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THERMOPHYSICAL PROPERTIES OF NICKEL-BASED CAST SUPERALLOYS

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The article presents tests results of specific heat storage capacity and oxidation resistance of nickel - based cast Mar M - 200, Mar - M - 247 and Rene 80 superalloys. Specific heat measurements were conducted with the use of differential scanning calorimetry (DSC), with the use of high - temperature calorimeter multi (HTC) Setaram. Oxidation resistance tests were conducted with the use of cyclic temperature change method. Each cycle consisted of heating by temperature of 1 100 °C and next quick cooling in air. It was proved that the biggest value of specific heat C_p was found in alloy Mar - M - 200, and the lowest in alloy Mar - M - 247. Relatively good oxidation resistance has been found in alloy Mar - M - 247.

Key words: nickel superalloys cast, specific heat, heat resistance

INTRODUCTION

Superalloys are classic materials developed for high-temperature usage where the big resistance to creep, fatigue and degradation under the influence of aggressive atmosphere is required. Development of superalloys is strictly related with the history of jet engine for which they were first designed [1, 2]. Currently those alloys are developed in other high-temperature applications – particularly as elements of turbines for energy industry [3 - 5]. A stimulus for further development of superalloys technology is the fact that the use of fuel is now too high in case of other currently applied materials and the aim is to lower that use as well as to limit the emission of pollution in case of aircraft engines. According to the law of thermodynamics it requires the use of higher working temperature. A characteristic feature of many nickel superalloys is the possibility of working both in high temperatures – at times up to 1 400 °C; as well as in cryogenic temperatures with simultaneous maintenance of perfect mechanical properties [2]. Other beneficial property of nickel superalloys is resistance to high temperature corrosion in aggressive environment of sulphur, nitrogen and carbon [6, 7]. The drawback of superalloys is low heat conductivity (10 - 30 % heat conductivity of nickel) [1], which may lead to the rise in temperature gradient, appearance of inner stresses and as a result the defect of the elements.

Alloy additives lead to increase of mechanical properties by precipitation strengthening (most often it is ordered phase γ’). The addition of Al, Ti, Ta is particularly important to create phase γ’. The addition of rare earth elements - Hf, La, Y - by bonding sulphur beneficially influence the increase of resistance to oxidation [8].

The aim of the article was to determine specific heat storage capacity and oxidation resistance of nickel superalloys Mar - M-200, Mar - M - 247 and Rene 80.

TEST MATERIALS AND METHODS

Tests were conducted on commercial nickel superalloys. Chemical composition is presented in Table 1.

Table 1 **Chemical composition of nickel superalloys / wt. %**

Alloy	C	Cr	Co	Mo	W	Nb	Ta	Ti	Al	Hf
M-200	0,14	9,1	10	-	12,5	1,1	-	2,0	5,1	1,1
M-247	0,16	8,2	10	0,6	10	-	3	1	5,5	1,5
Rene 80	0,16	14	9,0	4,0	4,0	-	-	4,7	3,0	0,8

Calorimetric tests were conducted with the use of high-temperature calorimeter, multi HTC Setaram. Determination of specific heat was based on comparison of the model, which had known weight and specific heat with the tested sample.

Specific heat of the model must be known with precision up to 0,5 % and should be measured by two different adiabatic calorimeters. It is suggested to use mono-crystal as a model to avoid appearance of a few peaks on DSC curve. In temperature range from 25 - 2 000 °C the model used is oxide α - Al_2O_3 – synthetic sapphire [9]. In order to determine the specific heat storage capacity, three measurements were conducted in identical conditions. First measurement was conducted with two empty melting pots, second with tested sample and third with model substance. Achieved curves of heat flow are the basis to mark the value of specific heat storage capacity c_p, which was calculated from the equation:

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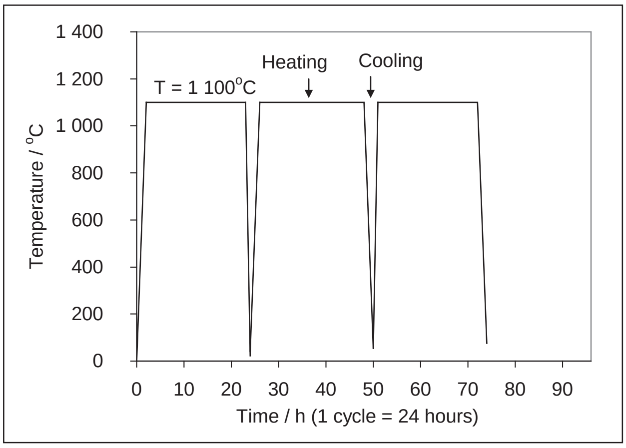

Figure 1 Diagram of heating and cooling cycle

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

where: C_{Ps}- specific heat of sample / J·(g·K)$^{-1}$, HF - heat flow respectively of sample, empty melting pots (blank), model (ref.) / µ·V, weight of the model and sample / g, $m_{ref.}$, m_{sample} - weight respectively reference, sample, / g C_{Pref} - heat storage capacity of the model (sapphire) / J·(g·K)$^{-1}$.

Calculations were conducted with the use of Setsoft program. Measurements were conducted in platinum crucibles with volume of 0,45 cm^3.

Heat resistance tests were conducted with the use of cyclic variable temperature method. One cycle included heating by temperature of 1 100 °C for 23 hours and next cooling for one hour in room temperature (Figure 1).

After each cycle, the samples were weighed on analytical balance with precision of 10 $^{-5}$g. Samples for tests were in the shape of cylinder with diameter d = 1,4 cm and height h = 0,45 cm. Before the process the samples were grinded with the use of abrasive paper SiC and next degreased in ethyl alcohol.

TESTS RESULTS AND DISCUSSION

Curves of specific heat storage capacity of tested nickel superalloys are presented in Figure 2.

Highest value of c_p is found in alloy Mar -M - 200, and lowest in alloy Mar - M - 247 (Table 2). Curves of C_p can be divided into three temperature ranges. In the first range from 150 °C to 550 °C, a moderate increase of heat storage capacity is observed. In second temperature range, from 550 °C to 800 °C, alloys Mar - M - 247 and Rene 80 absorb heat – increase of c_p value on curve, whereas alloy Mar - M - 200 give up the heat. In the third temperature range, > 800 °C, alloys absorb heat again. Higher value of c_p for alloy Mar - M - 200 may indicate the weaker bond of crystal lattice due to bigger thermal vibrations of atoms.

Weight change curves achieved after 6 heating and cooling cycles in temperature of 1 100 °C are presented in Figure 3.

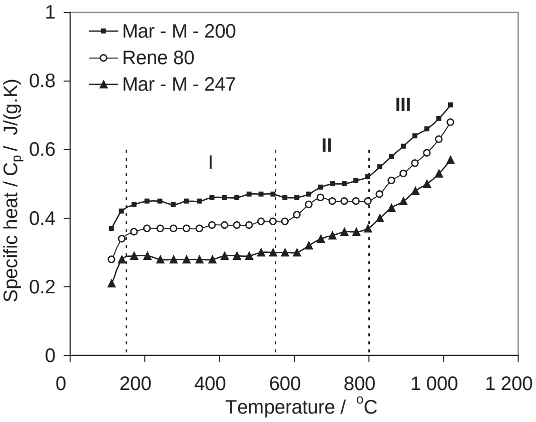

Figure 2 Specific heat storage capacity of nickel superalloy

Table 2 **Specific heat storage capacity of alloys on nickel matrix**

T / °C	Mar - M -200 / J×(g·K)-1	Rene 80 / J×(g·K)-1	Mar - M - 247 / J×(g·K)-1
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
1 000	0,71	0,65	0,55
1 050	0,73	0,68	0,58

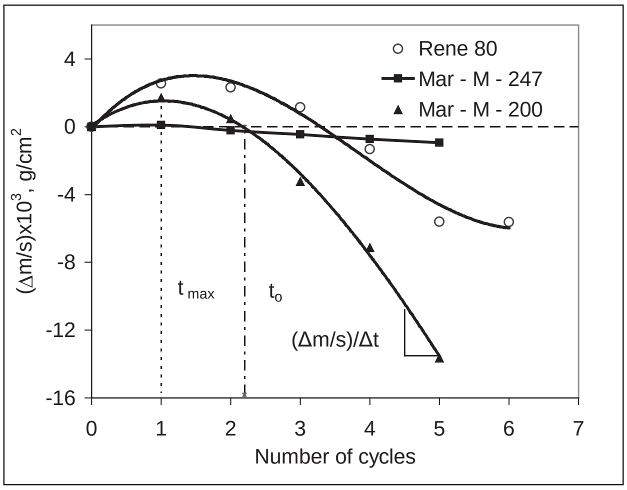

Figure 3 Course of cyclic oxidation of nickel superalloys T = 1 100 °C, air 1 cycle = 24 h

The author [10] has applied the following parameters characterizing weight change curves of samples: $(\Delta m/s)_{max}$ – biggest gain in sample weight, t_{max} – time until max. is reached, t_o – time of zero line crossing, $(\Delta m/s)/\Delta t_{and}$ – the speed of the final mass loss - are presented in Table 3.

Depending on the type of alloy the forming oxide scale can be one-, two- or three-layered (Figure 4).

Table 3 **Characteristic parameters of heat resistance assessment**

Alloy	$(\Delta m/s)_{max}$ 10^3 / g×cm^{-2}	t_{max} / h	t_o / h	$(\Delta m/s)/\Delta t$ / g×(cm^2·h)$^{-1}$
Rene 80	2,43	36	84	$2{,}88\cdot10^{-4}$
Mar - M - 200	1,70	24	52	$2{,}72\cdot10^{-4}$
Mar - M - 247	0,09	24	48	$8{,}31\cdot10^{-6}$

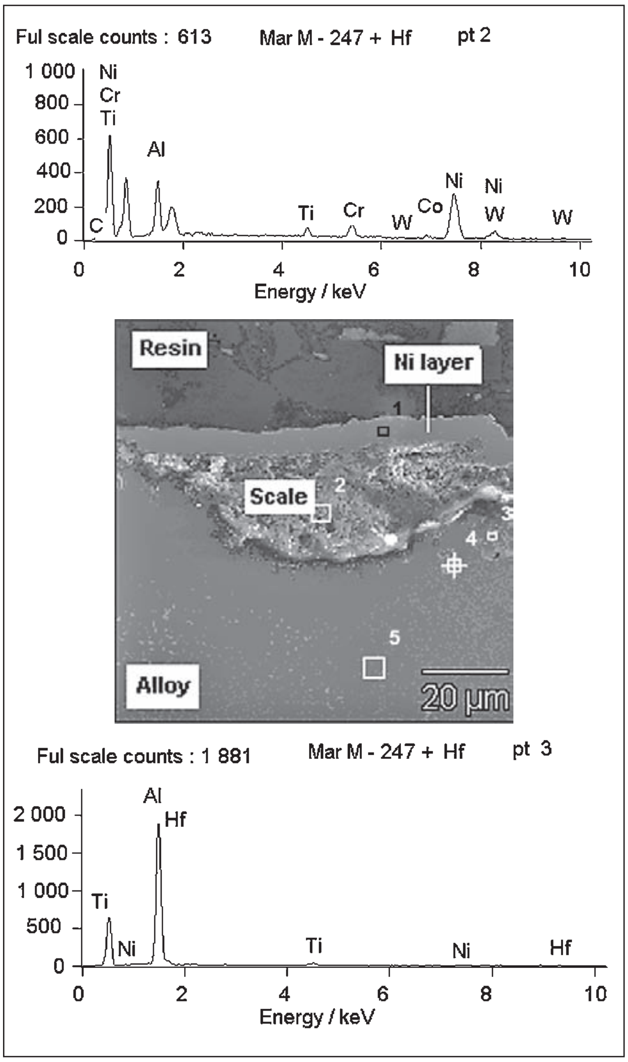

Figure 4 Transverse section of oxide scale on alloy Mar - M - 247 and analysis of chemical composition after cyclic oxidation by 1 100 °C

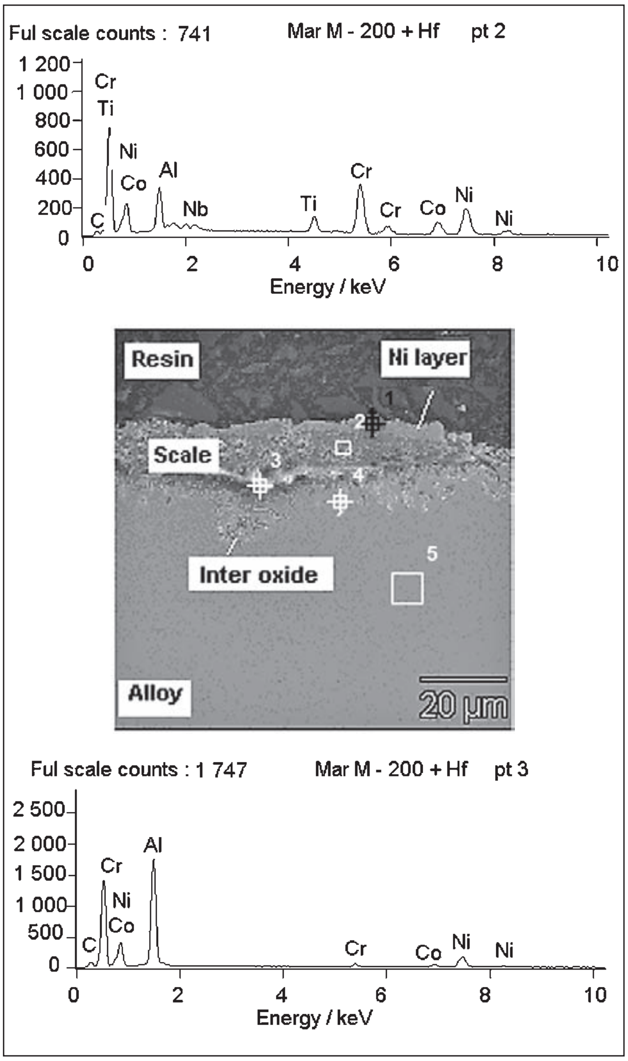

Figure 5 Transverse section of oxide scale on alloy Mar - M - 200 and the analysis of chemical composition after cyclic oxidation by 1 100 °C

According [10] the relatively good heat resistance is found in Mar - M - 247 alloy. Oxidation curve is characterized with slight decrease of weight. It is probably a result of increase of the Al content to 5,5 % by simultaneous decrease of titanium content to 1 %. Among three important oxides - Al_2O_3, Cr_2O_3, NiO - the most stable is Al_2O_3, and the least stable is NiO. Therefore, it can be expected that the first oxide, which will form on nickel superalloys, is Al_2O_3 oxide. Oxide scale formed from Al_2O_3 always shows slower speed of oxidation. On the contrary, titanium, which dissolves in aluminium oxide, increases the speed of its formation. Because ions Ti^{4+} and Al^{3+} have different electric charge, additional cationic vacancy defects are introduced into aluminium oxide lattice, the mobility of ions is increased and in this way the speed of oxidation accelerates. The appearance of internal oxidation zone (Figures 5 and 6) is characteristic for Mar - M - 200 and Rene 80 alloys. The presence of the mentioned zone indicates the possibility of dissolution of oxygen in alloys.

CONCLUSIONS

- Highest value of specific heat storage capacity is found in alloy Mar - M - 200, whereas the lowest value is present in Mar - M - 247. In temperature range from 550 °C to 800 °C alloys Rene 80 and Mar - M - 247 absorb heat, whereas alloy Mar - M - 200 gives up the heat.
- In conditions of cyclic variable temperature the tested nickel superalloys are characterised with relatively good heat resistance. The biggest heat resistance is found in alloy Mar - M - 247, the lowest in alloy Mar - M - 200.

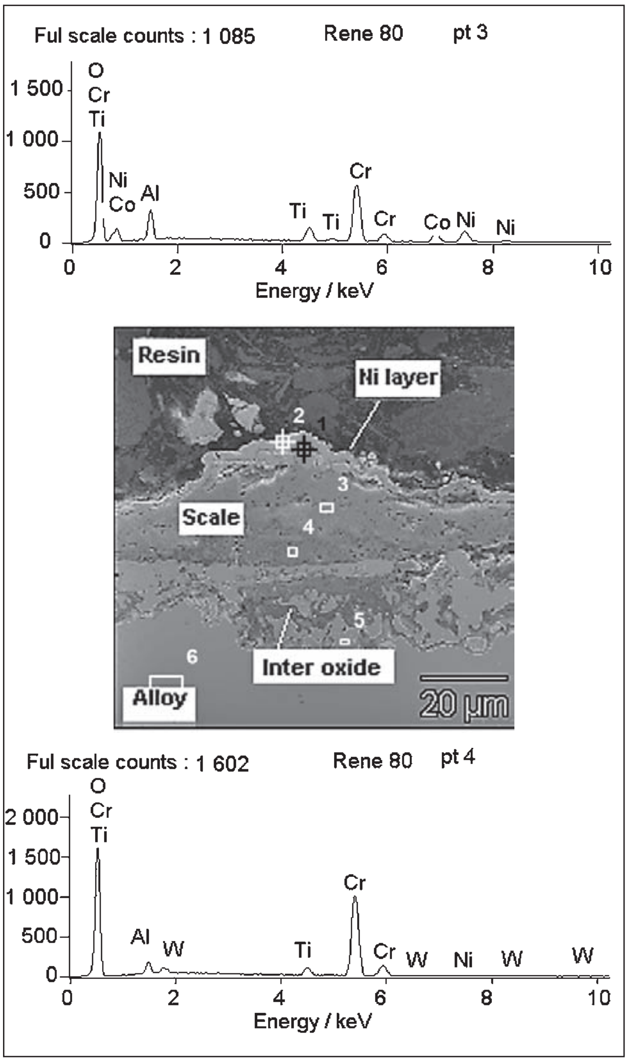

Figure 6 Transverse section of oxide scale on Rene 80 alloy and analysis of chemical composition after cyclic oxidation by 1 100 °C

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Note: The responsible translator for English language is Dorota Sidło, Poland