Alloy Design of Ni-based Single Crystal Superalloys for the Combination of Strength and Surface Stability at Elevated Temperatures

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Following the findings regarding the surface stability of superalloys recently obtained by the authors, three Ni-based single crystal (SC) superalloys containing Re are designed with the aid of d-electrons concept. Creep-rupture, hot-corrosion and oxidation tests are conducted with the designed alloys in order to investigate experimentally their high temperature properties. The superalloy containing 5.4 mass% Re and 3.8 mass% Cr (A-1) shows an excellent combination of high temperature creep strength and hot corrosion resistance in comparison with a commercial second generation SC superalloy containing 3 mass% Re. The A-1 alloy exhibits better creep rupture strength than the 3 mass% Re alloy under all the test conditions of 1313 K/137 MPa, 1193 K/314 MPa, 248 MPa, 206 MPa and 1123 K/441 MPa. Performance of the A-1 alloy is well comparable to the second generation alloy in the isothermal oxidation test but poor in the cyclic oxidation test. Another alloy (A-3) exhibits an excellent resistance to the cyclic oxidation test but its creep strength is not a level comparable to the second generation superalloy. Alloing balance is discussed for the excellent combination of high temperature creep rupture strength and good surface stability of superalloys.

KEY WORDS: Ni-based superalloy; creep rupture strength; rafting; surface stability.

1. Introduction

An increasing demand for the higher efficiency of gas turbines leads to the necessity of rising their operating temperatures and stresses, which requires a continued development of high strength superalloys for gas turbine components. Hot corrosion resistance is also important for industrial turbines, which are used for longer term than jet engines. Furthermore, oxidation resistance needs to be improved because of the general increase in the inlet-gas temperature of turbines. However, the improvement in one property by adding one or more elements into the alloy may be accompanied by the deterioration of another property. For example, the addition of Re improves both high-temperature creep strength and the hot corrosion resistance.1–3) However, increasing in the Re content in SC superalloys has the propensity to precipitate Re-rich topologically close packed (TCP) phases3,4) which is known to reduce creep rupture strength. Cr is an element to negatively affect the creep rupture life of superalloys,5) although Cr is indispensable alloying element in superalloys for maintaining the resistance to hot corrosion. Thus some difficulties arise when both the good surface stability and high temperature strength are simultaneously claimed.

From our previous experiments,6,7) it has been found that increase of Ti/Al compositional ratio improves hot corrosion resistance but has a detrimental influence on oxidation resistance. Also the alloys with the Ta/(W+Mo) compositional ratio closing to unity show good hot corrosion resistance.6,7) Furthermore, we have obtained that Re is rather harmful element for oxidation resistance but the adjustment of the Re/Al compositional ratio in mol% from zero to 0.1 leads to a good oxidation resistance.8,9) Following the recent findings from the studies made by us,6–9) three Ni-based superalloys have been designed and investigated in order to make clear a guide of alloy design for the excellent combination of strength and surface stability at elevated temperatures.

2. Experimental Procedure

2.1. Alloy Design

Three Ni-based single crystal superalloys are designed with the aid of d-electrons concept.1,10,11) The compositional average of the d-electrons parameters, B0 and MD are known to be related to the phase stability of Ni-based superalloys.1,12) In designing the present superalloys, the B0 and MD values are set as closely as possible to the values of the target region (MD: 0.985, B0: 0.665)1,12) where conventionally cast superalloys show maximum high-temperature
of each alloy after the aging heat treatments is measured compositional ratio to be close to unity. Moreover, hot present study is considered by setting a mol% Ta/(Mo ratio was close to unity. Thus hot corrosion resistance in the experimental alloys. Also the best resistance in burner-rig test was found in the alloys whose Ta/(W/R) compositional ratio of the alloys. The chemical compositions of the alloys. The heat-treatment conditions are shown in Table 2 together with alloying parameters. CMSX-4 is used as a reference alloy in this study.

2.2. Alloy Preparation

Master ingots of the designed alloys are made in a vacuum induction furnace. Then, using these ingots, single crystals (SC) with 16 mm in diameter and 150 mm in length are grown by a directionally solidified method. The conditions for the heat-treatments are determined on the bases of both the data obtained from the differential thermal analysis (DTA) and the result of microstructural examination of the alloys. The heat-treatment conditions are shown in Table 2. The ingots first undergo the solution heat treatment and then followed by the aging heat treatment. After these heat treatments, the single crystal specimens are supplied to a series of experiments.

2.3. Microstructural Observation

Microstructures of the SC alloys are observed with SEM before and after the creep rupture tests. At first, emery polishing of the specimens is done followed by buff polishing with Al2O3 powders down to 0.05 μm in diameter. The polished surface is etched chemically in a 1:1 volume% HCl–HNO3 solution for about 30 s. The volume fraction of each alloy after the aging heat treatments is measured from the SEM micrographs by means of a conventional image analyzing method. The cross section of the specimens after the hot corrosion test and the oxidation test are also observed using a SEM equipped with an EDX analyzer.

2.4. Creep Rupture Test

The heat-treated SC alloys are machined mechanically into the specimens for the creep rupture test. The gauge length of the specimen is 6 mm in diameter and 30 mm in length. The creep rupture tests are carried out under the temperature/stress conditions of 1313 K/137 MPa, 1193 K/248 MPa, 206 MPa and 1373 K/441 MPa.

2.5. Hot Corrosion and Oxidation Tests

For a hot corrosion test, a burner-rig test is carried out at 1123 K for a total time of 252 ks (10 cycles, each cycle is continued for 25.2 ks) with the specimen of 8 mm in diameter and 40 mm in length. A fuel gas with atomized brine of 80 ppm NaCl is used for this test. The mass change of the specimen before and after the corrosion test is measured. Also metallographic studies are done to measure the depth of penetration of corrosion products. The total thickness of the corroded layer is defined as the length measured from the external surface to the deepest corrosion pits of the corroded specimen. It is measured on the SEM images taken from the cross section of hot corroded specimens. The mass change as well as the total thickness data is used as a measure to show the hot corrosion performance of the alloys.

In order to examine the oxidation resistance, the plate specimens with the size of 25×10×1 mm are cut from the SC alloys by using an electro-spark machine. Two types of oxidation tests are performed in this study. One is the cyclic oxidation test, in which the specimen is kept into a furnace at 1373 K for 72 ks followed by air cooling in each cycle. This cycle is repeated 12 times and thus the total exposure time at 1373 K is 864 ks. The other is the isothermal oxidation test at 1313 K for 2.16 Ms. These test temperatures are much higher than the metal temperature in service condition of the superalloys, but we employed these temperature for the reasons: (1) the turbine inlet gas temperature is over

### Table 1. Chemical compositions and parameters of the experimental superalloys (mol%\text{/mass%}).

| Alloy | Ti | Cr | Co | Ni | Mo | Hf | Ta | W | Re | Al | Md | Bo | Ta/(Mo+W) * | Mo+W/Re * | Ti/Al * | Ref. |
|------|----|----|----|----|----|----|----|----|----|----|----|----|------------|------------|---------|------|
| A-1  | 1.95 | 4.55 | 11.62 | bal | 0.91 | 0.05 | 2.30 | 1.79 | 1.80 | 11.76 | 5.10 | 0.98 | 0.664 | 0.85 | 4.507 | 0.166 |
| A-2  | 2.33 | 5.97 | 9.69 | bal | 0.78 | 0.01 | 2.08 | 1.93 | 1.33 | 9.21 | 5.10 | 0.957 | 0.665 | 0.77 | 4.036 | 0.254 | 0.14 |
| A-3  | 1.50 | 9.50 | 3.00 | bal | 0.50 | 0.01 | 2.00 | 2.00 | 1.00 | 12.30 | 5.49 | 0.986 | 0.666 | 0.80 | 3.500 | 0.122 | 0.08 |
| (CMSX-4) | 1.27 | 7.60 | 9.30 | bal | 0.38 | 0.03 | 2.18 | 1.98 | 0.98 | 12.60 | 5.60 | 0.984 | 0.664 | 0.93 | 3.340 | 0.101 | 0.08 |

*Calculated on mol% basis.

### Table 2. Conditions for heat treatment.

| Alloy | Solution heat treatment | Aging heat treatment | 1st, step aging | 2nd, step aging |
|------|-------------------------|---------------------|----------------|----------------|
| A-1  | 1573K/03.2ks+1581K/03.2ks+1593K/86.4ks | 1431K/44.8ks, AC | 1431K/44.8ks, AC |
| A-2  | 1573K/03.2ks+1581K/03.2ks+1593K/86.4ks | 1431K/44.8ks, AC | 1144K/72cs, AC |
| A-3  | 1583K/14.4ks+1593K/14.4ks | 1573K/14.4ks, AC | 1573K/14.4ks, AC |
1 300 K; (2) when the TBC coating peels off the metal surface, the metal is exposed directly to such high temperatures; (3) advanced Ni-based superalloys show excellent oxidation resistance and hence meaningful data is not obtained by the tests below 1 273 K; (4) 1 313 K and 1 373 K are corresponding to the creep test temperatures. Furthermore, when a testing time is the same duration, total exposure time at a high temperature might be shorter in cyclic oxidation than that in isothermal oxidation. Then 1 373 K is employed in the cyclic oxidation test in this study.

The mass change of the specimen before and after the oxidation test is measured and used as a measure of the oxidation resistance of the alloy.

3. Results

3.1. Microstructure of Heat-treated Specimens

Irrespective of the difference in the chemical compositions among three alloys, no eutectic phase is observed in the microstructure of any alloys after the solution heat treatment, in agreement with the expectation from Bö and Mő parameters. Figure 1 shows the typical microstructures after the aging heat treatment, which consist of γ' phase precipitated homogeneously in the γ phase matrix. The measured γ' volume fraction of the alloys varies in the range of 60–69% as shown in Table 3.

3.2. Creep Rupture Strength

Creep rupture strengths of all the alloys are compared with each other using the Larson Miller Parameter (C = 20) as shown in Fig. 2. The A-1 alloy shows the highest creep rupture strength among all the experimental superalloys. Its rupture strength is better under all the temperature/stress conditions than that of a reference alloy, which is a commercial second generation superalloy containing 3 mass% Re. The creep strength of the A-2 alloy is also better or comparable to the reference alloy under all the test conditions, and its strength is the best among all the superalloys at the condition of 1 313 K/137 MPa. On the other hand, the strength of the A-3 alloy is not so high as the reference alloy under higher stress conditions but it shows better creep strength than the reference alloy at 1 313 K/137 MPa. The character of creep strength depending on the test conditions is related to the alloy chemistry and the microstructural evolution during creep, as will be discussed later.

3.3. Microstructure of Crept Specimens

We focus on the microstructural evolution during creep at 1 193 K, because this is the most important temperature for the turbine components for power plants. The micrographs taken from the cross section of the crept specimens at 1 193 K are shown in Fig. 3. The stress condition and the rupture time of each alloy are shown above and beneath the corresponding microstructure, respectively. The rafted structure is observed in the experimental alloys. Namely, the γ' precipitates are connected with each other normal to the stress axis. For the alloys, A-1 and A-2, the degree of the rafting varies depending on the stress value. The trend of rafting becomes less significant with decreasing stress. The variation of the degree of rafting with the stress value is, however, not distinct in the case of the A-3 alloy. The least amount of rafting is observed in the micrograph of the A-2 alloy at 206 MPa. This is related to the lattice misfit value of the A-2 alloy. As shown in Table 4, the largest misfit in the lattice parameter between γ and γ' phases leads to the break of the coherency between them, resulting...
in the poorest rafting. The microstructures of the A-1 and the A-2 alloys are free of any TCP phases, but a little needle-shaped TCP phase is observed in somewhere of the A-3 alloy after the creep test.

3.4. Hot Corrosion Test

3.4.1. Hot Corrosion Products

The SEM images and the corresponding characteristic X-ray images are taken from the cross section of hot corroded specimens after the burner-rig test, and the results are shown in Fig. 4 for the A-1 alloy containing high Re and Co contents and Fig. 5 for the A-3 alloy containing high Cr and low Co contents. Figure 4 is representative of the specimen having the corroded zone consisting of one layer, whereas Fig. 5 is representative of the specimens containing two layers (internal and external) in their corroded zone.

It is seen that corrosion is very limited for the A-1 alloy. From the Al image shown in Fig. 4, it is found that the Al-rich layer is dense and continuous in the hot corrosion zone of the A-1 alloy. On the other hand, corrosion penetrates into deep inside of the A-3 alloy. In the SEM image shown in Fig. 5, “t”, “t_int.” and “t_ext.” mean the thickness of the total corroded layer, the internal corroded layer and the external corroded layer, respectively. As shown in Fig. 5, the corroded zone is distinctly composed of external and internal layers. The Cr concentration in the external layer is higher than that in the internal layer. The region of the higher Al and Ti concentrations is observed in the corroded zone of the A-3 alloy, but in contrast to A-1 alloy the images are neither dense nor continuous, indicating that the Al and Ti-rich layer is porous.

In Figs. 4 and 5, the S signal inevitably includes Mo–L signal, because the corresponding electron energy levels are very close to each other. However, by comparing the S(\text{Mo}) image to the Mo image in Figs. 4 and 5, it is found that sulfur is enriched in the corroded layer of the A-3 alloy (Fig. 5) but it distributes homogeneously with a level of noise in the A-1 alloy (see Fig. 4). The relatively more dense S(\text{Mo}) image of the A-3 alloy is due to the S penetration which indicates that severe sulfidation occurs in the A-3 alloy during the hot corrosion.

Here, in the X-ray images, no Re enriched layer is observed in corrosion products formed on the Re containing alloys. This is probably due to a high vapor pressure of Re-oxide (Re₂O₇). Also, Ta is not enriched in the section of the corroded specimens as shown in Figs. 4 and 5.

3.4.2. Hot Corrosion Resistance

The mass change of the experimental alloys after the burner-rig test at 1 123 K for 252 ks is shown in Fig. 6. The A-1 alloy gains mass but the other alloys lose mass after the test. The mass gain and mass loss are associated with the retention and the spalling of the corrosion products on the
specimen surface after hot corrosion as to be explained later. Both the A-2 and the A-3 alloys exhibit larger mass changes than the reference alloy. The absolute value of the mass change is the largest in the A-3 alloy and the smallest in the A-1 alloy.

The corroded layer thickness is measured from the SEM images taken from the cross-section of hot corroded specimens. The measured values are summarized in Table 5.

3.5. Oxidation Test

3.5.1. Mass Change in Cyclic Oxidation

The measured mass change of the experimental alloys after the cyclic oxidation at 1 373 K for a total time of 864 ks is shown in Fig. 7. The A-3 alloy shows a steady mass change rate for all over the oxidation period (up to 864 ks). This alloy shows an indication of excellent oxidation resistance. Other experimental alloys show monotonous mass loss during oxidation, although the mass gain is observed in the first step of the oxidation test. At the end of the oxidation (864 ks), the A-2 alloy shows the maximum mass change among the experimental alloys. Compared to the reference alloy, the A-3 alloy is better but both the A-1 and A-2 alloys are worse in the oxidation resistance.

3.5.2. Cyclic Oxidation Products

After the cyclic oxidation test, SEM micrographs and the corresponding characteristic X-ray images are taken from the cross section of the oxidized specimens, and the results are shown in Fig. 8 for the A-2 alloy and in Fig. 9 for the A-3 alloy. These A-2 and A-3 alloys correspond to the alloy showing the largest and the smallest mass change in oxidation, respectively. Schematic illustration is also drawn in each figure. A porous Al image is seen in the oxidized scale of A-2 alloy as shown in Fig. 8. Ti and Cr images are also seen in the oxidized scale of this alloy. In contrast to the result of A-2 alloy, it is seen, from the characteristic X-ray images of A-3 alloy shown in Fig. 9, that the oxidized scale consists of a continuous Cr layer on the external side followed by a dense and continuous Al layer on the internal side and the two layers are entirely isolated from each other. The region of higher Ti concentration is not observed in the oxidized scale of A-3 alloy.
3.5.3. Mass Change in Isothermal Oxidation

Figure 10 shows the mass change of the experimental alloys after an isothermal oxidation at 1313 K for 2.16 Ms. The mass gain is observed in the A-2 alloy, which is different from other alloys showing mass loss after the oxidation test. The A-1 alloy shows a mass change nearly equal to that of the reference superalloy. It is obvious from Fig. 7 and Fig. 10 that the experimental alloys show different behavior in the mass change between cyclic and isothermal oxidation tests. For example, the A-2 alloy exhibits the smallest mass change among the experimental alloys in the isothermal test. Also, the mass change of A-3 alloy is the largest in the isothermal oxidation test but the smallest in the cyclic oxidation test. These results are probably related to the adhesiveness of oxide scales formed on the surface of experimental alloys.

Fig. 8. SEM image and the corresponding characteristic X-ray images taken from the cross section of the A-2 alloy after the cyclic oxidation test.

Fig. 9. SEM image and the corresponding characteristic X-ray images taken from the cross section of the A-3 alloy after the cyclic oxidation test.

Fig. 10. Mass change of the specimens measured after the isothermal oxidation test at 1313 K for 2.16 Ms.
4. Discussion

4.1. Rafted Structure

After the aging heat treatment, SC superalloys contain sub-micron size coherent cuboidal $\gamma'$ precipitates. The difference in lattice parameter between the $\gamma$ matrix and coherent $\gamma'$ precipitates in a Ni-based superalloy creates very high misfit stresses. During high temperature exposure, the misfit stresses can be relieved by the formation of networks of edge dislocations at the interfaces between the two phases. The dislocations arrange themselves such that their extra half planes are in the phase with the smaller lattice parameter, thus accommodating the lattice parameter mismatch between the phases.\(^{[14]}\) The formation of these networks induce the morphological evolution of the $\gamma'$ precipitates from cuboids to platelets (rafts).\(^{[15]}\) Along with the lattice misfit between the $\gamma$ and $\gamma'$ phases, the bulk diffusion rate is also considered to control the formation of rafted structure.\(^{[15]}\) The lattice misfit value of the designed alloys estimated by using a relationship between the lattice constant and the chemical composition\(^{[15],[18]}\) is shown in Table 4.

The lattice misfit value is the largest in the A-2 alloy and the smallest in the A-1 alloy. Due to a large lattice misfit value of A-2 alloy, coherency between $\gamma$ and $\gamma'$ phases is lost considerably and misfit dislocations are introduced into the interface.\(^{[15],[19]}\) The existence of such interfacial dislocations lowers the elastic energy between the two phases, so that the interfacial energy effect becomes more dominant than the elastic energy effect. As a result, the shape of the $\gamma'$ phase in the A-2 alloy becomes irregular at the lower stress values (248 MPa, 206 MPa) and the extent of rafting is rather decreased. However, the reason why the rafting of the A-2 alloy at higher stress value (314 MPa) is regular is not understood at the moment.

On the other hand, the least lattice misfit value produces the most continuous $\gamma'$ rafting in the A-1 alloy. This type of rafted structure containing continuous $\gamma'$ platelets improves the creep resistance effectively by providing barriers to dislocation climb around $\gamma'$ platelets.\(^{[20]}\) At a low stress value of 206 MPa, the extent of rafting is reduced, resulting in the reduced creep rupture life of A-1 alloy. This is consistent with the phenomena that the stress vs. LMP curve at 1 193 K becomes steep as the stress level changes from 248 to 206 MPa in the A-1 alloy as shown in Fig. 2. Poor creep rupture lives of the A-2 alloy both at 248 and 206 MPa are attributable to its low degree of rafting in the microstructure. Creep rupture strength of A-3 alloy is the poorest among all the experiment alloys. This is probably due to the appearance of a little amount of TCP phase during creep, since it deteriorates the creep strength largely.

The A-1 alloy contains a large Re content (5.4 mass%) which slows down all the diffusion-controlled processes and influences the creep behavior of the alloy.\(^{[21]}\) The coarsening rate of the $\gamma'$ precipitates is thus strongly reduced, resulting in the improvement of the creep rupture strength of the A-1 alloy.

4.2. Possible Protection Mechanism against Hot Corrosion

The element, Cr is well known to play an essential role in hot corrosion resistance, since it promotes the formation of a protective $\text{Cr}_2\text{O}_3$ scale.\(^{[22]}\) Although the A-1 alloy contains the minimum Cr content among the experimental alloys, it shows the best hot corrosion resistance. This is due to the high Re content (5.4 mass%). As already reported, Re is effective in improving hot corrosion resistance as well as creep rupture strength.\(^{[23],[24]}\) Furthermore, the Ta/(Mo+W) compositional ratio of the A-1 alloy (0.85) is close to unity. The best hot corrosion performance of this alloy supports our previous study\(^{[25]}\) that the alloys of the Ta/(Mo+W) compositional ratio close to unity show good hot corrosion resistance. The real reasons why Re is effective in hot-corrosion and why the Ta/(Mo+W) compositional ratio should be unity for keeping the hot-corrosion resistance, are still not clear. However, the Ta/(Mo+W) compositional ratio is probably related to arrange the chemical compositions between the $\gamma$ and $\gamma'$ phases, because both Mo and W are the $\gamma'$ phase forming elements and Ta is the $\gamma'$ phase forming element. In fact, it is known that the chemical compositions of the $\gamma$ and $\gamma'$ phases play an important role in the hot-corrosion resistance in nickel-based superalloys.\(^{[23]}\)

The presence of both $\text{Cr}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ on the surface is effective in improving the hot corrosion resistance of alloys. As far as the oxide scales are dense and continuous, these oxides provide barriers to spatially separate corrosive species and the underlying metals and to hinder the corrosive species from migrating into metals, resulting in the reduction in the rates of oxidation and sulfidation.\(^{[24]}\) As seen in Fig. 4, $\text{Cr}_2\text{O}_3$ is not formed in the corroded layer of the A-1 alloy possibly because of its low Cr content (3.8 mass%). Instead, dense and continuous $\text{Al}_2\text{O}_3$ layer is developed on the surface during hot corrosion, which is protective for the underlying alloy from hot corrosion. Thus the corrosion thickness is limited to 7.1 $\mu$m resulting in the excellent corrosion resistance of this alloy. On the other hand, the A-3 alloy has a high Cr content (8.18 mass%). Therefore, besides $\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$ and $\text{TiO}_2$ simultaneously form in the corroded zone of the A-3 alloy, resulting in the formation of porous oxides as shown in Fig. 5, since the competitive oxide forming reactions make oxides porous.\(^{[25]}\) The $\text{TiO}_2$ layer can scarcely hinder S intrusion\(^{[24]}\) and porous $\text{Cr}_2\text{O}_3$ or $\text{Al}_2\text{O}_3$ layer shows less ability to suppress internal oxidation and sulfidation, resulting in the low corrosion resistance of the A-3 alloy. In fact, the penetration of S from surface into deep inside of the A-3 alloy is seen from the S image of Fig. 5. As shown in Fig. 11, the hot corroded products of the A-3 alloy are identified by the X-ray diffraction method. The detection of sulfide compounds in the hot corroded scale confirms the occurrence of severe sulfidation during hot corrosion in this alloy.

As shown in Fig. 5, hot corroded layer of the A-3 alloy is distinctly composed of two layers. The dense oxidized layer is the external layer whereas the comparatively less dense oxidized layer is the internal layer, which implies that the internal layer corresponds to the sulfidized layer. The A-3 alloy has a high W content (6.09 mass%), which causes the adherence of the external oxide scales weaker by acidic fluxing reaction.\(^{[26]}\) Thus, the external layer of the A-3 alloy is removed easily, leading to the mass loss of the alloy as shown in Fig. 6.

No sulfur but the oxygen image appears in the corroded
reaction is the formation of TiO₂, but A-3 alloy has a very low Ti content as compared with the Cr content (Ti/Cr ratio is 0.16). Thus Al₂O₃, TiO₂ and Cr₂O₃ all form at the beginning of oxidation but the difference of the amount of reactants probably causes the predominant growth of the two oxides Al₂O₃ and Cr₂O₃ on the oxidized scale of the A-3 alloy; Al₂O₃ on the inner side followed by Cr₂O₃ on the outer side of the scale (Fig. 9). Both the layers are protective to the underlying alloy and thus the oxidation resistance of the A-3 alloy is improved. On the other hand, comparable amounts of Al, Ti and Cr contents of the A-2 alloy (Ti/Al and Ti/Cr ratios are 0.254 and 0.39 respectively) lead to the formation of the respective oxides in a competitive way, resulting in the formation of porous oxides as shown in Fig. 8. The coexistence of Al₂O₃, TiO₂ and Cr₂O₃ in the oxidized scale of the A-2 alloy after the cyclic oxidation test is confirmed in the X-ray diffraction pattern as shown in Fig. 12. The formation of porous oxides of the A-2 alloy is also due to its large Re content because of the large vapor pressure of Re-oxide. These porous oxides are non-protective and fail to save the underlying alloy effectively from oxidation.

4.4. Alloying Balance for Combination of High Temperature Strength and Surface Stability

As mentioned in the previous section, in the case of Ni-based superalloys, the cyclic oxidation tests are used commonly in order to evaluate the oxidation resistance of the alloys. Thus cyclic oxidation and hot corrosion resistance are considered as the surface stability of alloys.

When compared with the reference alloy, A-1 alloy shows an excellent performance in view of its creep rupture strength and corrosion resistance at elevated temperatures but its resistance in the cyclic oxidation is not good. On the contrary, A-3 alloy exhibits excellent resistance in the cyclic oxidation test but does not show a satisfactory performance either in high temperature creep rupture test or in hot corrosion test. The low value of the mol% Ti/Al ratio (0.122) as well as the Re/Al ratio (0.08)≤0.1 of A-3 alloy is supposed to be attributable to its excellent resistance in the cyclic oxidation. In contrast to A-3 alloy, the mol% Ti/Al and Re/Al compositional ratio of the A-1 alloy is 0.166 and 0.15 respectively. On the basis of the results of A-1 and A-3 alloys, a possible modification of the values of Ti/Al and Re/Al ratio of A-1 alloy approaching to 0.122.

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**Fig. 11.** X-ray diffraction pattern from the hot corroded scale of the A-3 alloy after the burner-rig test.

**Fig. 12.** X-ray diffraction pattern from the hot oxidized scale of the A-2 alloy after the cyclic oxidation test.
The formation of protective Al₂O₃ and Cr₂O₃ scales on the inner side and of Cr₂O₃ on the outer side of the oxide scale. Reactants causes the predominant growth of Al₂O₃ on the inner side and of Cr₂O₃ on the outer side of the oxide scale. The Ti/Al and Re/Al compositional ratio of A-1 alloy approach the balance for combination of high temperature strength and surface stability.

5. Conclusions

In this study, it is intended to design Ni-based single crystal (SC) superalloys with the aid of the d-electrons concept, which have the excellent creep rupture properties as well as the high temperature surface stability. The following results are obtained.

(1) One designed superalloy containing 5.4 mass% Re and 3.8 mass% Cr (A-1) exhibits an excellent combination of creep rupture strength and high temperature corrosion resistance which is superior to the second generation SC superalloy.

(2) The A-1 alloy shows similar performance to the reference second generation SC superalloy in continuous oxidation but its resistance to cyclic oxidation is not good.

(3) The A-3 alloy possesses the best resistance to cyclic oxidation. The difference in the amounts of oxide forming reactants causes the predominant growth of Al₂O₃ on the inner side and of Cr₂O₃ on the outer side of the oxide scale. The formation of protective Al₂O₃ and Cr₂O₃ scales on the A-3 alloy are attributable to its excellent oxidation resistance.

(4) A possible modification of the parameters of mol% Ti/Al and Re/Al compositional ratio of A-1 alloy approaching to 0.122 and ≤0.1 respectively is supposed to provide the balance for combination of high temperature strength and surface stability.

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