HOT CORROSION AND FRACTURE OF NICKEL–BASE SUPERALLOYS

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ABSTRACT

Nickel-base superalloys for stationary gas turbine hot part elements application must meet the requirements of sufficient hot corrosion resistance due to combustion product surface attack and high mechanical properties at exploitation temperatures. Thus nickel-base superalloys development was carried out taking into consideration hot corrosion processes studies and structural studies with elaboration of general concepts of alloying elements influence over hot corrosion and high temperature mechanical properties, including creep and fatigue. Hot corrosion resistance of model and commercial alloys was evaluated at specially designed low-pressure corrosion rig that ensured qualitative and quantitative correspondence of experimental result to these observed in experience. Turbine fuel containing 1 % sulphur was used together with sodium salts water solution injection into combustion products flow. Hot corrosion resistance was estimated due to average corrosion velocity V_q (g/m^2 s) and corrosion penetration depth h_{C2} (mm) taking into consideration environmentally assisted corrosion cracks. Structure formation and properties of nickel-base superalloys were studied within concentration limits that enhance sufficient hot corrosion resistance.

Comparison of experimental data of complex influence of alloying elements (chromium, titanium, aluminium, cobalt, columbium, tantalum, molybdenum, tungsten, rear-earth's) over hot corrosion surface stability and most important mechanical properties made it possible to propose concentration limits for hot corrosion - resistant nickel-base superalloys that were successfully used as materials for hot part gas turbine elements produced in Ukraine and Russia.

INTRODUCTION

Materialscience aspects of new superalloys development appeared to be extremely actual with the rapid growth of engineering high temperature systems application – in stationary and aviation gas turbines, gasification devices etc., – that work at high temperatures rising 1000–1100°C in contact with combustion products of impure fuels. Wide application of gas turbines is insured by prolonged exploitation term, high specific power, durability and fuel economy, all above mentioned features being achieved due to higher working temperatures. It's necessary to achieve 10000 hours for aviation gas turbines and 25000–50000 hours for stationary and energy gas turbines, thus making emphasis on high temperature materials technology. The key points are higher strength, lower density and increased corrosion resistance. For gas turbine materials hot corrosion failure processes cause certain temperature restrictions that negatively influence gas turbine efficiency.

As highly intensive corrosion processes can cause blade failure within very short period, the requirement of high corrosion resistance of superalloys appears not less important as guaranteed mechanical properties.

GENERAL INFORMATION

For exact hot corrosion resistance estimation of any material, exploitation tests are the only valid procedure, but duration of experiments together with fuel cost make such test as final for material evaluation. Thus in practice we increase environment corrosion effect thus reducing test time, neglecting sufficient changes in corrosion mechanisms. Turning to burner rig tests and crucible tests we require good correlation between their conditions and turbine environment influence resulting at least with qualitative similarity in surface layers composition and alloys rating.

That's why superalloys development in based on corrosion failure analysis of gas turbine blades used in practical conditions. Thus the detailed investigations of hot corrosion progressive forms in different types of foreign and domestic stationary and transporting gas turbine engines showed very intensive corrosion products formation on gas turbine blades working surfaces or on certain portions with higher temperature leading to formation of nonuniform layers and blade profile changes, especially at the edges. Corrosion products create two layers: thin inner layer composed of eutectic mixture $Ni–Ni_3S_2$ and disperse particles of chromium sulphide together with more complex chromium – titanium on nickel–chromium–titanium sulphides and thick outer layer consisting of oxides formed by practically all alloy components.

For gas transporting turbines extensive damages at 800°C prolonged exploitation were localized mainly on leading edge and concave surface. Main characteristic of corrosion products composition were due to presence of thin inner layer consisting of eutectic together with mixed sulfides of chromium, titanium and nickel. Multicomponent oxides formed outer layer having much larger thickness (up to 220 mkm) with NiO as principal component. Intermediate layer possessed maximum thickness reaching several millimeters was formed by oxide phases of spinel type. Such corrosion product presentation was found for gas turbine device GTN–16 used at compressive stations at powerful gas pipelines is Russia and natural samples produced of industrial superalloy EP 539 tested in "sea salt" corrosion conditions.

Generally speaking, study of morphology properties of outer layers of tested and real samples after exploitation or prolonged tests make evidence of certain general regularities for gas turbine engines of different types:

– outer layer being formed strictly in accordance to thermodynamic correspondence of oxide/sulfur activities and consisting mainly of oxide with different grade of compactness depending on spinel type oxides portion and base metal oxides (CoO, NiO);

– formation of zone with alloying elements loss that subdivides outer layer and base metal not influenced by corrosion processes;

– positioning of sulfide particles mainly in zone with alloying elements loss nearer to the frontier (base metal – corrosion products), and nickel eutectic $Ni–Ni_3S_2$ presence gives the evidence of catastrophic hot corrosion failure.

Comparing the corrosion products morphology one can come to a conclusion that burner rig tests inspite of comparative results are the most correct type of hot corrosion resistance and alloy failure evaluation. However, it appeared practically impossible to compare quantitative results of different burner rig tests, as it appears impossible to reproduce all test conditions, especially real pressures existing in gas turbine.

Analysis of hot corrosions evaluation results carried out by different authors [1–4] showed better correlation of experimental burner rig results with those observed in gas turbine practice especially from the point of view of corrosion products morphology similarity, also achieving comparable alloy ranking. That means that burner rig tests were to be used as principle method ensuring good qualitative similarity of outer layers morphology that is characteristic for real gas turbine materials, and crucible tests used as auxiliary method saving experiments expenditures.

Thus, general experiments were carried out using burner rig with low fuel consumption that contained specified volume of such corrosion–active elements, as sulfur, sodium, chlorum being main components in corrosion atmospheres existing in stationary and marine gas turbine [5].

Preliminary series of experiments were carried out with industrial gas turbine alloys widely used in domestic and foreign apparatus. Thus it was shown, that hot corrosion resistance level of superalloys, developed for aviation gas turbines (taking into consideration aviation fuel properties and composition), appeared to be unsatisfactory for application in stationary and marine conditions. All industrial alloys can be ranked as those of catastrophic corrosion failure and those possessing sufficient corrosion resistance. Generally saying, it's not possible to improve drastically hot corrosion resistance level of industrial alloys just changing separate elements content without conceptual changes of alloying principles corresponding to gas turbine exploitation conditions.

For initial analysis the results of several burner rig tests were taken, e.g. [6–9]

$V_q^{900} 10^5 = 19{,}66 - 0{,}34[Cr] - 0{,}4[Ti] + 1{,}34[Al] + 0{,}72[Nb]$,

$V_q^{850} \cdot 10^4 = 10{,}16[Al] + 2{,}71[Ti] - 4{,}13[Nb] - 1{,}26[Ta] - 1{,}96[Al][Ti] + 1{,}56[Al][Nb] - 11{,}28$,

$V_q^{900} \cdot 10^4 = 15{,}75[Al] + 4{,}85[Ti] + 5{,}13[Nb] - 3{,}14[Ta] - 2{,}88[Al][Ti] + 2{,}85[Al][Nb] - 2{,}87[Nb][Ti] - 20{,}29$,

$V_q^{950} \cdot 10^4 = 25{,}52 + 3{,}58[Al] - 3{,}89[Ti] - 12{,}99[Nb] - 7{,}74[Ta] + 0{,}73[Al][Ti] + 9{,}45[Al][Nb] - 1{,}99[Nb][Ti]$.

Using modern computer techniques, it appeared possible to propose based alloys which composition was used for further studies looking for new compositional ratios between γ'–forming elements (Al, Ti, Nb, Ta), solid solution strengthening elements (V, Mo, Ta), grain boundary strengthening elements (B, Zr) together with sufficient corrosion resistance ensuring elements (Cr, Ti) and microalloying elements (Ce, Y).

Taking into consideration the intercrystalline character of alloy rapture at creep, the structure factor that governs the level of excess phases precipitation of grain boundaries having unsatisfactory morphology together with topologically close packed (TCP) phases inside grain, was obtained to estimate the possibility of TCP phases formation, system PHACOMP was used for calculation of average number of electron holes. Thus for highly alloyed nickel-base superalloys (with 60-70 % (vol) γ'- phase) the dependence between properties level and average electron hole concentration was gained (with three areas of different character of alloying element's influence).

Here we can distinguish the following zones:

– area of high temperature strength rise due to solid solution and dispersion strengthening It is characterized with continuous improvement structural characteristics of γ'–phese particles and optimal morphology of grain carbides (I);

– area of high temperature strength drop due to formation of carbide (or carbo–boride) net at grain boundaries. It might be accompanied improvement (II);

– area of high temperature strength catastrophical drop at TCP phases precipitation (III).

As area II always precede area III due to kinetical peculiarities of TCP phases formation one must pay extreme attention to structural–energetical conditions of grain boundaries together with methods of its regulation.

To achieve better correlation between hot corrosion resistance and mechanical properties of superalloys chromium content can be varied between 12–16%, thus the lower level being recommended for alloys with satisfactory hot corrosion resistance and improved creep and fatigue strength. Ratio between principal γ'–forming elements – titanium and aluminum is to be organized depending on chromium content, in atomic concentrations $n_a = \frac{Ti}{Al} > 1$, also paying attention to high temperature strength as limited factor for above mentioned ratio, not exceeding double titanium concentration compared to aluminum, keeping the latter at 2–4%.

Solid solution strengthening elements influence negatively hot corrosion resistance, so one must limit both separate and total amounts of molybdenum and tungsten, with some additional possibilities of fatigue strength improvement with cobalt additions in wide range of concentrations because it practically doesn't influence corrosion properties. Microalloying generally improve hot corrosion resistance especially with cerium and yttrium additions, but it is necessary to restrict their concentration because of possible mechanical properties drop connected with overalloying of grain boundaries.

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