance efficiently. Furthermore, crack self-healing effects in the microalloyed zone are also confirmed.

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