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Creep rupture strength of Re and Ru containing experimental nickel-base superalloys

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Abstract. The influence of Re and Ru on creep rupture strength has been investigated using a new in-house designed alloy-series comprising 9 experimental nickel-base superalloys with stepwise increased Re and Ru additions. The presented creep data reveals a significant increase in creep rupture strength by additions of Re. For additions of Ru an increase of creep rupture strength can only be found for low Re contents. The present article, which is part of an extensive and systematic investigation on Re and Ru influences, shows, that an improved creep resistance by an influence of Re and Ru on the γ'-solvus temperature is rather improbable. Likewise, the influence of Re and Ru on liquidus temperature is not expected to play an important role. However, the creep rupture strength is suggested to be highly modified by γ/γ'-microstructure changes.

Introduction

The performance of turbines is governed by the properties of nickel-base superalloys, which can sustain severe thermal and mechanical stresses under extreme environmental conditions. For turbine efficiency improvements by increased gas inlet temperatures, it is thus important to enhance the temperature capability of the assembled single crystal turbine blades. At this junction, alloy development plays an important role, as the achieved temperature improvement of more than 100 °C during the last 30 years demonstrates [1]. A major progress in alloy chemistry is marked by the addition of Re, which promotes higher tensile strength, as well as better creep properties [1-3]. However, the addition of Re is limited by the highly increased susceptibility to form brittle and harming TCP-phases. To overcome this problem, the most recent alloy development led to the addition of Ru, which appears to be advantageous through microstructure stabilization with respect to TCP-formation [3-11]. However, additions of the elements Re and Ru also give rise to economic concerns, since both elements are short in availability and thus also fairly expensive. Unfortunately, the mechanisms of the key benefits of Re and Ru additions are still not well understood, so that the optimization of the desired Re and Ru amount is challenging. The present article is part of an extensive investigation of a newly designed alloy series, with the aim to systematically determine the element influence on solidification properties [12,13], thermophysical properties and casting conditions [14], γ/γ'-microstructure changes [15], creep resistance, and phase stability [16-18]. The alloys are based on the commercial alloy CMSX-4 and contain different contents of Re and Ru which were added in well-defined atomic percent contents to guarantee a systematic investigation of the element influence. In the present article, the creep rupture strength of the alloys in dependence of Re and Ru additions is shown and discussed with respect to the element influence on observed microstructure changes and creep relevant thermophysical properties.

Experimental

The composition of the investigated experimental alloy-series exhibits minor changes in the Al, Mo and Cr content compared to the parent alloy CMSX-4. Ti and Hf additions were removed completely. Re and Ru were added stepwise in the range of 0-2 at.-% to the base alloy Astra1-00 at the expense of Ni, while all other alloying elements are retained at constant at.-% levels (Table 1). Further details about in-house alloy fabrication, implemented quality controls and casting conditions are stated elsewhere [12,13]. To assure a statistically meaningful number of tensile creep samples with identical casting conditions, the experimental alloys and the reference alloy CMSX-4 were directionally solidified (DS) as a set of three cylindrical bars (12 mm in diameter and 180 mm in length).

Table 1: Composition of Astra1-series, based on constant at.-%. The alloys are named by two numbers, referring to the added Re (first) and Ru content (latter). For better comparison to other alloys, the composition in wt.-% as well as the composition of CMSX-4 (without Ti and Hf) is given.

element →	**Al**		**Co**		**Cr**		**Mo**		**Re**		**Ru**		**Ta**		**W**		**Ni**
alloy ↓	at.-%	wt.-%	at.-%	wt.-%	at.-%	wt.-%	at.-%	wt.-%	at.-%	wt.-%	at.-%	wt.-%	at.-%	wt.-%	at.-%	wt.-%	
Astra1-00	13,50	6,13	9,00	8,92	6,00	5,25	0,60	0,97					2,20	6,70	2,00	6,19	base
Astra1-01	13,50	6,08	9,00	8,86	6,00	5,21	0,60	0,96			1,00	1,69	2,20	6,65	2,00	6,14	base
Astra1-02	13,50	6,04	9,00	8,80	6,00	5,17	0,60	0,95			2,00	3,35	2,20	6,60	2,00	6,10	base
Astra1-10	13,50	6,00	9,00	8,73	6,00	5,14	0,60	0,95	1,00	3,07			2,20	6,56	2,00	6,06	base
Astra1-11	13,50	5,96	9,00	8,67	6,00	5,10	0,60	0,94	1,00	3,05	1,00	1,65	2,20	6,51	2,00	6,01	base
Astra1-12	13,50	5,92	9,00	8,61	6,00	5,07	0,60	0,94	1,00	3,02	2,00	3,28	2,20	6,47	2,00	5,97	base
Astra1-20	13,50	5,88	9,00	8,56	6,00	5,03	0,60	0,93	2,00	6,01			2,20	6,42	2,00	5,93	base
Astra1-21	13,50	5,84	9,00	8,50	6,00	5,00	0,60	0,92	2,00	5,97	1,00	1,62	2,20	6,38	2,00	5,89	base
Astra1-22	13,50	5,80	9,00	8,44	6,00	4,96	0,60	0,92	2,00	5,93	2,00	3,22	2,20	6,34	2,00	5,85	base
CMSX4	12,58	5,60	9,26	9,00	7,58	6,50	0,38	0,60	0,98	3,00			2,18	6,50	1,98	6,00	base

The investigation of liquidus and γ' solvus temperatures in dependence of Re and Ru were performed on a differential scanning calorimetry instrument (DSC, Netzsch STA 409, Netzsch Gerätebau GmbH, Selb, Germany) with a heating and cooling rate of 5 K/min. Further details are given in [12], where also quasi-binary phase diagrams determined from the cooling curves of DSC-measurements in the as cast state are reported. In this work, additional measurements of homogenised samples (DSC-heating curves of fully heat treated alloys) have been made in order to allow a comparison to the liquidus and γ' solvus temperatures obtained for the solidification process (DSC-cooling curve data). Both results were also compared to calculated ThermoCalc data (ThermoCalc Software, Stockholm, Sweden).

The quasi-binary phase diagrams from DSC-cooling curves [12] were used to identify the incipient melting point of the Astra1-alloys. Together with supplemental experiments in the temperature range around the incipient melting point, a consistent solution heat treatment temperature of 1340 °C was selected for all Astra-1 alloys as maximum temperature without partial melting. The required solution heat treatment time has been determined by the investigation of the segregation distribution coefficients k_s after solution heat treatment times of 1, 4, 8, 16, 24 and 32 h at 1340 °C. For this purpose, EPMA analyses (electron probe microanalyzer JXA-8100, JEOL, Tokyo, Japan) of all elements were carried out by mappings of a 750x750 μm^2 area (measuring details can be found in [12]). Averaged element concentrations within the dendrite core (c_D) and in the interdendritic region (c_{ID}) have been determined by at least ten measurements in each case. k_s was subsequently calculated as c_D/c_{ID}. The Astra1-k_s-data after different solution heat treatment times was compared to the remaining microsegregation of the standard heat treated reference alloy CMSX-4 (Fig. 1). Since the remaining Re-segregation in Astra1-alloys with 2 at.-% Re is still detectable after economically unreasonable solution heat treatment times of 32 h, a duration of 16 h was selected as standard heat treatment time for all Astra1-alloys. This duration is also comparable to the remaining Re-segregation of the standard heat treated CMSX-4. The following aging heat treatments were adopted to the standard process for CMSX-4 with 2 h at 1140 °C in a first step and 24 h at 870 °C in a second step.

Microstructure investigation was carried out on a scanning electron microscope (SEM XL30, Phillips Electronics, Eindhoven, Netherlands) with an acceleration voltage of 25 kV. For sample preparation a procedure comprising the polishing steps 6 µm MD-Allegro, 3 µm DP-Mol (both with lubricant green) and 0.25 µm MD-Chem with OP-U/H_2O 1:5 suspension was used. Slight etching was performed using a V2A-etchant (100 mL H_2O, 100mL HCl (32%), 10mL HNO_3 (65%) and 0.3 ml Vogels Sparbeize at 60 °C. Microstructure evaluation was realized with the image evaluation software ImageC (Version 5.0, Aquinto AG, Berlin, Germany).

Tensile creep specimens were fabricated in accordance to DIN 10291 in <001> orientation of fully heat treated cylindrical bars. Lever-arm tensile test equipment (lever-arm 2330-CC, ATS Applied Test Systems Inc., Butler, PA, USA) with displacement transducer (Linearencoder St12, Heidenhain

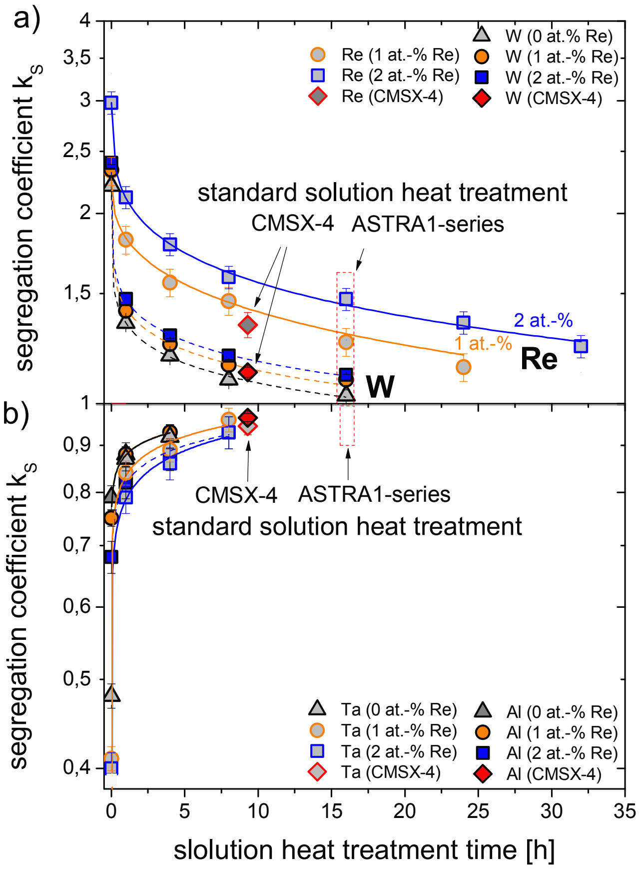

Figure 1: Segregation distribution coefficients k_s (c_D/c_{ID}) in dependence of solution heat treatment time for (a) Re and W and (b) Al and Ta.

GmbH, Traunreut, Germany) was used to perform creep tests under constant load at 950 °C and 1050 °C. The furnace temperature with discrepancies of < 5 K was controlled by thermo couples attached to the creep samples. Applied stresses varied between 150-400 MPa. All tests have been conducted as uninterrupted creep tests in air. Data evaluation for Larson-Miller-plots has been carried out for creep times until 1% plastic deformation.

Results

The creep results in dependence of the Ru content are shown in Fig. 2 for 1 at.-% Re (a) and 2at.-% Re (b), respectively, as Larson-Miller-plots. No creep data could be determined for Astra1-alloys without Re, since almost all specimens failed immediately during load apply. Fig. 2a reveals a significant improvement of creep resistance by increasing Ru contents for present low Re contents. Thus, a higher temperature capability of the alloys is reached (stated temperature increase calculated for $\sigma = 250$ MPa and $t_{1\%} = 100$ h). However, in typical 3rd and 4th Generation nickel-base superalloys with higher Re-contents of 2 at.-% (Fig. 2b), the influence of Ru is clearly diminished. Obviously in these alloys a possible improvement of creep resistance is restricted to the effect of Re-additions. Compared to the Astra1-alloys, the commercial alloy CMSX-4 shows a remarkably high creep resistance. In terms of alloy composition, CMSX-4 is beside additional Ti and minor Hf contents, the counterpart to the experimental Astra1-10 alloy (1 at.-% Re, 0 at.-% Ru). However, its creep strength is comparable to the Astra1-12 alloy with additional 2 at.-% Ru.

As reported in relation to the previously published quasi-binary phase diagrams [12], additions of Ru do not significantly influence the thermophysical properties of the alloys. By contrast, for additions of Re, an increase in liquidus temperature of about 6 K/at.-% can be found for the solidification data taken from DSC-cooling curves (Fig. 3a). However, after alloy heat treatment, this increase drops by a factor 3 to 2 K/at.-% Re, as can be seen in Fig. 3a. For creep temperatures T above 950 °C and liquidus temperatures T_L around 1380 °C, this consequently leads to a negligible homologous temperature increase $T_H = T/T_L$ of < 0.15 %/at.-% Re. The comparison in Fig. 3a also shows that T_L of the heat treated samples is more than 10 °C lower than for the solidification process. Considering a necessary undercooling of about 5 K for solidification [19], the difference is likely even higher. Surprisingly, this result is in disagreement to studies on CMSX-10 from Fuchs and Boutwell [20] who found a T_L increase after heat treatment process.

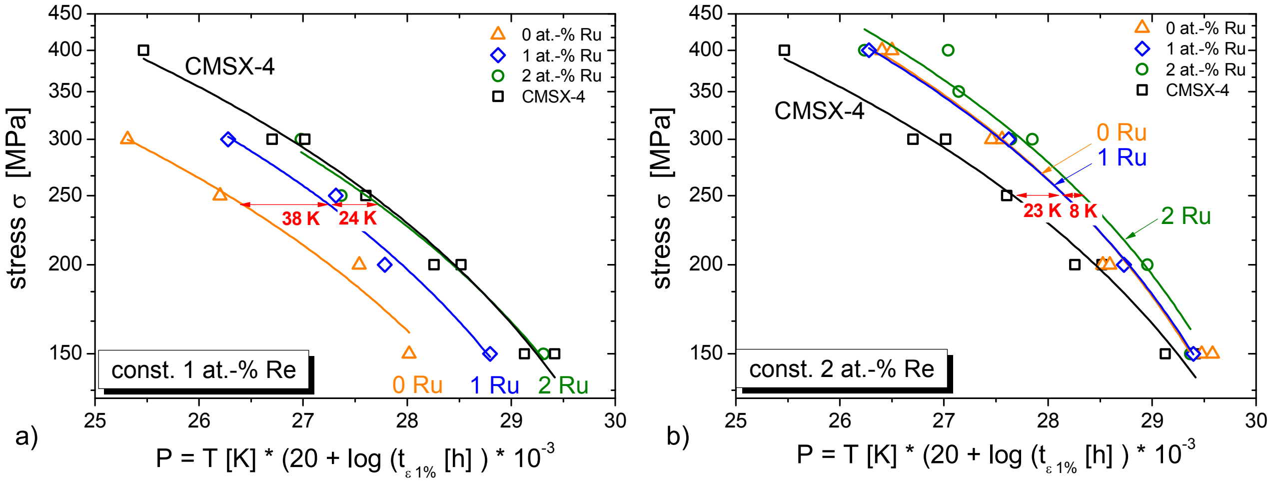

Figure 2: Larson-Miller-plots for DS-Astra1-alloys with constant 1 at.-% Re (a) and constant 2 at.-% Re (b). For comparison, experimentally derived creep data for DS-CMSX-4 is given. An improved creep resistance for Ru additions is mainly restricted to low Re-contents.

Fig. 3b displays the comparison of experimentally derived γ’ solvus temperature $T_{\gamma'\text{-Sol}}$ for alloy solidification (derived from DSC-cooling curves) and homogenized samples (data derived from DSC-heating-curves of heat treated samples). It is remarkable, that the distinct decrease in $T_{\gamma'\text{-Sol}}$ of about 15 K/at.-% Re for solidification-data fully disappeared in the heat treated alloys. The comparison in Fig. 3b furthermore reveals, that the ThermoCalc calculation for $T_{\gamma'\text{-Sol}}$ is in good agreement with the experimental data for $T_{\gamma'\text{-Sol}}$ in heat treated samples. However, the uniform $T_{\gamma'\text{-Sol}}$ for different Re-contents after heat treatment can not be displayed by ThermoCalc calculations. Solidification data indicates a constant discrepancy of about 50 °C to the simulated $T_{\gamma'\text{-Sol}}$, which is due to the fact, that the simulation characterizes the γ’ precipitation start temperature, whereas the measured DSC-values could only be extracted for peak of maximum precipitation rate [12].
The influence of Re and Ru on the γ/γ’-microstructure is shown in Fig. 4. It can be seen in Fig. 4a, that the remaining Re-segregation in heat treated Astra1-alloys with high Re-amounts (Fig. 1) affects the γ’-size within the dendritic and interdendritic regions. However, the difference in γ’-size is tolerable,

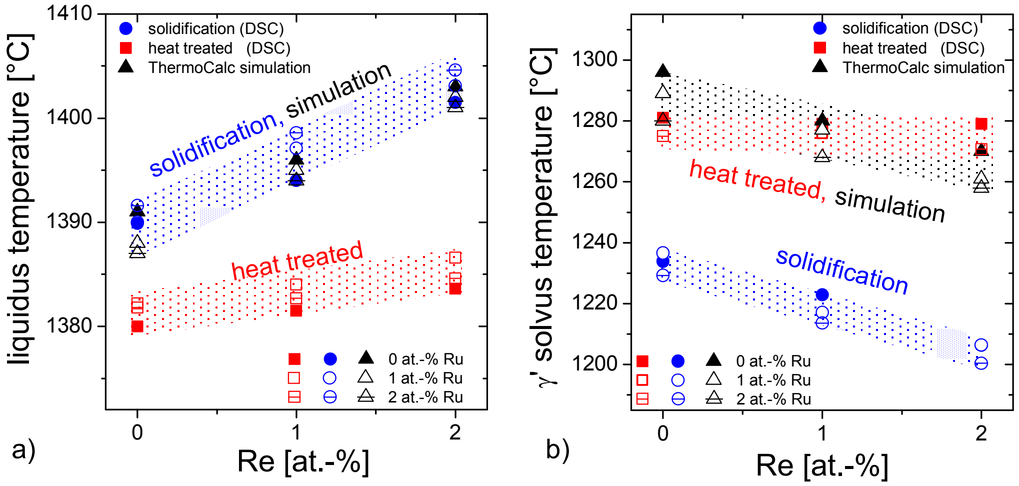

Figure 3: Comparison of experimentally derived liquidus temperature (a) and γ’ solvus temperature $T_{\gamma'\text{-Sol}}$ (b) for solidification and after homogenization in dependence of Re content. The influence of Re on thermophysical properties decreases after heat treatment.

since the variation is within the measuring tolerance. Thus, it can be concluded, that a remaining Re segregation distribution coefficient k_s of < 1,5 is sufficient for heat treatment processes. Fig. 4 also demonstrates the significant effect of Re-additions on γ’-size and -morphology, which cannot be

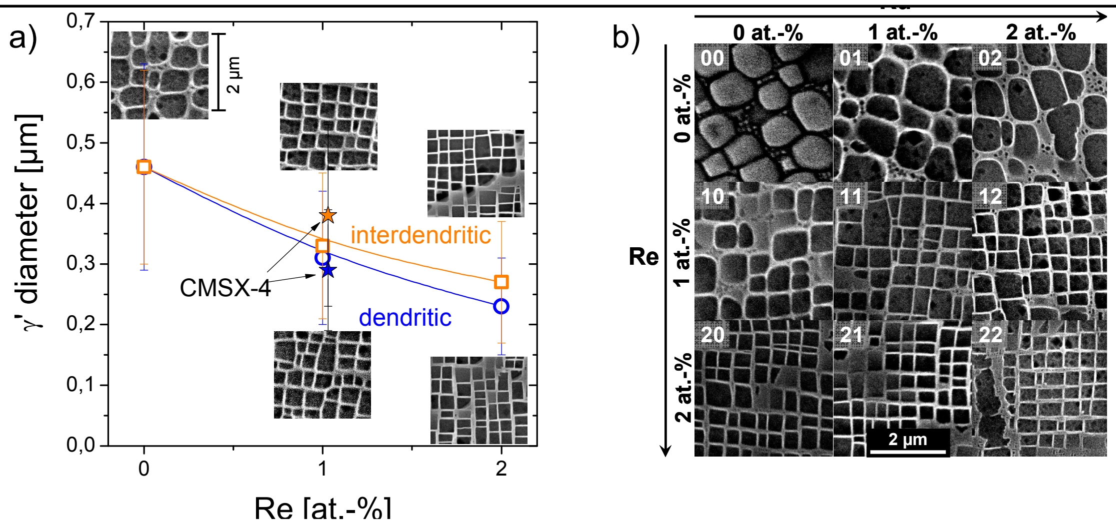

Figure 4: γ/γ'-Microstructure evolution of standard heat treated Astra1-alloys and CMSX-4. (a) γ'-size in dependence of the Re content and its variation between interdendritic and dendritic regions due to rest segregation (also see Fig. 1). (b) γ/γ' morphology in dependence of Re and Ru (given numbers equal the alloy-number).

found for Ru-additions. The γ'-size after a consistent heat treatment process decreases considerably with increasing Re contents, as is also approved elsewhere [21, 22]. Likewise the γ'-morphology changes from spherical to cubic and sharp edged γ'-precipitates with increasing Re content due to misfit changes [23]. A full quantitative γ/γ' microcharacterization with respect to the Re and Ru influence on γ'-size, γ'-volume content, γ/γ' misfit and γ/γ' distribution coefficients will be reported in a forthcoming article [15].

Discussion

The difference in liquidus temperature T_L between as-cast and heat treated alloys is most likely an effect of microsegregation. As known from literature, refractory elements in general, and Re in particular, feature a high segregation tendency to the dendrite core during solidification [12, 24-26]. Since the dendrite is the first solid formed, the high dendritic refractory fraction accordingly causes high T_L. After homogenization of the alloys, the refractory concentration is more evenly distributed and thus, the maximum T_L decreases. Consequently, the T_L difference before and after heat treatment rises with increasing microsegregation. As previously reported [12], such an overall ascent of microsegregation is caused by Re-additions, which in turn explains the increasing T_L-difference with increasing Re-contents in Fig. 3a. For experimental evaluations of element influences on T_L, these results make clear, that it is essential to pay attention to the influence of microsegregation on thermophysical data. Concerning the effect of an increased T_L as an argument for higher creep resistance, the effect by Re and Ru additions can be stated as insignificant due to the results presented in Fig. 3a.

An influence of γ'-solvus temperature $T_{\gamma'\text{-Sol}}$ on creep resistance could be given by a lower γ'-volume fraction emerging from earlier γ'-dissolution with increasing temperature. Considering the distinct data obtained for solidification or inhomogeneous as-cast samples (Fig. 3b), the decreasing $T_{\gamma'\text{-Sol}}$ with increasing Re-content could assume a negative effect for creep resistance. However, the $T_{\gamma'\text{-Sol}}$ decrease disappears fully after heat treatment. This result again points out the importance to recognize the distorting effect on thermophysical properties due to microsegregation in the as-cast state. According to the unaffected $T_{\gamma'\text{-Sol}}$ by Re and Ru additions after heat treatment, an influence on creep resistance by $T_{\gamma'\text{-Sol}}$ can be regarded as implausible in the Astra1-alloys, since there is also no effect on γ'-dissolution behaviour with increasing temperature, as found by Caron [27].

In contrast to the negligible effect of thermophysical properties, a major influence of Re and Ru on the γ/γ'-microstructure can be found. Hence, there is also a strong effect of the γ/γ' microstructure on the experimentally derived creep resistance of the Astra1-alloys. The main possible influence parameter can be given by the Re-dependent γ'-size, which is illustrated in Fig. 4a. Studies from Nathal [28] and Neumeier [29] prove, that there is a maximum creep resistance for optimized γ'-sizes. In nickel-base superalloys of the 3rd and 4th generation, this optimum is around 320 nm [29]. Thus, the γ'-size in Astra1-alloys with additions of 2 at.-% Re is possibly too small to obtain optimized creep properties. Furthermore, there is also an influence on creep rupture strength given by the γ'-coarsening rate, the γ'-volume content, the γ/γ' misfit and the elemental distribution between the γ and γ' phase, which make the interrelations quite complex. All these microstructural parameters influencing creep resistance and their quantitative modification by Re and Ru will be shown in detail in a forthcoming publication, which also discusses the exceptional creep resistance of CMSX-4.

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