Analysis of localized oxides and oxide films formed on alloy 625 and 617 in supercritical water and superheated steam environments at 750°C

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Abstract
Oxidation tests using coupon specimens of alloy 625 and alloy 617, and four-point bending tests for a duration of 100 hrs were carried out in supercritical water (SCW) environment at a pressure of 24 MPa and in superheated steam (SHS) environments at 750°C. The noticeable difference between the oxidation in two environments appeared in the oxidation behavior of primary precipitates like Nb rich MC carbide for alloy 625. In the SCW environment, a large number of pitting was observed. Those were thought to be made by electrochemical reactions, while in SHS most of the carbides were oxidized as Nb oxides with some extent of volume expansion. In the case of alloy 617, the pitting formation was also observed in both environments. It seemed to have a dependence on the oxidation behavior of the primary carbides similar to that of alloy 625. The effect of the applied stress was not apparent under current experimental conditions because permanent deformation was observed in all the specimens and stress relaxation subsequently occurred during the test. In addition, no cracks were observed on both alloys after four-point bending tests. In the outer layer of the oxide film formed in the SCW, the Cr content exhibit to have smaller in both alloys, and the oxide thicknesses were 0.53 to 0.88 times thinner than those in the SHS.

Keywords: A-USC, Alloy 625, Alloy 617, Supercritical water, oxidation, Four-point bending test, Weight gain, Pitting, AES

1. Introduction

Ni-base superalloys have been considered as candidate structural material in high temperature section in advanced ultra-supercritical (A-USC) power generation. Those materials are exposed to high temperature and high pressure steam beyond 700°C. In most of the studies concerning life time and strength of the materials at high temperature, creep tests in air and oxidation tests in superheated steam had been performed (Viswanathan et al., 2010; Rosler et al. 2003). However, the materials’ behavior in high temperature and high pressure environments in that materials will be subjected during the plant operation are not well known due to experimental difficulties. The effect of steam pressure on the oxidation behavior has been considered less important than the temperature and the surface finish because it had been expected that solubility is reduced in supercritical water (SCW) at higher temperatures (Kritzer, 2004). This means that the oxidation behavior in SCW is predicted to become more similar to that in steam at pressure below the critical pressure (22.1MPa). However, recent researches particularly in the field of nuclear power generation have reported the differences in surface oxide morphologies on Ni-base superalloys in superheated steam (SHS) and SCW environments (McClure et al., 2015). For example, the oxides formed on alloy 625 after exposed to SCW at 29 MPa and 600°C for 1000 hrs were composed of two types of oxides. One was an oxide enriched in Cr and the other was enriched in Ni. In contrast, almost no oxides were observed in SHS at 0.1 MPa for 1000 hrs (Garcia, et al., 2015). However, very few investigations have been seen in that focused on the difference of the oxidation behavior between in SCW and SHS environment beyond 700°C (Marrone, 2009).
Crack initiation and its subsequent propagation are considered as one of the primary degradations concerning life time of turbine or boiler components. It should be affected by some extent of oxidation because those surfaces are exposed to SCW. The SCC tests using Ni-base superalloys in SCW have been carried out by Teyssseyre and Was (2006). They performed constant extension rate tests (CERT) in a range of 400 to 550°C at 25.5 MPa, and concluded that alloy 625 exhibited a crack density of 5 to 36 times higher than that of other alloys including Fe-base alloys. However, the dependence of crack initiation on the SCW environmental were not examined in that study. Recently, it has been concerned that crack initiation by stress assisted grain boundary oxidation (SAGBO) (Carpenter et al., 1997) on polycrystal Ni-base superalloys. In actual plant operation, the materials used in the high temperature and high pressure section are subjected to experience on temperature and pressure cyclic and irregular change due to start-up/shut-down of the plant. Consequently, the damage of the exfoliation and the thermal fatigue appear to be more severe than expected from laboratory studies. In addition to that, Ni-base superalloys have been used rarely in large parts such as casing, piping, rotor. In other words, there is little practical experience of the long term exposure in the SCW environment beyond 700°C. Thus, it is necessary to gain fundamental understandings on the oxidation behavior in SCW assumed actual A-USC steam condition in order to evaluate the long term reliability of materials.

In this current study, alloy 625 and alloy 617 was used for oxidation tests in SCW and SHS at 750°C in order to evaluate the effect of pressure on oxidation behavior. In addition, four-point bending tests were performed for the durations of 100 hrs. With aiming to help developing prediction methodology from the data in air to plant operating condition, comparison of surface oxide morphologies and oxide film structures between two different environments were made in both alloys. The oxidation mechanisms including dissolution with focused on composition of the precipitations were discussed to reveal the dependence on stress and environments.

2. Materials and experimental procedures

2.1 Materials and specimens

Two wrought Ni-base superalloys, alloy 625 and 617 were used for the tests. The chemical compositions of the alloys are shown in Table 1. Both alloys are solid-solution strengthened superalloys with high Cr and Ni contents which provide good oxidation resistance. Al included especially in alloy 617 also contributes to the oxidation resistance at high temperatures. In addition, Al forms an intermetallic compound γ'-Ni3Al over a range of temperatures, which results in precipitation strengthening on top of the solid-solution strengthening imparted by Co and Mo (Ren and Swindeman, 2009). On the other hand, alloy 625 is also an age-hardenable superalloy which is achieved by metastable γ" phase, having Ni3Nb composition. Moreover, the improvement of creep strength is attained by especially Mo and Nb (+Ta) addition (Eiselstein and Tillack, 1991).

The size of specimens for four-point bending tests was 90 mm×10 mm×1 mm in SHS environment, and was 50 mm×10 mm×1 mm in SCW environment. Coupon specimens (10 mm×10 mm×1 mm) were prepared and used as non-stressed condition in order to evaluate the influence of the applied stress by comparing with four-point bending specimens. Firstly, all specimen surfaces were finished with abrasive paper to 1000 grid. Those surfaces were subsequently polished up with silica to nearly 0.02 μm. Before the tests, they were ultrasonically cleaned in ethanol.

| Table 1 Chemical compositions of alloy 625 and alloy 617 [wt.%]. |
|-----------------|---|---|---|---|---|---|---|---|---|---|
|                | Ni | Cr | Mo | Co | Fe | Al | Ti | C  | Si | Mn | Nb+Ta |
| Alloy 625      | 61.4|  21.8|  8.19|  0.04|  4.35|  0.13|  0.19|  0.08|  0.2|  0.18|  3.42 |
| Alloy 617      | 53.0|  22.6|  9.67|  11.4|  1.29|  1.12|  0.33|  0.09|  0.07|  0.07|   -   |

2.2 Oxidation tests at 750°C

Tests in SHS environment were conducted in a sealed furnace tube with a steam generator which has a water recirculation loop. This apparatus consists of the water tank, pump, ion exchanger and water quality measurement circuit. Tests in SCW environment were performed in an autoclave which had a water recirculation loop. Fully deaerated pure water was used for both environments. Tests conditions are given in Table 2.

The four-point bending stress was set to 337 MPa for alloy 625 and 175 MPa for alloy 617, which was the 90% of the 0.2% proof stress at 750°C for each alloy. Figure 1 shows bolt loading fixture used in SHS environment. The spans
of the inner and outer points were 20 mm and 80 mm, respectively. In SCW environment, the four-point bending fixture was integrated with the autoclave, and also designed with inner and outer spans of 10 mm and 40 mm, respectively. The applied stress was set by adjusting the flexure to achieve the desired displacement at room temperature. Coupon specimens were fixed into each test section using platinum wires.

Table 2 Environmental parameters for oxidation test.

| Environment | Test temperature [°C] | Test duration [hr] | Pressure [MPa] | Dissolved oxygen |
|-------------|------------------------|--------------------|----------------|-----------------|
| SCW         | 750                    | 100                | 24             | Fully deaerated  |
| SHS         | 750                    | 100                | 0.1            | < 5 ppb         |

Fig. 1 Schematic illustration of fixture for four-point bending test used in superheated steam environment.

2.3 Analysis

After the tests, the surfaces of the specimens were observed using the scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) to characterize the surface morphology and elemental distribution. Cross sections of particular region of the surface were fabricated by using the Focused Ion Beam (FIB) to observe the cross section of the localized oxides. The weight of the coupon specimens was measured to a precision of 0.01 mg before and after each test, and then the weight changes per unit area were calculated. Elemental depth profiling was performed by the Auger electro spectroscopy (AES) analysis. Argon ion milling with 3.0 keV was used for sputtering. The spot area for measurement was approximately 53 µm² for alloy 625 and 4.0×10³ µm² for alloy 617 respectively. The etching rate was obtained by depth profiling of the thin SiO₂ film (6.82 nm/min). Oxide thicknesses were estimated by multiplying the required sputtering time for the oxygen concentration decreased to a half of the value at the outermost layer and the etching rate of the SiO₂ film.

3. Results and discussion

3.1 Surface morphology

3.1.1 Oxide formed on coupon specimens in SCW

Figure 2 shows surface morphologies of mirror finished coupon specimen of alloy 625 after the test in SCW. Two types of grain that showed different contrast were observed as can be seen in Fig. 2(a). A large number of pitting was recognized on alloy 625 after the test in SCW. The pitting formation on alloy 625 in SCW has been extensively reported in other investigations in the other temperature ranges (Chang et al., 2012, 2014; Garcia et al., 2015). As shown in Fig. 2(b), the diameter of the pitting was approximately 10 µm and angular oxide particles had a micron size were distributed around there. Such localized oxides observed on 625 in SCW are examined in more detail in the later section. A magnified image of darker grain region is shown in Fig. 2(c). The shape of oxides was triangular and flaky type. Their oxides were oriented in the same direction. In other word, the diffusion of the specific element become flaky oxides was thought to be oriented following the crystal orientation. Therefore, it is considered that the damaged layer has been almost removed by polishing. On the other hand, the lighter grain area was covered with finer particles with sub-micron size. This formation was also considered to be affected by the crystal orientation of the grain.

SEM images of surface morphology of alloy 617 after the test in SCW were represented in Fig. 3. It is widely known that alloy 617 is composed of twin crystals. Those twin crystals can be seen into difference of contrast in a grain from overview picture shown in Fig. 3(a). Difference in contrast between grains were also applicable to alloy 617. The same type of pitting was observed typically on or near grain boundaries. However, the size of pittings on alloy 617 is much...
smaller than that formed on alloy 625. In addition, almost all of pittings were formed adjacent to the certain large localized oxide. The interaction between pitting formation and large localized oxides is not clear at this time.

Fig. 2 SEM images of (a) overview showing different apparent contrasts in each grain, (b) typical example of pitting, which diameter was approximately 10 µm, (c) triangular and flaky shape oxides in darker grain and (d) angular with sub-micron sized particle oxides in lighter grain on coupon specimens of alloy 625 after 100 hrs in deaerated SCW at 750°C.

Fig. 3 SEM images of (a) overview showing different apparent contrasts in each grain, (b) pitting formed adjacent to grain boundary, (c) oxides in a darker grain, (d) oxides in a lighter grain on coupon specimens of alloy 617 after 100 hrs in deaerated SCW at 750°C. Most of the pittings were distributed on or adjacent to grain boundaries.

3.1.2 Oxide formed on coupon specimens in SHS

SEM images of surface oxide layer on alloy 625 exposed to the SHS at 750°C for 100 hrs are illustrated in Fig. 4. In contrast to the SCW, the surface was covered with uniform oxides consisting of submicron-sized particles as shown in Fig. 4(b). As seen in Fig. 4(c), the nodule-like oxides formed expansively outward with delaminated oxide film. The distribution of those oxides in SHS for 100 hrs was very similar to that of pittings seen in Fig. 2. Figure 5 shows the
elemental distribution on the surface of alloy 625 around the nodule-like oxide formed in SHS. The enrichment of Nb and Mo and the depletion of Ni and Cr was confirmed in the nodule-like oxide. In addition, the grain boundary on alloy 625 was found to be enriched in Cr and depleted in Ni.

On the other hand, the outer oxide layer on alloy 617 exposed to SHS at 750°C for 100 hrs is presented in Fig. 6. As observed in alloy 625 exposed to SHS, the surface was decorated with the uniform oxide except along the grain boundary. Figure 6(b) illustrates the SEM image of the surface oxide in the grain at higher magnification. The oxide particles had a rounded and granular shape. The morphology of localized oxide formed on alloy 617 exposed to SHS was represented in Fig. 6(c). In contrast to those in SCW, the blister-like oxide formed around the pitting was found to typically be exfoliated. The EDS maps around the localized oxide formed on alloy 617 in SHS were shown in Fig. 7. The part of exfoliation was enriched almost only in Mo, and depleted in Ni, Co and Cr. Then the rest of the blister-like oxides next to the exfoliation was confirmed to be enriched in Cr. The elemental composition of the oxides along grain boundary of alloy 617 was thought to be similar to that of alloy 625.

Based on the morphologies of localized oxides observed in each environment, the primary precipitates seem to have been the initiation site of those oxides. Actually, the range of density of pitting and nodule-like oxides have a good agreement with that of Nb rich carbide, likely MC (Floreen et al., 1994) on etched alloy 625 before the test shown in Fig. 8. Therefore, the nodule-like oxides were considered to be Nb2O5 which is most stable in Nb oxides. Since the Nb2O5 have a large Pilling-Bedworth ratio of 2.69, it is considered that the oxidation of Nb carbides resulted in that expansive growth outward on alloy 625. Similarly, the oxidation of Cr rich M23C6 and Mo rich M6C known widely as primary carbides (Mankins et al., 1974) was considered in the formation of blister-like oxides on alloy 617.

Fig. 4 SEM images of (a) overview showing uniform distribution of surface oxide on each grain, (b) sub-micron size oxide particles, (c) localized oxides formed expansively outward with delaminated oxide film on coupon specimens of alloy 625 after 100 hrs in deaerated SHS at 750°C.

Fig. 5 Qualitative elemental analysis by EDS in the localized oxide shown in figure 5(c). The localized oxide was enriched in Nb and Mo. Along grain boundaries, Ni was depleted and Cr was enriched.
Fig. 6  SEM images of (a) overview, (b) oxides on a grain consisted of rounded and granular particle oxides, (c) pitting including some extent of exfoliation of the blister-like oxide on coupon specimens of alloy 617 after 100 hrs in deaerated SHS at 750°C.

Fig. 7  Qualitative elemental analysis by EDS in the localized oxide shown in figure 6(c). The part of exfoliation was enriched almost only in Mo, and depleted in Ni, Co and Cr. The rest of the blister-like oxides next to the exfoliation was enriched in Cr.

Fig. 8  SEM image of the Nb rich primary carbide on as-received alloy 625 after etching and spectrum obtained by EDS.

3.1.3 Influence of stress on oxide morphologies in SCW and SHS

Figure 9 represents SEM images of overview and localized oxides in the tensile part of four-point bending specimens of alloy 625 and alloy 617 exposed to the SCW and SHS at 750°C for 100 hrs. Compared to the non-stressed coupon specimens, it seemed that the grain boundary oxidized to be thicker than that on coupon specimens of alloy 625 in both environments. As can be seen in Fig. 5 and Fig. 6, considering the oxide on grain boundary is composed of mainly Cr
oxide, the Cr diffusion in grain boundary was likely to be influenced by applied stress. However, the remarkable difference in morphologies of oxides on grain and localized oxides on both alloys was not seen in either environment. In addition, no cracks and spallation were observed on both alloys in the tensile part of four-point bending specimens. Based on these results, the effect of applied stress was found to be considerably limited except on grain boundaries in this work. As a evidence of that, all the specimens were found to be permanently deformed after the test in SCW and SHS environment, which is possibly suggesting that the stress relaxation have occurred during the tests.

3.2 Localized oxidation on alloy 625

In order to investigate the detail of localized oxide formed on alloy 625 in SCW and SHS at 750°C for 100 hrs, The cross-sectional observation was performed to the localized oxides in each environment shown in Fig. 10. The trenches were made by FIB sputtering. The surfaces were protected with tungsten deposition coating in advance. In SCW, the pitting was found to be probably formed by dissolution of carbides according to the image obtained from the cross-section shown in Fig. 10. Based on this image, estimation of average depth and area of this pitting was made. This pitting volume was tentatively calculated to be approximately 2.6×10⁻¹⁰ cm³. In addition to that oxide particles with coarse micron-sized diameter were predominant around the pitting, almost no oxide film was observed partially there. Considering these morphologies on the localized oxide, it is plausible that the dissolution of carbides was caused by electrochemical reaction due to the composition difference between the substrate and carbides. However, it is still not decided at this time.

In contrast to the SCW environment, as mentioned before, the oxidation of Nb carbides was the cause of the formation nodule-like oxides. The Nb oxides, which can be seen in inner area of the carbide with the lighter contrast shown in Fig. 10, reached the bottom of the Nb carbide with the depth of more than 10 µm. Therefore, it seemed that the oxygen could easily penetrated into the carbide compared to the substrate of alloy 625. In the elemental map shown in Fig. 5, the radial enrichment of Nb around the nodule-like oxide was considered to be due to the collapse of the Nb oxide extended over the surface and consequently the deposition around there. Similarly, the spallation of the blister-like oxides seemed to be caused by steam flow due to lower strength of oxide/carbide interface, likely developing large amount of voids.

The pitting site is considered to be a crack initiation site due to the stress concentration. On the other hand, since the Nb oxides are brittle (King et al., 1990), and said to be mostly affected to the crack propagation (Wei et al., 2009), they also might be somewhat influenced on crack initiation. Therefore, more detailed analyses on carbide dissolution, oxidation and its role in the oxidation of the matrix adjacent to those are necessary.
Fig. 10 SEM images of cross section of localized oxides in tensile part of four-point bending specimen of alloy 625 after 100 hrs in deaerated SCW and SHS at 750°C. White part is the tungsten coating. In SCW, there were few oxides at the coating/carbide interface and were partially almost no oxide film around the pitting, while in SHS, oxides with lighter contrast formed with the depth of more than 10 µm.

### 3.3 Weight Gain

Gravimetric analysis was performed in coupon specimens of both alloys by measuring their weights before and after the oxidation tests in SHS and SCW environment respectively. Figure 11 presents the result of the weight gain per unit area calculated. The weight gain obtained in SCW was found to be almost 50% less than that in SHS for both alloys. Considering these differences of weight gain in each environment as a result of dissolution of material, there are three areas in which the dissolution might take place: grain boundaries, grains, and primary precipitates. Here the contribution of the pitting formation on alloy 625 in SCW toward the total amount of dissolution was examined. Firstly, the pitting density ($N_{pit}$ [1/mm$^2$]) on the coupon of alloy 625 in SCW was measured by counting the number of pitting in a unit area from the SEM image at low magnification. The average pitting volume ($V_{pit}$ [m$^3$]) was substituted for the volume obtained from pitting on alloy 625 in the tensile part of four-point bending specimen shown in Fig. 10. The density of NbC ($\rho_{NbC}$ [g/m$^3$]) was assumed to be 7.73~7.80 (Cuppari and Santos, 2016). Then the NbC mass have solved to the SCW environment from coupon specimen of alloy 625 was calculated under condition that all of primary carbides are composed of NbC. The values obtained from these measurements were summarized in Table 3.

As can be seen in Fig. 11, the total amount of dissolution ($M_d$ [mg/cm$^2$]) on Alloy 625 is approximately $6.1 \times 10^{-2}$, obtained by the calculation of (weight gain in SHS – weight gain in SCW). Therefore, the fraction of dissolution by pitting formation ($f_{pit}$) was estimated to be at most 39.5 % using Eq. (1) shown below.

$$f_{pit} = \frac{N_{pit} \cdot V_{pit} \cdot \rho_{NbC}}{M_d} \times 100$$  \hspace{1cm} (1)

Actually, because in SHS environment the NbC carbides oxidized to be Nb$_2$O$_5$ to some extent, this value estimated seemed to be changeable. However, the tendency that the amount of dissolution by pitting formation on alloy 625 highly contributed to the total would not change.
Fig. 11 Weight gain of coupon specimens of alloy 625 and 617 in SCW showing smaller values than those of SHS after oxidation tests for 100 hrs at 750°C.

Table 3 Summary of parameters used for the calculation and the fraction of dissolution by pitting formation on alloy 625 in SCW.

| $V_p$ [cm$^3$] | $p_{NOC}$ [g/cm$^3$] | $N_{pit}$ [1/mm$^2$] | $M_d$ [mg/cm$^2$] | $f_{pit}$ [%] |
|--------------|-----------------|----------------|-------------|----------|
| 2.6×10$^{-10}$ | 7.73~7.80 | 118 | 6.1×10$^{-2}$ | 39.5 |

3.4 Oxide structure and oxide thickness

To evaluate the amount of dissolution in the grains, AES depth profiling was carried out on the surface of both alloys exposed to SCW and SHS at 750°C for 100 hrs. As mentioned before, the grains in SCW was distinguished from darker one and lighter one. Therefore, the profiling was performed in both regions. It is noted that the oxide thickness obtained was calculated using the SiO$_2$ sputter rate with the same Ar-ion sputter condition. Since the sputter rate varies between the oxides, the thickness was different from the actual value. Obtained elemental distributions are shown in Fig. 12 and Fig. 13. It is indicated that alloy 625 in SCW would form duplex layer, which inner layer is Cr$_2$O$_3$ and/or Cr$_2$O$_3$ + spinel and outer layer is spinel like Ni(Cr, Fe)$_2$O$_4$ (Chang et al., 2012; Ren et al., 2007). As seen in Fig. 12(a) and Fig. 12(b), the lighter grain was slightly thicker than the darker one, especially in the outer layer thought to be composed of spinel. The estimated oxide thickness was 0.477 µm and 0.355 µm respectively. Based on these results, it is suggested that the diffusion rate of Ni in the grain of alloy 625 against the oxidation was influenced by its crystal orientation. In the outer layer in SCW, the concentration of Cr decreased to approximately 10% instead of the increase of Ni. The profiling in SHS illustrated in Fig. 12(c) explains that the estimated oxide thickness is 0.539 µm and the spinel layer much thicker than Cr$_2$O$_3$ layer compared to that in SCW. On the other hand, Fig. 13(a) and Fig. 13(b) shows that difference of the oxide thickness in grains with lighter and darker contrast was not appeared clearly (0.300 µm and 0.327 µm respectively). However, as the same alloy 625, the lighter grain was slightly enriched in Ni on outer oxide layer. In SHS, the uniform oxide composed of mainly Cr and small amount of Co was observed on alloy 617 shown in Fig. 13(c), which is almost single outer layer and its oxide thickness is 0.614 µm. According to the study on the solubility of nonconductive oxide in SCW at 25 MPa up to 600°C, it is reported that the Cr oxide has a higher solubility compared to the Ni oxide (Cook and Guzonas, 2012). Supposing that this tendency remains on to 750°C, the decrease in Cr contents in outer layer on both alloys can be explained to some extent. Moreover, this trends agrees with the AES result of alloy 625 after SCW oxidation test at 600°C reported by Ren et al. (2007).

Oxide thicknesses obtained from both materials exposed to the SCW and SHS at 750°C for 100 hrs were summarized in Fig. 14. The oxide thickness of alloy 625 in SCW was 0.89 times thinner than that in SHS. On the other hand, the oxide thickness of alloy 617 in SCW is 0.53 times thinner than the one in SHS. Compared to the results in two alloys, the amount of dissolution in a grain of alloy 617 was considered to be larger than that of alloy 625 instead of the small contribution by the pitting formation. In order to discuss the relationship between the weight change and oxide thickness, a test with a much longer duration is necessary because the localized oxidation might affect the total weight loss. In addition, after a long time exposure beyond 700°C, these materials should have certain precipitates such as M$_2$C$_6$, μ-phase, and coarsening γ’ phase, etc. in their bulk alloy (Krisha et al., 2015; Garcia-Fresnillo et al., 2014). Therefore,

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their susceptibility against the dissolution in SCW also needs to be investigated in depth.

Fig. 12  Elemental depth profiles obtained by AES analysis (a) in a lighter grain and (b) darker grain in deaerated SCW, (c) in a grain in SHS at 750°C for the duration of 100hrs for alloy 625. Atomic concentration was shown by O (black), Ni (red), Cr (blue), Mo (pink) and Fe (green) content. In SCW, the oxide film was composed of the duplex layer, and the lighter grain was slightly thicker than the darker one. The outer layer in SHS was much thicker compared to that in SCW.

Fig. 13  Elemental depth profiles by AES (a) in a lighter grain and (b) darker grain in deaerated SCW, (c) in a grain in SHS at 750°C for the duration of 100hr for alloy 617. Atomic concentration was shown by O (black), Ni (red), Cr (blue), Mo (pink) and Co (green) content. In SCW, there were almost no difference in the oxide thickness and oxide film structure between the lighter and the darker grain. In SHS, The oxide layer was composed of mainly Cr and small amount of Co.
Fig. 14 Oxide thickness comparison with each environment on alloy 625 and alloy 617 estimated by AES analysis. The thickness from lighter and darker grains were respectively shown for SCW. All obtained oxide thickness from SCW exhibited thinner than those from SHS.

4. Conclusions

In this study, oxidation tests of alloy 625 and alloy 617 using coupon specimens and four-point bending tests were performed in SHS (0.1 MPa) and SCW (24 MPa) environments at 750°C. The noticeable findings are described as below.

[1] The remarkable difference in the oxidation behavior between SCW and SHS environments appeared in the primary carbide (likely NbC) in alloy 625. The pitting observed in SCW was assumed to be formed by the dissolution of carbides. In contrast, the Nb carbide oxidized to be Nb oxides with a large Pilling-Bedworth ratio in the SHS environment, which resulted in the formation of nodule-like oxides with a delaminated oxide film. Both localized oxidation sites might be potential crack initiation sites, more detailed analyses on carbide dissolution, oxidation, and its role in the oxidation of the matrix adjacent to those sites are necessary. In alloy 617, the pitting was observed in each environment. In SHS, the blister-like oxide around the pitting tended to be exfoliated presumably due to the steam flow. As for alloy 625, the primary carbides might cause the pitting formation.

[2] No cracks or spallation were observed in the outer oxide layer in the tensile part of the four-point bending specimens of both alloys. All the specimens were crept and the stress relaxation seemed to have occurred during the test. Therefore, the effect of the applied stress would be considerably limited.

[3] The weight gain was consisted with the oxide thicknesses acquired in SCW and SHS for both alloys. In the test duration of 100 hrs, the amount of the dissolution by pitting formation on alloy 625 account for a somewhat large proportion in total weight loss by dissolution. In contrast, it is considered that there was a large contribution by the dissolution of oxides on the grains of alloy 617 because the oxide thickness in SCW was much thinner than that in SHS compared to those of alloy 625. Consequently, the total weight loss by dissolution obtained in SCW on both alloys seems to be similar each other. Even at 750°C, the tendency for the preferential dissolution of Cr$_2$O$_3$ to occur in SCW was seen on both alloys in an elemental depth profile by AES. Tests with a much longer duration will help to investigate the relationship between the weight gain and oxide thickness. Moreover, the influence of the precipitates that appear in long time exposure on the oxidation and dissolution behavior also needs to be examined systematically.

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