

WATER VAPOUR EFFECT ON HIGH TEMPERATURE OXIDATION BEHAVIOUR OF SUPERALLOY RENE 80

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Summary

The commercial Ni-base superalloy Rene 80 was isothermally oxidized at 1050°C in synthetic air and synthetic air with addition of H₂O in two types of experiments: during oxidation in a thermobalance for 50 h and during oxidation in a tube furnace. During thermobalance oxidation the water vapour content was 7% while during tube furnace oxidation 20%. The samples were exposed up to 100 hours. The obtained results revealed that Rene 80 formed the oxide scale consisting of TiO₂ and Cr₂O₃ in the outer and BCrO₃ in the inner part of the oxide scale. Below the latter oxides internal Al₂O₃ precipitates are visible. Such an oxide scale morphology was observed on samples exposed in both atmospheres. For material oxidised in dry synthetic air an additional phase, namely TiN below the zone of internal oxidation of aluminium was found for all of the times. The internal TiN phase was suppressed due to the presence of water vapour in the atmosphere. The obtained results showed that such a suppression is observed up to at least 100 hours.

Keywords: superalloy Rene 80, high temperature oxidation, water vapour

Wpływ pary wodnej na proces utleniania wysokotemperaturowego nadstopu niklu Rene 80

Streszczenie

W pracy przedstawiono wyniki badań kinetyki procesu utleniania wysokotemperaturowego nadstopu niklu Rene 80 w temperaturze 1050°C i w czasie 100 h, w środowisku syntetycznego powietrza z i bez dodatku pary wodnej. Do utleniania stosowano dwa rodzaje pieców: komorowy – próba termograwimetryczna i piec rurowy. Przyjęto zawartość pary wodnej w powietrzu syntetycznym podczas próby w komorze termograwimetrycznej – 7%, natomiast w piecu rurowym 20%. Analiza wyników badań składu chemicznego metodami emisyjnej spektroskopii optycznej z wyładowaniem jarzeniowym (GD-OES) i skaningowej mikroskopii elektronowej (SEM) na przekroju warstwy utlenionej wykazała, że na podłożu nadstopu niklu Rene 80 tworzy się wielostrefowa zgorzelina złożona z tlenków TiO₂ i Cr₂O₃ w strefie zewnętrznej oraz tlenek BCrO₃ w strefie wewnętrznej. Poniżej warstwy wierzchniej zgorzeliny stwierdzono strefy wydzieleni nieciągłych tlenku Al₂O₃. Przedstawiona morfologia zgorzeliny jest charakterystyczna dla utleniania w obydwu atmosferach zarówno dla powietrza syntetycznego, jak również powietrza z parą wodną. Stwierdzono, że podczas utleniania w powietrzu syntetycznym (bez pary wodnej) tworzą się azotki TiN poniżej warstwy tlenku Al₂O₃. Azotki TiN nie wytworzyły się

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w warstwie utlenianej w atmosferze pary wodnej. Jest to spowodowane preferencyjną adsorpcją cząstek pary wodnej na powierzchni zgorzeliny.

Słowa kluczowe: nadstop niklu Rene 80, korozja wysokotemperaturowa, para wodna

1. Introduction

Gas turbines are one of the most important sector of electricity production. One of the major problems associated with electricity generation is CO₂ emission, therefore in near future gas turbines power plants should be able to operate at higher temperature range with non-conventional gases e.g. hydrogen rich Syngas or other fuels with higher amount of water vapour compared to natural gas. For construction the hottest parts of gas turbines Ni-based superalloys are the most widely used. Ni-based superalloys are as popular, because of their very good mechanical properties, high thermal fatigue strength, good tensile properties and high temperature creep resistance. However to increase further resistance of superalloys to high temperature oxidation different types of oxidation resistant coatings are used. For second stage of the blades and vanes Ni-based superalloys with MCrAlY (where M=Ni, Co) coating are used. For first row of turbine blades and vanes more advanced thermal barrier coating (TBC) are necessary.

Presence of water vapour in the atmosphere is known to alter the high-temperature oxidation behaviour of material used in the hot sections of the turbine. Based on research on pure Cr and Fe-based alloys it has been found that water vapour significantly increased chromia scale growth rate [1-7]. The water vapour effect on oxide scale adherence was also investigated. The results showed that oxide scale formed on specimens oxidized in water vapour containing gases showed better oxide scale adherence compare to that formed in dry atmospheres [1, 2, 8]. One of proposed explanation for better adherence of oxides formed under water vapour containing atmospheres was enhancement of oxide scale plasticity by water vapor [9, 10]. In spite of positive influence of water vapour on oxide scale adherence also negative effects can be observed. Increasing of chromium oxide evaporation was found in many studies [11-13]. Water vapour enhancement of chromium oxide evaporation was found by forming of chromium oxyhydroxide. However studies of Ti-containing Ni-based alloys under water vapour containing showed that vaporization of chromium oxyhydroxide can be to some extent suppressed by formation of continuous outer TiO₂ layer [14]. Results obtained from investigation about influence of oxygen partial pressure on oxidation behaviour of alloys showed, that in atmospheres with low pO₂ Cr evaporation should not be significant; it can have a significant impact on oxidation process only in high pO₂ atmospheres [12-18]. It has been also found that Ti-solubility in chromia scale can be dependent on pO₂ [19].

The aim of present work is to investigate the effect of water vapour in synthetic air atmosphere on oxide scale formation on commercially available Ni-based superalloy Rene 80.

2. Experimental

Chemical analysis of Rene 80 determined by inductive coupled plasma – optical emission spectroscopy (ICP-OES) showed that the composition of the used alloy batch is very close to the nominal one (Table 1). Rectangular specimens were machined with a size of 20 x 10 x 2 mm. The surfaces were ground on SiC papers till 1200 grit finish and then ultrasonically cleaned in ethanol prior to oxidation.

Table 1. Chemical composition of studied batch of Rene 80 analysed by ICP-OES and combustion analysis (for carbon) and ICP-MS (for boron) compared with the nominal composition (wt%)

Method	Ni	Cr	Co	Ti	Al	Mo	W	C	B	Zr
Nominal	Base	14.0	9.5	5.0	3.0	4.0	4.0	0.17	0.015	0.03
ICP-OES	Base	13.2	9.16	4.6	2.85	3.92	3.81	0.15	0.009	<0.01

Isothermal oxidation tests were performed using TGA 92-16.18 Setaram thermobalance. The test was performed at 1050°C up to 50 hours in two atmospheres: synthetic air and synthetic air + 7% H₂O. The heating rate was 90 K/min, the cooling rate 10K/min and the gas flow rate 2 l/h.

A second type of the oxidation tests were performed at 1050°C in a tube furnace with a heating rate of 10 K/min and a cooling rate of 2 K/min in two atmospheres:

- synthetic air (N₂ + 21% O₂)
- synthetic air + 20% H₂O.

Prior to cross-sections preparation oxidized specimens were cut in the middle, sputtered with very thin gold layer using cathodic evaporation, electrolytically coated with nickel and mounted in resin. Metallographic cross sections were prepared by series of grinding and polishing steps, finishing with a fine polishing in SiO₂ suspension with 0.25 µm granulation. The cross sections were analysed using optical microscope and scanning electron microscope (SEM). Selected samples were investigated X-ray diffraction (XRD) and glow discharge – optical emission spectrometry (GD-OES). The GD-OES depth profiles were quantified using the procedure described in references [20, 21].

3. Results and discussion

Figure 1 shows the microstructure of Rene 80 in the as-received condition. It is visible, that the alloy consists of γ' -Ni₃Al cubic precipitates distributed within γ -Ni matrix. Moreover at the grain boundaries coarsening of γ' phase is observed.

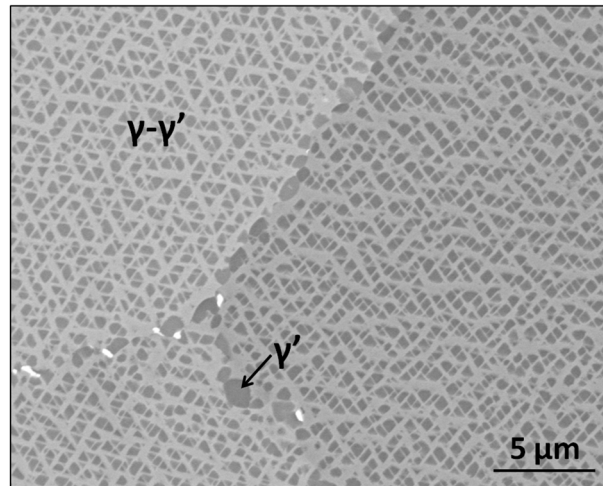


Fig. 1. SEM backscattered electron image showing cross-section of Rene 80 in the as received condition

Figure 2a shows the mass change of Rene 80 oxidized up to 50 h in dry and wet synthetic air. The instantaneous k_w calculated based on the mass changes obtained from Figure 1 is shown on Figure 2b. The procedure for the k_w calculation is described in Ref [22]. The obtained results showed no dramatic effect of water vapour on the mass gain as well as on instantaneous k_w . Moreover, the value of calculated instantaneous k_w which is of about $0.17 \text{ mg}\cdot\text{cm}^{-4}\cdot\text{h}^{-1}$ at the end of the experiment and it is comparable to the data available in literature published e.g. by Jalowicka [23].

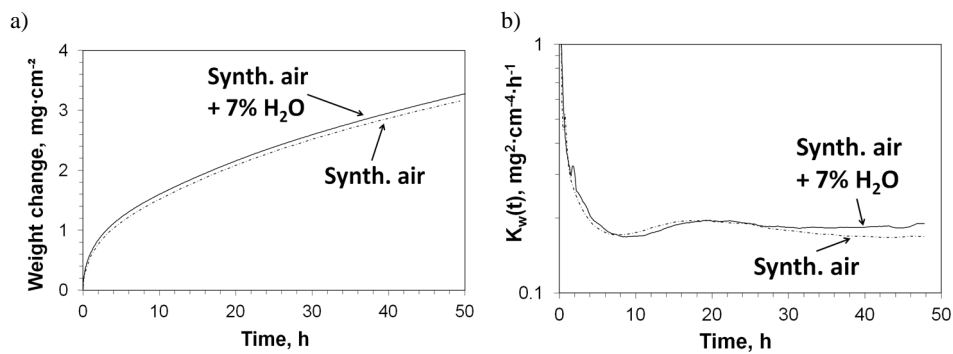


Fig. 2. Thermogravimetric test results obtained for Rene 80 during isothermal exposure at 1050°C in synthetic air with and without 7% H_2O for 50 h: a) mass change as function of time and b) instantaneous parabolic rate constant k_w calculated using data in according to procedure described in Ref., based on [22]

The results of the GD-OES analysis performed on Rene 80 isothermally exposed at 1050°C up to 50 hours (Fig. 3 and 4 respectively), showed that material formed oxide scale with quantitatively similar composition in dry and wet synthetic air. On both depth profiles in the outer oxide region one can observe enrichment of Ti below which Cr is enriched. Following Al profile one can observe enrichment of Al in the inner part of the oxide scale which corresponds to the internal precipitates of Al_2O_3 . Between the peaks of Cr and Al a high peak

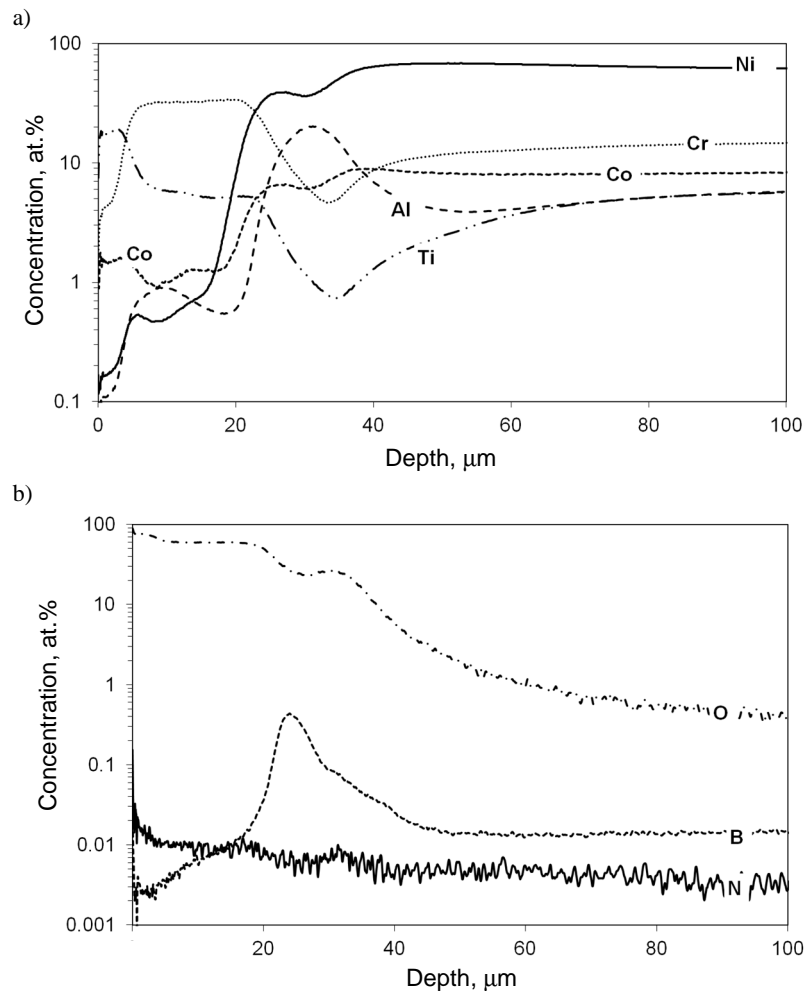


Fig. 3. GD-OES depth profiles of Rene 80 after oxidation at 1050°C in synthetic air for 50 h showing depth profiles of: a) metallic elements and b) selected non-metallic elements

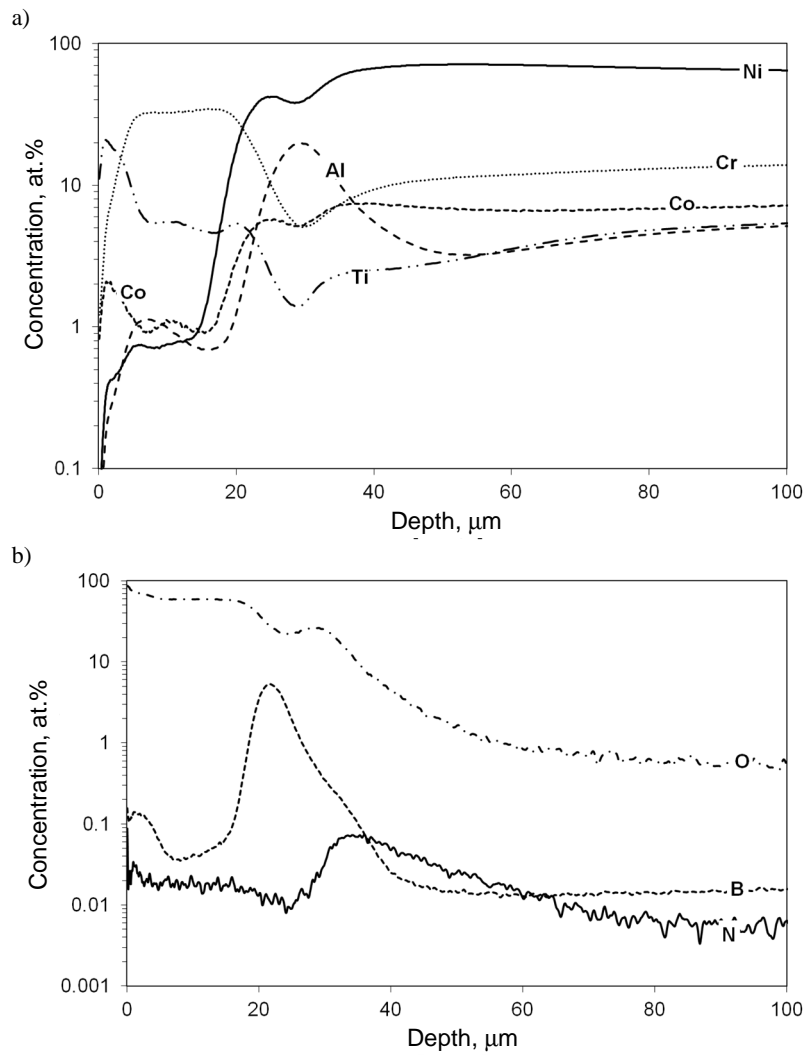


Fig. 4. GD-OES depth profiles of Rene 80 after oxidation at 1050°C in synthetic air + 7% H₂O for 50 h showing depth profiles of: a) metallic elements and b) selected non-metallic elements

of B is found above which enrichment of Ti is observed. This suggests formation of BCrO_3 and CrTi_2O_5 phases which were recently identified by Jalowicka et. al. [24]. As mentioned, the oxide scale composition looks similar in both atmospheres, however the main difference is observed in the nitrogen profile. For the specimen oxidized in dry synthetic air an enrichment of nitrogen is observed below the zone of internal oxidation of aluminum, while for the sample exposed in wet synthetic air the nitrogen profile is flat, which means that no enrichment is found. Enrichment of nitrogen in the sample exposed in dry atmosphere

corresponds to a kink in Ti profile, which indicates formation of TiN precipitates below the oxide scale. This observation is confirmed by the SEM analysis of the cross sections of the materials exposed in both atmospheres (Fig. 5) in which formation of TiN is clearly visible in case of dry atmosphere while in case of water vapour presence the latter phase is absent. The SEM images of the cross sections of Rene 80 oxidised during oxidation tests at 1050°C in synthetic air and synthetic air + 20% H₂O (Fig. 6) showed that the observation of internal TiN and its absence in dry and wet gas respectively is reproducible. Formation of TiN was additionally confirmed by SEM/EDX elemental mapping presented in Fig. 7.

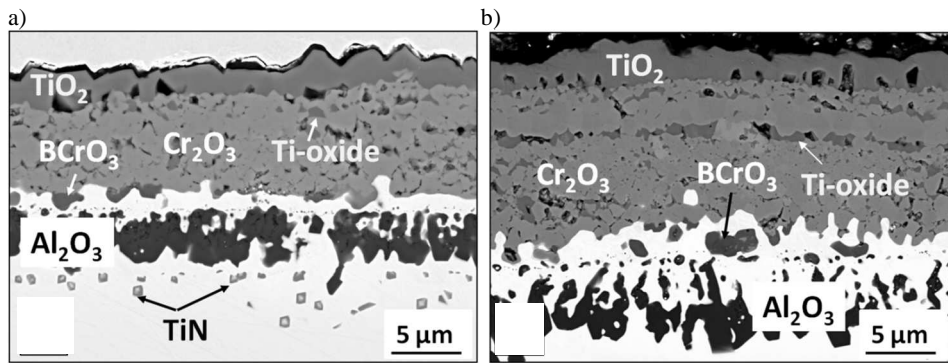


Fig. 5. SEM/BSE images of the cross-sections of Rene 80 after isothermal oxidation test at 1050°C for 50 hours in: a) synthetic air and b) synthetic air + 7% H₂O

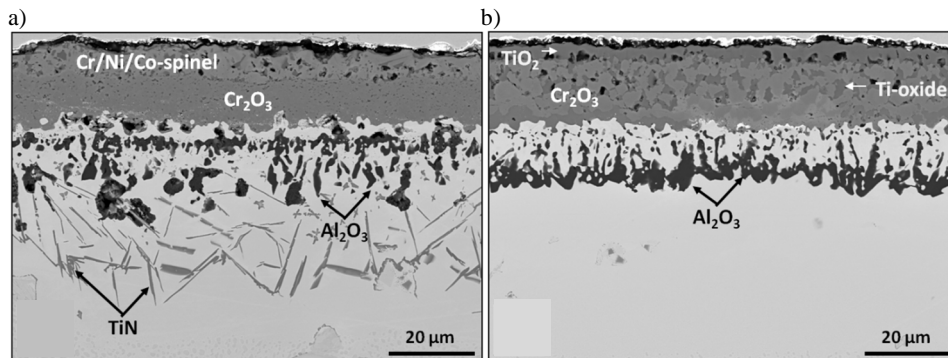


Fig. 6. SEM/BSE images of the cross-sections of Rene 80 after discontinuous oxidation test at 1050°C for 100 hours in: a) synthetic air and b) synthetic air + 20% H₂O

Krupp and Christ [24, 25] studied internal nitridation phenomena on binary and ternary [24] as well as quaternary alloys [25]. The exposure atmosphere was a mixture of 45% He – 5% H₂ – 50% N₂. For Cr concentration below 20 wt.% no Cr nitrides could be observed. Similar observation was noticed for ternary and

quaternary alloys. However for quaternary alloys Ni-10Cr-2Al-2Ti two types of nitrides were found: TiN and AlN. In contrary in the present work only TiN formation is observed, Al-nitrides are not present; Al_2O_3 formed. Figure 8 illustrates stability diagram for the system Ti-Al-O-N at 1050°C . Within the oxide scale $p\text{O}_2$ decreases from gas side to oxide/superalloy interface. Figure 8 shows that when $p\text{O}_2$ decreases TiN will be formed prior to AlN, because TiN is more stable.

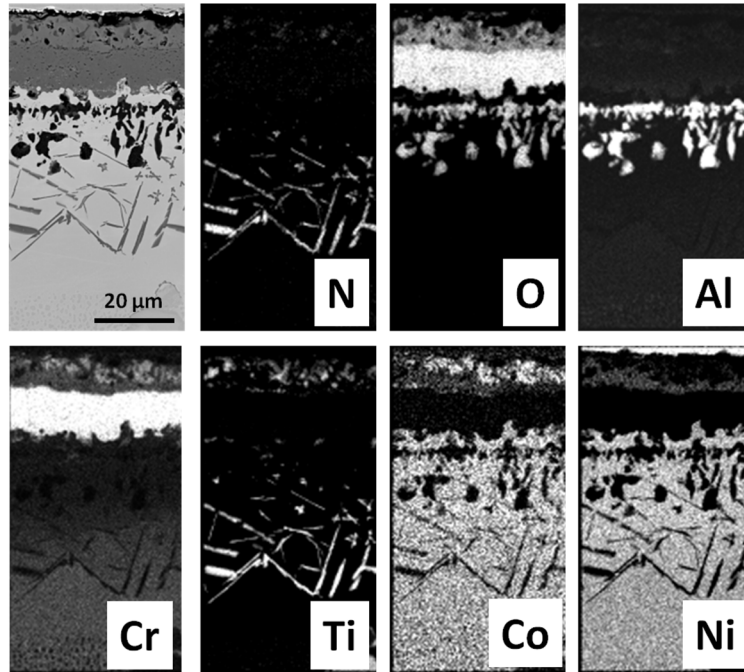


Fig. 7. SEM/BSE image and SEM/EDX corresponding maps of the cross-sections of Rene 80 after discontinuous oxidation test at 1050°C for 100 hours in synthetic air

Considering the very low N-solubility in chromia, the N-penetration is related to molecular transport via defects in the oxide scale, such as pores or microcracks. In contrast, in case of chromia scales which are free of such defects, nitridation does not occur [24, 25]. Therefore it is obvious that the substantial porosity in the oxide scales on Rene 80 as a result of Ti-doping of chromia as described in detail by Jalowicka et al. [26] promotes the nitridation.

Contrary to the experiment in dry synthetic air no internal TiN formation is observed in the synthetic air + 7% H_2O . Suppression of internal nitridation by water vapour has been observed by Michalik et al. [27] during oxidation of pure chromium in $\text{N}_2 - 1\% \text{O}_2$ with and without different amounts of water vapour. The authors explained this phenomenon by the fact that polar water vapour molecule

absorbs on the surface of the oxide scale much more strongly than the non-polar molecule of N_2 . It was also suggested that any contribution made by molecular water to oxygen mass transport within the chromia will also be enhanced.

Tying up Ti in the form of TiN results in suppression of Ti incorporation into the chromia scale. Therefore it can be expected that the adverse effect of Ti on the chromia scale growth rate described in [27] might be to some extent suppressed during exposure in dry synthetic air. Indications for the latter were found in the cross-sections: a thinner outer TiO_2 layer, a thinner Cr_2O_3 scale and coarser internal Al_2O_3 precipitates were found after exposure in synthetic air than in synthetic air + 7% H_2O (Figures 5 and 6).

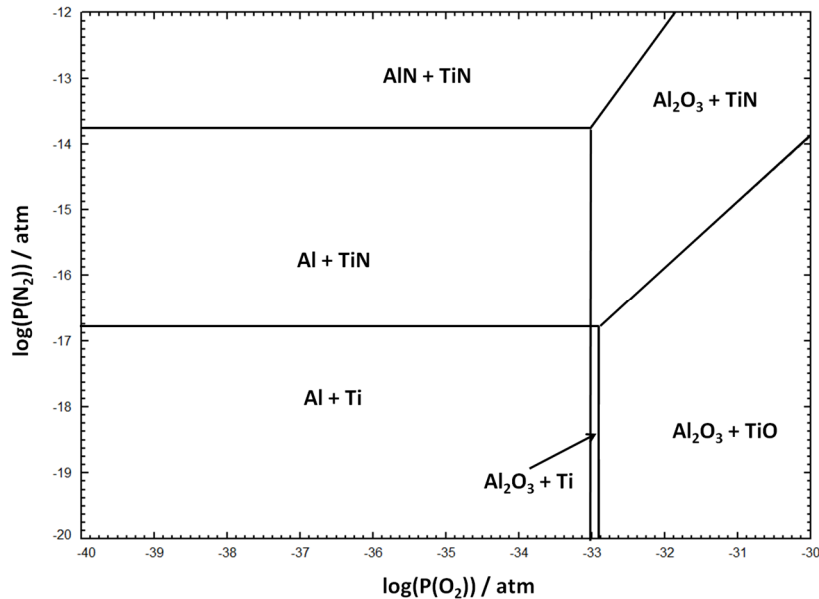


Fig. 8. Stability diagram for the system Ti-Al-O-N at 1050°C (calculations carried out with the Program Fact Sage)

4. Conclusions

In Rene 80 exposed in dry synthetic air formation of TiN below the internally oxidized Al_2O_3 precipitates was found. Formation of coarser Al_2O_3 precipitates which locally grow together into a virtually continuous sub-scale might be correlated with suppressed Ti incorporation into the chromia based scale due to formation of TiN.

Addition of water vapour (7%) resulted in suppression of TiN formation. This was explained by preferential adsorption of polar water vapour molecules or H-associated species in the oxide scale than non-polar N_2 molecules.

Addition of 20% H₂O into synthetic air during isothermal test up to 100 hours was found to affect the oxidation behaviour of Rene 80 in similar manner as observed in isothermal oxidation test with 7% H₂O. Hampering of TiN formation by the presence of water vapour was observed as well.

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