Evaluation of Heat Capacity and Resistance to Cyclic Oxidation of Nickel Superalloys

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Abstract

Paper presents the results of evaluation of heat resistance and specific heat capacity of MAR-M-200, MAR-M-247 and Rene 80 nickel superalloys. Heat resistance was evaluated using cyclic method. Every cycle included heating in 1100°C for 23 hours and cooling for 1 hour in air. Microstructure of the scale was observed using electron microscope. Specific heat capacity was measured using DSC calorimeter. It was found that under conditions of cyclically changing temperature alloy MAR-M-247 exhibits highest heat resistance. Formed oxide scale is heterophasic mixture of alloying elements, under which an internal oxidation zone was present. MAR-M-200 alloy has higher specific heat capacity compared to MAR-M-247. For tested alloys in the temperature range from 550°C to 800°C precipitation processes (γ', γ'') are probably occurring, resulting in a sudden increase in the observed heat capacity.

1. Introduction

Superalloys are a group of materials used mainly in high temperature conditions, where high creep, corrosion and fatigue resistances are required. The development of superalloys is closely connected with the history of the jet engine, for which they were first designed [1,2]. Conditions inside the jet engine turbine are extreme, elements are subjected to high temperature, corrosive atmosphere of the exhaust and high mechanical strain. Currently, superalloys are being used in other high temperature applications, especially for turbine components for power plants [3-5]. The temperature of steam in supercritical power plant installations can compare to the temperature inside a jet engine. The desire to reduce fuel consumption and emissions is a powerful incentive for continued development of superalloys. This requires even higher work temperatures. A characteristic feature of many nickel superalloys is the ability to work in both the very high temperatures (up to 1400°C) as well as in very low, cryogenic temperatures while maintaining the excellent mechanical properties [2]. Another advantageous feature of nickel superalloys is high-temperature corrosion resistance in aggressive environments of sulfur, nitrogen and carbon [6,7]. Disadvantageous feature of superalloys can be a low thermal conductivity (10-30% of nickels thermal conductivity) [1], which may lead to increased temperature gradient and rise of internal stresses resulting in component failure. Properties of nickel at high temperatures depend mainly on the choice of alloying elements. Alloying additions may lead to an increase of mechanical properties by precipitation hardening (typically by an ordered phase γ'). The additions of Al, Ti and Ta are particularly important in the formation of the γ' phase. In turn, the rare earth metals such as Hf, La, Y have a positive influence on oxidation resistance mainly by bounding sulphur impurities [8].

2. Materials and methods of investigation

The test ware carried out using commercial grade superalloys of following chemical composition:

MAR-M-200: 0.14% C, 9% Cr, 10% Co, 12.5% W, 1% Nb, 2% Ti, 5% Al, 1.1% Hf, 0.05% Zr, rest Ni.

MAR-M-246: 0.16% C, 8.2% Cr, 10% Co, 0.6% Mo, 10% W, 3% Ta, 1% Ti, 5.5% Al, 1.5% Hf, 0.05% Zr, rest Ni.

Rene 80: 0.16% C, 14% Cr, 9% Co, 4% Mo, 4% W, 4.7% Ti, 3% Al, 0.8% Hf, rest Ni.

Heat resistance tests were carried out using cyclically fluctuating temperature method. Once cycle consisted of heating in 1100°C for 23 hours and then cooling for 1 hour in room temperature (Figure 1).
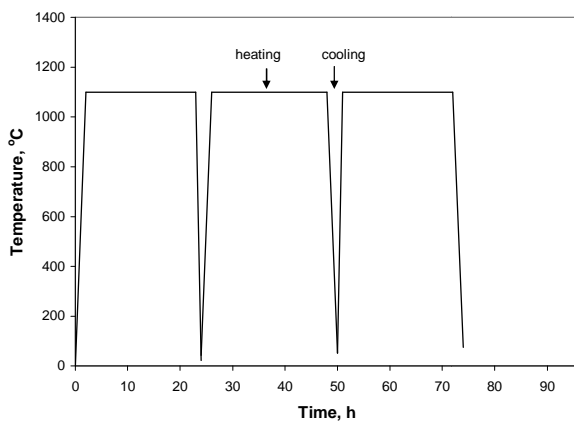

Fig. 1. Oxidation cycles

Test samples were manufactured in the form of cylinder of diameter d = 14 mm and height h = 4.5 mm. Before the tests, samples were polished using SiC abrasive papers (grit 800) and degreased in ethyl alcohol. After each cycle, the mass of the test samples was measured with a precision of 10^{-5} g.

Metallographic studies of the scale were performed on cross-sections of samples using HITACHI S-4200 SEM microscope. External surface of the samples was electroplated with nickel. After cutting, the samples were mounted in resin.

Evaluation of heat capacity involves comparison of reference substance of known mass and specific heat capacity with the test sample. The reference substance should have known characteristics and, if possible, a certificate [9]. Specific heat capacity of the reference substance should be specified with precision of 0.5%, and should be measured using two different adiabatic calorimeters. Monocrystals are preferred for reference substances in order to avoid the appearance of multiple peaks on the DSC curve. In the temperature range of 25°C – 2000°C the α-Al_2O_3 oxide (synthetic sapphire) is used as a reference substance.

In order to determine the specific heat capacity three measurements were carried out under identical conditions. The first measurement was performed with two empty crucibles, the second with the test sample and the third with the reference

substance. The resulting heat flux curves are the basis for determining the value of the specific heat capacity c_p, which was calculated from the following relationship:

$$C_{P_s}(T) = \frac{HF_{sample} - HF_{blank}}{HF_{ref.} - HF_{blank}} \cdot \frac{m_{ref.}}{m_{sample}} \cdot C_{P_{ref}}(T) \qquad (1)$$

where: C_{P_s} – specific heat capacity of the test sample, J/(g·K); HF – heat flux respectively for test sample (sample), empty crucibles (blank) and reference substance (ref.), μV; m – mass of the sample and the reference substance, g; $C_{P\ ref.}$ – heat capacity of the reference substance (sapphire), J/(g·K).

The measurements were carried out using platinum crucibles with a capacity of 0.45 cm^3. Calculations were performed using a Setsoft software package provided by the manufacturer of the calorimeter.

3. The results of investigations and discussion of results

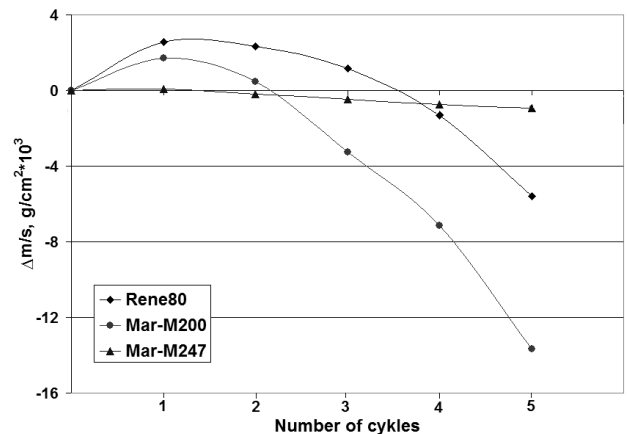Mass change curves obtained after 5 oxidation cycles are shown in Figure 2.

Fig. 2. Cyclic oxidation of the nickel superalloys samples

Table 1.
Characteristic parameters for heat resistance evaluation

Alloy	$(\Delta m/s)_{max}$ [g/cm^2]	t_{max} [h]	t_0 [h]	$(\Delta m/s)/\Delta t$ [g/(cm^2·h)]
MAR-M-200	1.70	24	52	$2.72 \cdot 10^{-4}$
MAR-M-247	0.09	24	48	$8.31 \cdot 10^{-6}$
Rene 80	2.56	24	84	$1.14 \cdot 10^{-6}$

According to the heat-resistance evaluation criterion proposed in [10] investigated alloys have relatively good surface scale adhesion. Another method of the heat resistance evaluation for alloys in conditions of cyclically changing temperature was proposed by Smialek [11]. The author has

adopted the following parameters characterizing the mass change curves of samples: $(\Delta m/s)_{max}$ – highest mass increase, t_{max} – time to reach the maximum, t_0 – time of the zero-line intersection, $(\Delta m/s)/\Delta t$ – rate of final mass loss. The values of these parameters for the tested alloys are shown in Table 1.

The oxide scale on MAR-M-200 is monophasic. Beneath the surface scale an internal oxidation zone has formed (Figure 3).

The existence of the aforementioned zone indicates the possibility of oxygen dissolution in the alloy. Outer layer and internal oxidation zone are heterophasic mixtures of almost all alloying elements. But there was no presence of hafnium, both in the outer layer and in the internal oxidation zone. In case of MAR-M-247 the peeling of the scale occurred already after the first oxidizing cycle. Remaining scale was uneven and an internal oxidation zone was present (Figure 4).
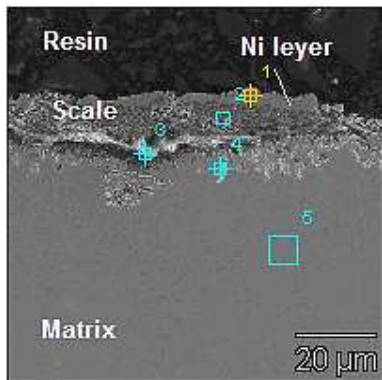

Fig. 3. Cross-section of oxide scale on the surface
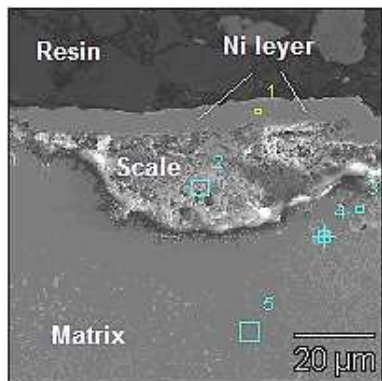of the MAR-M-200 sample

Fig. 4. Cross-section of oxide scale on the surface
of the MAR-M-247 sample

The presence of hafnium was revealed in the internal oxidation zone. Oxidation curves show that MAR-M-247 has greater heat resistance in comparison to MAR-M-200, which exhibited increased mass loss. This is probably a result of the increase in aluminium concentration from 5 to 5.5% and decrease in titanium concentration from 2 to 1%. Of the three significant oxides (Al_2O_3, Cr_2O_3, NiO), Al_2O_3 is the most stable and NiO the least. It can therefore be expected that in nickel superalloys the Al_2O_3 will be formed first.

In addition to the thermodynamic aspect, the oxidation kinetics is an important factor in the evaluation of heat resistance. NiO oxide is a semiconductor with disordered cation sub-lattice, so it will be formed very fast as a result of upward diffusion of nickel ions through cation vacancies. The scale can fall off easily causing continuous corrosion. In turn, the dissolution of TiO_2 in Al_2O_3 may increase the rate of formation of aluminum oxide, as Ti^{4+} and Al^{3+} have a different charge. Inclusion of additional vacancies into Al_2O_3 increase the mobility of aluminium ions, and thus increase the rate of oxidation.

Changes of the specific heat capacity of investigated nickel superalloys are shown on Figure 5 and, for the specific temperature, in Table 2.
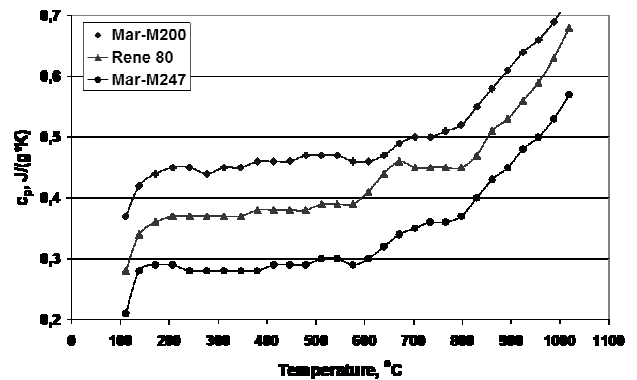

Fig. 5. Specific heat capacity of nickel superalloys as a function
of temperature

Table 2.
Specific heat capacity investigated nickel alloys

Temp. [°C]	Specific heat capacity c_p [J/(g·K)]		
	MAR-M-200	Rene 80	MAR-M-247
150	0.43	0.35	0.29
200	0.45	0.37	0.29
300	0.45	0.37	0.28
400	0.46	0.38	0.28
500	0.47	0.38	0.30
600	0.46	0.40	0.30
700	0.50	0.45	0.35
800	0.52	0.45	0.38
900	0.62	0.54	0.46
1000	0.71	0.65	0.55
1050	0.73	0.68	0.58

Alloy MAR-M-200 has a higher value of the specific heat capacity c_p, as compared to the alloys MAR-M-247 and Rene 80.

The changes in specific heat capacity for investigated alloys can be divided into three distinct temperature ranges. In the first range from 150°C to 550°C a moderate increase of heat capacity can be observed. In the second range from 550°C to 800°C the heat capacity decreases slightly at first, and then increases to the

maximum at the temperature of approximately 700°C. These change is probably due to precipitation of γ″ phase, which occur in the temperature range from 500°C to 750°C, as has been shown in [12]. In the third range, above 800°C heat capacity of the samples increase linearly. Higher c_p value for MAR-M-200 and Rene 80 alloys may lead to lower heat gradient and thus higher thermal shock resistance. This is confirmed only for few initial oxidation cycles.

4. Conclusions

Under the conditions of cyclically changing temperature nickel superalloys have a relatively good oxidation resistance. MAR-M-247 shows better heat resistance. For MAR-M-200 alloy the oxidation curves are close to parabolic law until it reaches the maximum mass loss. Similar behaviour was observed for Rene 80 sample. Oxide scale formed on nickel superalloys is a heterophasic mixture of oxides of most alloying elements. Under the scale an internal oxidation zone were formed.

MAR-M-200 have highest specific heat capacity, while MAR-M-247 lowest. In the temperature range from 550°C to 800°C in the investigated alloys the γ″ phase probably precipitates, which results in a slight decrease, followed by a strong increase of specific heat capacity.

Acknowledgements

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