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Improving the Effectiveness of the Solid-Solution-Strengthening Elements Mo, Re, Ru and W in Single-Crystalline Nickel-Based Superalloys

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Abstract: Tailoring the partitioning behavior of solid solution strengtheners is a crucial design strategy for advanced Ni-based superalloys. The goal of this study was to maximize the enrichment of Mo, Re, Ru and W in the γ-matrix phase. To determine the composition dependency of the partitioning behavior, a set of polycrystalline superalloys with varying contents of these solid solution-strengthening elements and a W-containing single-crystalline alloy series with varying concentrations of the γ′-forming elements Ta and Ti was produced. Assessed properties include phase compositions by electron-probe micro-analysis, phase transformation temperatures by differential scanning calorimetry and creep behavior. Re exhibits the most pronounced enrichment in the γ-matrix, followed by Mo, Ru and W. Due to the preference of the Al-sites in the γ′-phase in the order Ta > Ti > W > Mo > Re, the solid solution strengthening elements Mo, Re and W are displaced from the γ′-phase by increasing Ti and Ta contents. The investigated solutes do not directly influence the partitioning behavior of Ru as it prefers Ni-sites in the γ′-phase. Compressive creep experiments reveal a correlation between the content of solid solution strengtheners in the γ-phase and creep performance.

Keywords: Ni-based superalloys; creep; solid solution strengthening; partitioning behavior; DSC; CALPHAD

1. Introduction

During the last three decades, alloy development for blade applications in gas turbines for stationary and especially aeronautical applications has mainly focused on increasing the content of refractory elements such as Mo, Ta, W, Re and Ru [1–3]. This has led to improved high temperature creep performance but came with various drawbacks, including increased mass density, higher cost and formation of topological close-packed phases (TCP) [4–7]. A more efficient usage of alloying elements could improve Ni-based superalloys while avoiding some of these complications.

Ni-based cast superalloys derive their excellent high temperature creep resistance from the two-phase microstructure consisting of a ductile γ-matrix phase strengthened by a high volume fraction of ordered intermetallic γ′-precipitates. The main strengthening mechanisms are precipitation strengthening through the γ′-phase as well as solid solution strengthening (SSS) of the γ-phase matrix. Alloy design must consider both of these mechanisms to achieve sufficient creep resistance at elevated temperatures (1000–1150 °C). Creep of superalloys in the high-temperature-low-stress (HTLS) regime is controlled by thermally activated dislocation–motion in the γ-phase (e.g., [8]). Mo, Re, Ru and W have
binary Ni-X diffusion coefficients much smaller than Ni self-diffusion or Ni-Cr and Ni-Co diffusion coefficients [9–13] and are therefore beneficial for creep resistance. Especially Re, but also Mo and W, are used in many alloys for this purpose [14], whereas Ru was mainly introduced to counteract TCP formation [15].

In recent years, our research group has found that the partitioning behavior of the solid solution strengthening element W can be altered by γ′-stabilizing elements such as Ti and Ta [16–18]. Based on this concept, the alloys ERBO/13 (ERBO is an acronym for alloys developed in the DFG collaborative research center/transregio SFB/TR 103 resulting from the initial letters of the cities Erlangen and Bochum where the two partnering universities FAU and RUB are located.) [19] and ERBO/15 [20] were designed using our multi-criteria optimization software tool MultOpt [19]. They exhibit creep resistance similar to ERBO/1 (a CMSX-4 derivative) but without costly Re and at a much lower mass density in the case of ERBO/15. To understand the mechanisms behind the modification of the partitioning behavior in more detail, two model alloy series have been designed

(i) with varying amounts of the solid solution strengthening elements Mo, Re, Ru and W to investigate the differences of these elements among each other and
(ii) containing exclusively W as solid solution strengthener with varying amounts of the γ′-forming elements Ta and Ti to evaluate their efficiency in displacing W from the γ′ precipitates into the γ matrix.

This experiment builds on a previous study investigating only the effect of the γ′-forming element Ti [17]. In another publication [21], we had shown that Ta is more efficient than Ti regarding the re-partitioning of W, but adding a combination of the two exceeds the effect they have individually.

The properties of the model alloys are discussed and compared with the alloys ERBO/15 and ERBO/13 (designed in an optimization procedure) and the industrial reference ERBO/1 (CMSX-4). Creep results for SX alloys will be shown and discussed based on the partitioning behavior.

2. Materials and Methods

2.1. Alloy Chemistry and Processing

This study presents two series of alloys:

One set of polycrystalline alloys (referred to as EXP10 to EXP18) was fabricated by arc melting. The alloys are based on Ni-12.5Al-12.5Co-7.5Cr-2.5Ta (at.-%) and contain Mo, Re, Ru and W in amounts varying between 0, 1 and 2 at.-% (see Table 1). The two-step heat treatment of the as-solidified specimens consisted of a homogenization heat treatment (10 K/min up to 1300 °C/1 h, 1310 °C/1 h and 1320 °C/4 h, air-cooling to RT) and an aging heat treatment (4 K/min up to 860 °C, 1 K/min up to 900 °C/30 h, air-cooling to RT).

The second group of alloys was produced in a single-crystalline (SX) form and is referred to as ERBO/#. This set of alloys consists of the reference alloy ERBO/1 (CMSX-4 derivative), the recently designed reference alloys ERBO/13 (Rettig2015) and ERBO/15 (Rettig2016), as well as a model alloy system derived from a constant base composition Ni-10Co–5Cr–4W–15(Al + Ta + Ti) (at.-%) with the Ta- and Ti-content varying between 0 at.-% and 2.5 at.-%. Their designations are ERBO/17 . . . ERBO/19 and ERBO/32 (see Table 1). The fabrication of the SX alloys consisted of pre-alloying in an arc-furnace and subsequent casting in a laboratory-scale Bridgman furnace (for more details about the equipment, see [22]) followed by a two-step heat treatment comprising homogenization and aging. The casting procedure of all alloys was identical. Details about ERBO/1, ERBO/13, ERBO/15 and ERBO/17 . . . ERBO/19 have already been published in [19–21]. However, the heat treatments of some alloys have been modified and are summarized in Table 2. The multiple-step solution heat treatment was conducted to maximize the homogenization and slightly varies among the alloys due to their different thermophysical properties. A two-step aging heat treatment was conducted for all alloys. This was identical for all SX alloys except for ERBO/15, which was subjected to a lower temperature of 1040 °C during the first aging
step to avoid undesired $\gamma'$ morphologies and ERBO/32, which had to be aged in a single step at 800 °C due to challenging microstructure-coarsening behavior.

### Table 1. Chemical composition of the investigated alloys in at.-%. * ERBO/1 additionally contains 0.03 at.% Hf.

| Designation | Additional Designation | Al  | Co  | Cr  | Mo  | Re  | Ru  | Ta  | Ti  | W   | Ni   |
|-------------|------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| ERBO/1 *    | Reference              | 12.7| 9.9 | 7.5 | 0.4 | 1.0 | 2.2 | 1.3 | 2.2 | Bal. |
| ERBO/13     | Reference              | 11.2| 9.2 | 6.0 | 0.9 | 3.5 | 1.6 | 3.0 | Bal. |
| ERBO/15     | Reference              | 11.3| 3.1 | 7.6 | 2.6 |     |     |     |     |     |
| ERBO/32     | Model                  | 15.0| 10.0| 5.0 |     |     |     |     |     |     |
| ERBO/17     | Model                  | 12.5| 10.0| 5.0 |     |     |     |     |     |
| ERBO/18     | Model                  | 12.5| 10.0| 5.0 |     |     |     |     |     |
| ERBO/19     | Model                  | 10.0| 10.0| 5.0 |     |     |     |     |     |
| EXP10       | Experimental           | 12.5| 12.5| 7.5 |     |     |     |     |     |
| EXP11       | Experimental           | 12.5| 12.5| 7.5 | 1.0 |     |     |     |     |
| EXP12       | Experimental           | 12.5| 12.5| 7.5 | 2.5 |     |     |     |     |
| EXP13       | Experimental           | 12.5| 12.5| 7.5 | 1.0 |     |     |     |     |
| EXP14       | Experimental           | 12.5| 12.5| 7.5 | 2.5 |     |     |     |     |
| EXP15       | Experimental           | 12.5| 12.5| 7.5 | 1.0 |     |     |     |     |
| EXP16       | Experimental           | 12.5| 12.5| 7.5 | 2.5 |     |     |     |     |
| EXP17       | Experimental           | 12.5| 12.5| 7.5 | 2.5 |     |     |     |     |
| EXP18       | Experimental           | 12.5| 12.5| 7.5 |     |     |     |     |

### Table 2. Overview of heat-treatment procedure for all single crystalline alloys. AC is short for air-cooling at room temperature.

| Alloy      | Homogenization Heat Treatment                                                                 | Aging Heat Treatment                                                                 |
|------------|------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| ERBO/1     | 10 K/min to 1280 °C, 1 K/min to 1300 °C, hold 2 h, 1 K/min to 1310 °C, hold 2 h, 1 K/min to 1320 °C, hold 10 h AC | 4 K/min to 1100 °C, 1 K/min to 1140 °C, hold 2 h, 4 K/min to 830 °C, 1 K/min to 870 °C, hold 24 h, AC |
| ERBO/13    | 10 K/min to 1280 °C, 1 K/min to 1305 °C, hold 2 h, 1 K/min to 1315 °C, hold 10 h AC             | 4 K/min to 1100 °C, 1 K/min to 1140 °C, hold 2 h, 4 K/min to 830 °C, 1 K/min to 870 °C, hold 24 h, AC |
| ERBO/15    | 10 K/min to 1280 °C, 1 K/min to 1300 °C, hold 2 h, 1 K/min to 1310 °C, hold 10 h AC             | 4 K/min to 1000 °C, 1 K/min to 1040 °C, hold 2 h, 4 K/min to 830 °C, 1 K/min to 870 °C, hold 24 h, AC |
| ERBO/32    | 10 K/min to 1280 °C, 1 K/min to 1305 °C, hold 2 h, 1 K/min to 1315 °C, hold 2 h, 1 K/min to 1325 °C, hold 2 h, 1 K/min to 1335 °C, hold 10 h AC | 4 K/min to 760 °C, 1 K/min to 800 °C, hold 100 h, AC                                     |
| ERBO/17    | 10 K/min to 1280 °C, 1 K/min to 1305 °C, hold 2 h, 1 K/min to 1315 °C, hold 2 h, 1 K/min to 1325 °C, hold 2 h, 1 K/min to 1335 °C, hold 10 h AC | 4 K/min to 1100 °C, 1 K/min to 1140 °C, hold 2 h, 4 K/min to 830 °C, 1 K/min to 870 °C, hold 24 h, AC |
| ERBO/18    | 10 K/min to 1280 °C, 1 K/min to 1305 °C, hold 2 h, 1 K/min to 1315 °C, hold 2 h, 1 K/min to 1325 °C, hold 2 h, 1 K/min to 1335 °C, hold 10 h AC | 4 K/min to 1100 °C, 1 K/min to 1140 °C, hold 2 h, 4 K/min to 830 °C, 1 K/min to 870 °C, hold 24 h, AC |
Table 2. Cont.

| Alloy    | Homogenization Heat Treatment | Aging Heat Treatment          |
|----------|-------------------------------|-------------------------------|
| ERBO/19  | 10 K/min to 1280 °C, 1 K/min to 1305 °C, hold 2 h | 4 K/min to 1100 °C, 1 K/min to 1140 °C, hold 2 h, AC |
|          | 1 K/min to 1315 °C, hold 2 h | 4 K/min to 830 °C, 1 K/min to 870 °C, hold 24 h, AC |
|          | 1 K/min to 1325 °C, hold 2 h |                               |
|          | 1 K/min to 1335 °C, hold 10 h |                               |

2.2. DSC, EPMA Measurement and Metallography

The phase transformation temperatures have been determined using differential scanning calorimetry (DSC) measurements of fully heat-treated 3 × 3 × 3 mm³ cube-shaped specimens using a Netzsch STA 409C/CD device (Netzsch GmbH, Selb, Germany). All alloys were investigated in a heat-treated state to obtain a stronger signal of the γ'-solvus peak and determine the equilibrium solidus temperature instead of the incipient melting temperature in interdendritic regions (compare Figure 1). For the SX alloys, the as-cast state was measured additionally. The transformation temperatures were determined by plotting the DSC signal (W/mg) against temperature (°C) and tracking the first deviation from the local baseline. An exemplary DSC curve of the alloy ERBO/19 can be seen in Figure 1. For further information on the analysis technique and the accuracy of this method, the reader is referred to Ritter et al. [23].

![DSC curve of the alloy ERBO/19](image)

Figure 1. Example for the determination of phase transformation temperatures based on DSC measurements. The figure shows the DSC response of the alloy ERBO/19 in the as-cast (ac) and the heat treated + aged (ht + a) state. The arrows indicate the temperatures of phase transformations.

For electron-probe micro-analysis (EPMA), the γ’-precipitates were coarsened to a size of several micrometers by a special heat treatment, initially developed by Heckl et al. [24]. The fully heat-treated state was heated up to 1280 °C (1300 °C—for the SX alloys) with 10 K/min and further to 1290 °C (1310 °C—for the SX alloys) at 1 K/min. To achieve complete dissolution of the γ'-phase, the temperature was subsequently kept constant for 1 h. Afterward, a slow cool-down with approximately 20 K/h to 1100 °C (1150 °C—for the SX alloys) was performed to nucleate a small number of γ'-precipitates. A 12 h holding time followed to coarsen the precipitates. Finally, subsequent furnace cooling to 700 °C in 8 h minimized the amount of tertiary γ' precipitation. The final precipitate size was measured to be up to 5 μm. The composition of the γ'-matrix and γ' precipitate phase were calculated analogously to the sorting algorithms to determine segregation coefficients as reported in Ganesan et al. [25], Kößmann et al. [26] and Ritter et al. [21]. The compositional data of the EPMA mapping were sorted by their average concentration-weighted tendency.
to partition to either the γ- or γ'-phase. The mean of the first and last 2% of the sorted data points were then taken to be the γ- and γ'-phase composition, respectively.

The partitioning behavior between the γ'-precipitate and the γ-matrix is often described in terms of the γ'/γ partitioning coefficient

$$K_i = \frac{c_{i,\gamma'}}{c_{i,\gamma}}$$

(1)

where $c_{i,\gamma}$ and $c_{i,\gamma'}$ represent the concentration of element $i$ in γ and γ', respectively. In addition, the concentration of an element $i$ in the matrix phase can, of course, also be increased by increasing its nominal content $c_{i,nom}$ in the alloy. Thus, the amount of a solid solution strengthener (SSS) in the γ-matrix-phase is determined by $c_{i,nom}$ and $K_i$. In this work, we define another quantity to include the dependence on $c_{i,nom}$ as previously described in Ritter et al. [21]. The partitioning efficiency $K_{i,\gamma/nom}$ represents how efficient a certain amount of a solid solution strengthening element is accumulated in the γ-matrix phase:

$$K_{i,\gamma/nom} = \frac{c_{i,\gamma}}{c_{i,nom}}$$

(2)

An efficient solid solution strengthening element should therefore have a concentration in the γ-matrix as large as possible, e.g., $K_{i,\gamma/nom}$ should be large. On the other hand, an element that is equally distributed between the γ- and γ'-phase has a partitioning efficiency of $K_{i,\gamma/nom} = 1$.

Additionally, completely heat-treated specimens of all SX alloys were heat-treated at 1100 °C for 24 h and subsequently water-quenched. All specimens were ground, polished and etched. The γ' area-fraction was determined by image analysis of four secondary-electron micrographs per alloy, acquired on an FEI Quanta 450 scanning electron microscope. The γ' volume-fraction was additionally calculated from the EPMA phase compositions using the lever-rule approach described by Blavette et al. [27].

2.3. Creep Testing

Heat-treated samples were spark-eroded to produce cylindrical compressive creep specimens with a height of 6.4 mm and a diameter of 4 mm. Top and bottom surfaces were turned down to a height of 6.0 mm to ensure that contact surfaces were parallel. The compressive creep tests were performed at constant temperature and constant true stress under the following conditions: 1100 °C/137 MPa, 1050 °C/200 MPa, 950 °C/300 MPa and 950 °C/400 MPa.

2.4. Numerical Methods

For each alloy listed in Table 1, a property diagram (temperature vs. phase amount) was calculated using the CALPHAD software ThermoCalc, version 2016b (ThermoCalc AB, Stockholm, Sweden) with the TTNi8 database (ThermoTech, Surrey, UK) to determine the γ'-solvus, solidus and liquidus temperatures. To access the compositions of the γ-matrix and γ'-precipitate phases, a metastable property diagram was calculated by selecting only the γ-matrix-phase, γ'-phase and liquid phase and rejecting all other phases. The B-sublattice occupation data in the ordered γ' A3B lattice were also derived from these calculations.

2.5. Terminology

The terms efficiency, effectivity and efficacy can be used to phrase related meanings. Regarding describing partitioning behavior and solid solution strengthening, multiple of these terms may be applicable based on the point of view. Eventually, this can lead to some confusion. Therefore, in order to clarify the usage of these terms in this work, we define the following:
(i) The **Partitioning Efficiency** describes how much of a given nominal concentration of a SSS element is accumulated within the $\gamma$-matrix. The partitioning efficiency is represented by $K_{i,\gamma}/\text{nom}$ (see Equation (2)).

(ii) The **Repartitioning Efficiency** describes how much $K_{i,\gamma}/\text{nom}$ of a SSS element is affected by the addition of $\gamma'$-formers.

(iii) The **Solid Solution Strengthening (SSS) Effectivity** describes how large the effect of a SSS element is on the alloy’s total macroscopic solid solution strengthening. This is represented by the Solid Solution Strengthening Index ($I_{\text{SSS}}$) developed by Fleischmann et al. [28], in which the respective SSS element concentration in the $\gamma$-matrix is weighted by the element’s efficacy regarding creep strength. This is summarized by the following equation [19]:

$$I_{\text{SSS}} = 2.44c_{\text{Re,}\gamma} + 1.22c_{\text{W,}\gamma} + c_{\text{Mo,}\gamma}. \quad (3)$$

### 3. Results

All alloys display a two-phase $\gamma/\gamma'$-microstructure. Figure 2 shows SEM micrographs of the $\gamma/\gamma'$-microstructure that can be observed for all alloys in the homogenized and aged state. The $\gamma'$-precipitates have a clearly defined cuboidal shape for the reference alloys ERBO/1, ERBO/13 and ERBO/15. The precipitates of the model alloys ERBO/17 . . . 19 and ERBO/32 have more rounded corners than the reference alloys, which is most likely the result of a smaller absolute value of the $\gamma/\gamma'$ lattice misfit. The experimental polycrystalline alloys EXP10 . . . 18 show $\gamma/\gamma'$-microstructure varying from the cuboidal morphology. The differences include sectioning orientations deviating from $[001]$ (EXP15 and EXP13), precipitates shapes closer to spherical (EXP12, EXP14 and EXP18) and a larger amount of tertiary precipitates (EXP12 . . . 15). Neither topological close-packed phases (TCP) nor carbides were observed in all alloys.

![SEM micrographs of the $\gamma/\gamma'$ microstructure of all alloys in the homogenized and aged state.](image)
In the following, first, the results of the polycrystalline experimental alloy analysis are presented. Second, the properties of the single crystalline reference and model alloys are detailed.

3.1. Polycrystalline Alloys (EXP Alloy Series)

The differential scanning calorimetry (DSC) measurements in Figure 3 show that Re, Ru and W slightly increase the solidus temperature, whereas Mo strongly decreases it when the elements are added at the expense of Ni. In contrast, Mo, as well as W and Re, increase the γ′-solvus temperature while Ru slightly lowers it. The effect of W on the γ′-solvus temperature is much more significant than the comparatively small effects of Re and Mo.

![Figure 3](image)

**Figure 3.** Influence of solid solution strengthening elements on the transformation temperatures measured by DSC of the EXP alloy series.

In Figure 4, the partitioning behavior of Mo, Re, Ru and W is analyzed according to their partitioning efficiency. Seven out of the eight alloy derivatives show $K_{i/\gamma_{\text{nom}}}$ values significantly above one and therefore a clear enrichment of SSS elements in the γ-matrix phase. Only alloy EXP17 with one at.% W shows a value close to one for W, indicating its equal distribution between the phases γ and γ′. An increase in the nominal content of the solid solution strengtheners from 1 to 2.5 at.% leads to a stronger displacement from the γ′ phase in the case of Mo, Re and W. In contrast, the preferential partitioning of Ru remains unaffected by its nominal content in the alloy. The partitioning efficiency is highest for Re and lowest for W, whereas the order of Ru and Mo changes by increasing the nominal content. Mo shows a larger $K_{i/\gamma_{\text{nom}}}$ than Ru at a larger nominal concentration. The highest partitioning efficiency is approximately 1.6 and occurs in alloy EXP14 which means that—in contrast to the 2.5 at.% nominal Re content—the γ-matrix contains four at.% Re in that alloy.

![Figure 4](image)

**Figure 4.** Partitioning behavior of solid solution strengthening elements in the polycrystalline EXP alloy series described by the partitioning efficiency.
Different behavior of Ru compared to the three other elements is also visible in Figure 5a. The sum of Al, Ta, Cr and solid solution strengthening elements in the γ′-phase is close to 25 at.-% for the alloys containing Re, W and Mo, whereas the sum for the Ru-containing alloy reaches values larger than 26 at.-%. Figure 5b presents the absolute concentration values of alloying elements measured for the γ′-phase (left column), calculated for the γ′-phase (middle column) as well as the calculated values for the occupation of Al-sites in the γ′-phase (right column) for the base alloy and all 2.5 at.-% derivative versions. While the total γ′-composition is close to 25 at.-% for all three data sets, the Cr content shows larger discrepancies between experimental values and ThermoCalc calculations. The Cr content in γ′, as determined by EPMA measurements, is about twice as high as the thermodynamic predictions. In contrast, the calculations seem to overestimate the Al content in γ′ for the derivative EXP alloys. However, considering the much larger total concentration of Al (12.5 at.-%), this is only a minor relative deviation compared to the Cr concentration discrepancy.

![Figure 5. Element concentrations in the γ′-phase: (a) The alloys containing Mo, Re and W show decreasing sums of experimentally determined (EPMA) Al + Ta concentrations and a relatively constant value of about 25 at.-% for the sum of Al + Ta + Cr + SSS elements, whereas the Ru effect is different; (b) comparison of the experimentally measured composition (left column) with ThermoCalc calculated (middle column) composition of the γ′-phase. The right column shows the occupation of Al sites in the γ′-phase calculated with ThermoCalc.](image)

3.2. Single-Crystalline Alloys (ERBO Alloy Series)

The DSC measurement results for the SX-alloys are summarized in Figure 6 for the as-cast state (first column), the heat-treated and aged state (middle column) and the solidification process (right column). The solidus temperature increases due to the heat treatment from the as-cast state to the heat-treated and aged state, whereas the liquidus temperature does not change significantly. Solidus and liquidus temperatures are highest in ERBO/32 (Al) and decrease in the order ERBO/17 (Ta), ERBO/18 (Ti), ERBO/19 (Ta + Ti) and are lowest in the three reference alloys ERBO/1, ERBO/13 and ERBO/15. For the model alloy series, the alloys ERBO/17 (Ta) and ERBO/19 (Ta + Ti) show the highest γ′-solvus temperatures (1303 and 1305 °C), while it decreases for ERBO/18 (1278 °C) and is the lowest in ERBO/32 (Al) (1250 °C). The γ′-solvus temperature of ERBO/1 reaches a similar level (1309 °C) as ERBO/17 (Ta) and ERBO/19 (Ta + Ti), ERBO/13 shows the highest value (1323 °C) and ERBO/15 (only containing Ti and Al) offers the lowest γ′-solvus temperature (1282 °C) of the reference alloys. In all alloys except ERBO/13, the eutectic formation temperature during solidification is higher than the measured γ′-solvus temperature in the heat-treated state. DSC measurements and metallographic investigation of ERBO/32 (Al) show no evidence of eutectic formation.
The previous subchapter presented the influence of solid solution strengthening elements on their partitioning behavior. Figure 8 shows the influence of Ta and Ti on the partitioning behavior of W in the model single-crystal alloy series. The nominal four at.-% W partitions the least between the γ-matrix and the γ′-phase in the Ta- and Ti-free base system ERBO/32 (Al). By adding 2.5 at.-% Ta or 2.5 at.-% Ti at the expense of Al, W is repelled from the γ′-precipitates into the γ-matrix. The effect is more prominent for
ERBO/17 (Ta) compared to ERBO/18 (Ti) but highest in ERBO/19 (Ta + Ti), containing only 10 at.-% Al but 2.5 at.-% Ta and 2.5 at.-% Ti.

Figure 8. Analysis of the partitioning efficiency $W$ for the single-crystalline model alloy series. The alloying elements Ti and Ta in ERBO/17, ERBO/18 and ERBO/19 replace some of the Al content compared to the base alloy ERBO/32, such that a $\gamma'$-forming elements sum (Al + Ta + Ti) of 15 at.-% is retained.

Figure 9a shows the partitioning behavior for the reference alloys ERBO/1, ERBO/13 and ERBO/15. The order of partitioning efficiency of solid solution strengthening elements is $\text{Re} > \text{Mo} > W$ and is therefore identical to the polycrystalline experimental alloy system shown before. The displacement of $W$ is the weakest in ERBO/15 and ERBO/1. The best partitioning efficiency of $W$ and Mo is achieved in ERBO/13, an alloy containing 3.5 at.-% Ta and 1.6 at.-% Ti.

Figure 9b displays the direct comparison of the nominal SSS concentration (left column), the measured concentration within the $\gamma$-matrix phase (middle column) and the solid solution strengthening index (I_{SSS}) in Equation (3)).

Figure 9b displays the direct comparison of the nominal SSS concentration (left column), the measured concentration within the $\gamma$-matrix phase (middle column) and the solid solution strengthening index (I_{SSS}). ERBO/1 with the lowest overall content of solid solution strengthener achieves the largest I_{SSS}. The main reasons are the strong partitioning

Equation (3)).
of Re towards the matrix phase and the extraordinary efficacy as a solid solution strengthening element compared to W and Mo. ERBO/15 reaches a similar Isss as ERBO/1 but has the highest overall content of solid solution strengthener. W is not as strongly enriched in the γ-matrix phase as in the other alloys, and Mo—although strongly enriched in the γ-phase—has the lowest general efficacy as a solid solution strengthener in the description of Isss.

Creep Results

Figure 10a shows the creep curves for all alloys tested in compression at 1100 °C and 137 MPa. The single-crystalline reference alloys ERBO/1 and ERBO/15 show the best creep performance with minimum strain rates below $10^{-7}$ 1/s, followed by ERBO/13 with slightly lower creep resistance. Due to their non-optimal alloy composition, the other single-crystalline model alloys display lower creep resistance in the form of higher strain rates. ERBO/32 (Al) has the overall largest strain rates. The Larson-Miller Parameter (LMP) graph in Figure 10b summarizes the creep experiments for the reference alloy series. ERBO/1 still displays the best creep performance even after including the other creep test conditions. However, ERBO/13 and ERBO/15—optimized to have similar creep performance as ERBO/1—show similar results.

Figure 10. Creep results and their interpretation: (a) creep curves showing strain rate vs. true strain for the single-crystalline alloys. (b) Larson-Miller Plot of the reference alloy series to compare the creep performance between different creep test conditions, (c) Larson-Miller Plot of the model alloy series to clarify the influence of the partitioning efficiency of W and repartitioning efficiency of Ti and Ta on creep properties, which is also shown in (d) as a graph of the minimum strain rate as a function of the partitioning efficiency of W.
Figure 10c shows the creep performance of the alloys ERBO/32 and ERBO/17...ERBO/19 in a LMP diagram. ERBO/32 shows the lowest creep resistance, whereas ERBO/19 has the best creep properties in this alloy series. The minimum strain rate vs. the partitioning efficiency of W in Figure 10d clarifies the correlation between the creep performance and the partitioning behavior of W. ERBO/32 and ERBO/18, which have similar values for $K_{i,\gamma/\gamma}$, show similar minimum creep rates. The increasing partitioning efficiency of the alloys ERBO/17 and ERBO/19 results in lower minimum strain rates.

4. Discussion

4.1. $\gamma/\gamma'$-Partitioning Behavior

The experimental results in Figures 4 and 9a reveal an order regarding the partitioning efficiency of the solid solution strengthening (SSS) elements: Re > Mo > W. Taking the results of Amouyal et al. [18] into account, showing that W energetically prefers Al sites in $\gamma'$-phase the most, it can be concluded that also Re and Mo show similar behavior to W, which was also shown in Ding et al. [29]. Figure 5b also depicts the incorporation of solid solution strengthening elements in the $\gamma'$-phase on the Al sublattice. In the $\gamma'$-phase, based on the stoichiometric composition $\text{Ni}_3\text{Al}(A_3\text{B})$, Al is found on the corners (B-positions) and Ni on the faces (A-positions) of the cubic unit cell. Therefore, the corner positions correspond to 25 at.-% of the alloying elements. As $\gamma'$-formers, Al and Ta primarily occupy the B sublattice. Their combined amount reaches approximately 21.8 at.-% for the base system EXP10 and decreases with increasing additions of Mo, Re and W while being only slightly affected by Ru (see Figure 5a). This indicates that other alloying elements replace Al and Ta. The constant sum of Al + Ta + Cr + solid-solution-strengthening element in $\gamma'$ of approximately 25 at.-% reveals that W, Re and Mo indeed replace Al and Ta on the Al sublattice. Regarding the Ru-containing alloys, this behavior deviates by increasing the sum, indicating that Ru does not replace Al and Ta in $\gamma'$ and is somewhat preferably incorporated in the Ni sublattice in the $\gamma'$-phase as shown in Ding et al. [29].

Murakami et al. [30,31] have shown by simulation and experimental investigation of multiple Ni-base superalloys that Ta, Al, Ti, Mo, Re and W prefer Al-sites in $\gamma'$-phase, and Ni and Co the Ni-sites. The results for Cr were less clear. Their simulations showed a preference of Cr for the Al-sites. However, their experiments revealed a Ni-site preference of Cr. Similar findings are confirmed by Blavette et al. [27] on CMSX-2 and PWA 1980 as well as Duval et al. [32] for MC2 alloy using an atom probe technique. Liebscher et al. found an Al-site preference for Cr in a ternary Ni–Al–Cr alloy which changed to no site preference in the singly crystalline CMSX-4 alloy [33]. The results of this study (Figure 5a,b) seem to imply that Cr weakly prefers Al-sites as otherwise the 25 at.-% of the Al sublattice would not be filled with the sum of the remaining Al-site preferring elements. The observed behavior is already partially included in the CALPHAD database TTN18 (compare Figure 5b). Ta, Al, W, Mo and to some extent, Cr are placed on Al sites, whereas Ni, Co, Re and Ru are placed on the Ni sublattice. The calculated results for Re and Ru might be less accurate than for other elements as they were introduced to the CALPHAD system quite late and therefore are based on a smaller amount of experimental and simulation data. However, Re and Ru have been critical alloying elements in advanced single crystal alloys for a long time and were almost always found in the $\gamma$-matrix phase instead of $\gamma'$-phase [16,34–36]. Volek et al. [37] showed for ternary NiAl-X systems that Re accumulates in the $\gamma'$-phase whereas Ru is enriched in the $\gamma$-matrix. Therefore, it can be concluded that Re indeed energetically prefers the Al-site in the $\gamma'$-phase. However, due to the energetically more favorable occupancy through most other solutes such as Ta, W or Mo, the Re atoms are almost exclusively found in the matrix phase.

Adding the results presented in Figure 8 to the discussed topic, the order partitioning efficiency should be modified to an order of Al-site preference in the $\gamma'$-phase: Ta > Ti > W > Mo > Re. The position of Cr and Al in this order remains unclear. Using the established order of Al sublattice preference in the $\gamma'$-phase, alloys can be designed with efficient use...
of solid-solution-strengthening elements such as W and Mo in ERBO/13 and ERBO/15. Thereby, Ta displays a more significant repartitioning efficiency than Ti.

4.2. Correlation of Solid Solution Strengthening and Creep Performance

Creep resistance in nickel-based superalloys is derived from the main strengthening mechanisms, precipitation strengthening and solid solution strengthening, as well as a complex interaction of the two-phase microstructure. Since dislocation motion at high temperature creep mainly occurs in the $\gamma$-matrix, the solid solution strengthening elements need to be enriched there to achieve the optimal creep performance. The single-crystalline model alloy series results showed that Ta affects the partitioning behavior of W more efficiently than Ti, e.g., it exhibits a more pronounced repartitioning efficiency, which correlates to the creep performance (see Figure 10d).

However, the concentration of solid solution strengthening elements in the $\gamma$-matrix phase alone cannot explain the similar creep performance of ERBO/1 compared to ERBO/15. ERBO/15 has a much higher concentration of W and Mo in the $\gamma$-matrix than W, Re and Mo in ERBO/1 (see Figure 9b). The missing factor in explaining this behavior is the solid solution strengthening efficacy of the SSS elements, which is related to the interdiffusion coefficient of those elements [38], the reduction in stacking fault energy and the increase in the elastic modulus [28]. Re is the slowest diffusion element compared to W and Mo [38] and therefore has the highest efficacy on solid solution strengthening, which is also reflected by the highest weighting factor within the definition of $I_{\text{SSS}}$.

This highlights the two possible strategies to achieve high creep resistance by solid solution strengthening in superalloy design:

(i) Use the highly efficacious solid solutions strengthening element Re or
(ii) Optimize the partitioning behavior, and increase the amount of Mo and W.

The second strategy was successfully employed to design the alloys ERBO/13 and ERBO/15, which are less expensive due to Re’s absence, and still reach similar creep resistance, as shown in Figure 10b.

5. Conclusions

- Solute prefer the Al-sites in the $\gamma'$-phase in the order Ta > Ti > W > Mo > Re. This can be exploited to repel solid-solution-strengthening elements W, Mo and Re from the $\gamma'$-precipitates to the $\gamma$-matrix.
- Ni, Co and Ru prefer the Ni-sites in the $\gamma'$-phase but preferentially accumulate in the $\gamma$-matrix phase. Therefore, an increase in the Ru solid solution strengthening effectivity by repartitioning is not feasible.
- A direct correlation between the content of solid-solution-strengthening elements in the $\gamma$-matrix phase and the creep performance is demonstrated.
- The possible strategies to achieve large solid-solution-strengthening effectivities by optimizing the partitioning efficiency or using the highly efficacious SSS element Re are highlighted.

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