Quantitative Experimental Determination of the Solid Solution Hardening Potential of Rhenium, Tungsten and Molybdenum in Single Crystal Nickel-Based Superalloys

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Abstract

The solid solution hardening potential of the refractory elements rhenium, tungsten and molybdenum in the matrix of single crystal nickel-based superalloys was experimentally quantified. Single phase alloys with the composition of the nickel solid solution matrix of superalloys were cast as single crystals, and tested in creep at 980°C and 30 - 75 MPa. The use of single phase single crystalline material ensures very clean data because no grain boundary or particle strengthening effects interfere with the solid solution hardening. This makes it possible to quantify the amount of rhenium, tungsten and molybdenum necessary to reduce the creep rate by a factor of ten. Rhenium is more than two times more effective for matrix strengthening than either tungsten or molybdenum. The existence of rhenium clusters as a possible reason for the strong strengthening effect, is excluded as a result of atom probe tomography measurements. If the partitioning coefficient of rhenium, tungsten and molybdenum between the γ matrix and the γ' precipitates is taken into account, the effectiveness of the alloying elements in two phase superalloys can be calculated and the rhenium effect can be explained.

Keywords: solid solution, single crystal, creep, nickel-based superalloys, rhenium

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1. Introduction

Materials used in the hot section of stationary turbines and aero-engines have to fulfill high demands. They have to withstand high material temperatures of up to 1100°C under high mechanical loads. For several decades, the materials of choice have been nickel-based superalloys, as they exhibit excellent high temperature mechanical properties, such as creep and oxidation resistance [1]. The temperature resistance has been increased by new processing routes, i.e., changing from wrought to single crystal alloys, and by modification of the alloy composition. Many investigations have concentrated on the optimization of the microstructure, which consists of cuboidal L1₂-ordered γ' precipitates separated by narrow channels of face-centered cubic solid solution γ matrix [2]. It is well known that the ideal microstructure shows an initial γ' particle size of $d_{\gamma'} = 0.45 \mu\text{m}$, a γ' volume fraction $f_{\gamma'} = 70\%$, and a misfit of matrix and γ' lattice parameter of $\delta = -(1...3) \cdot 10^{-3}$, where $\delta = 2 \cdot (a_{\gamma'} - a_{\gamma}) / (a_{\gamma'} + a_{\gamma})$ [3,4]. These values are often met by modern single crystal superalloys, i.e. the precipitation strengthening is exploited to its maximum. Thus, solid solution strengthening of the soft γ matrix is of high interest to further increase the mechanical properties. Re, W and Mo are the most effective solid solution hardening elements, with Re being the strongest, which led to the classification in superalloy generations [5]. But there are also several problems that arise by increasing the Re content: the alloys show poor oxidation resistance [6] and are prone to the formation of brittle topologically close-packed phases, which have detrimental effects on the mechanical properties [7]. Furthermore, Re is a scarce strategic element and is subjected to large price fluctuations [8] leading to high alloy costs. Currently, huge development efforts are being undertaken to identify single crystal superalloys without rhenium that retain similar or

better mechanical properties than second generation superalloys containing 3 wt.% Re [8,9].

Therefore, it is crucial to know the magnitude of the effect of rhenium as a solid solution hardener in the single crystalline γ matrix, where the additional strengthening will originate, and if Re can be replaced by other solid solution hardening elements, such as W and Mo.

The present investigation addresses these questions. Six alloys with the typical γ matrix composition of a nickel-based superalloy but with different contents of rhenium, tungsten and molybdenum, were cast as single crystals and tested in creep. For the first time single phase single crystalline material with systematically varied content of heavy elements were tested in creep. The results are very clean data for the solid solution strengthening potential, which are not falsified by any grain boundary or particle strengthening effects. This allows a quantification of the effectiveness of the refractory elements on solid solution hardening of the matrix phase.

In combination with the partitioning coefficient, which describes the distribution of the elements between the matrix and γ' particles, the amount of refractory elements for the strengthening of two phase superalloys can be calculated.

The influence of alloying elements on diffusivity and stacking fault energy are discussed as possible reasons for solid solution hardening. Another possible explanation for the large Re-effect on the creep rate is the formation of rhenium clusters in the matrix. These clusters act as obstacles against dislocation movement. The existence of these clusters remains controversial: rhenium clusters were claimed by several researchers [10,11] and were identified using 1D-atom probe field ion microscopy, but this was later refuted by Mottura et al. using the extended X-ray absorption fine structure technique [12] and more sophisticated statistical analysis of modern atom probe tomography [13]. Using the same

method described by Mottura et al. [13], a Re containing matrix alloy was observed to detect possible clusters.

2. Materials and Methods

Alloy Selection

Seven different matrix alloys with a composition close to the matrix of two-phase single crystal superalloys were chosen and designated according to their rhenium or tungsten content with MSX (matrix single crystal). The corresponding two-phase alloys are either different in their commercial use (CMSX-4 and MC2) or are model alloys. The compositions (see table 1) were calculated by Thermo-Calc [14] with the TTNi7 database [15] at the equilibrium temperature of 800°C. This method generated good agreement with the measured matrix compositions in commercial superalloys [10,16], which are included in table 1 for comparison.

A wide range of the most important solid solution strengthening elements, rhenium, tungsten and molybdenum is represented: the rhenium content varies in-between 0 - 9 wt.% (the upper limit corresponds to the matrix content of the second generation nickel-based superalloy CMSX-4), the tungsten content varies in-between 5.4 - 16.3 wt.%, and the molybdenum content in-between 1.3 - 4.4 wt.%. All values are typical for first and second generation nickel-based superalloys.

SX casting and heat treatment

Prior to single crystal casting, the master alloys were melted from high purity elements (>99.9%) in an arc furnace under 500 mbar argon atmosphere. Subsequent single crystal casting was carried out in a proprietary Bridgman investment casting furnace [17,18] with a temperature gradient of 6 K/mm and a withdrawal rate of 3 mm/min. The single crystal rods had a diameter of 15 mm and a length of 130 mm. The alloys were diffusion heat

treated for 60 h at 1280°C to obtain a homogenous distribution of rhenium and tungsten, which strongly segregate to the dendrite cores [19].

Creep testing

Flat creep specimens (for geometry see [20]) were cut from the single-crystal rods by wire electro-discharge machining, and then ground flat to a surface roughness of $R_a < 0.2 \mu\text{m}$. The specimens were machined parallel to the axis of symmetry of the rod to coincide with the orientation resulting from the casting process. The deviation between the axis of the applied stress and the $\langle 001 \rangle$ crystallographic direction equals the maximum angle between the cylindrical axis and the dendrites. The crystallographic sample orientation was measured from etched rods in the as-cast condition, where the etching conditions were 3 min. in a solution of 200 ml H_2O , 200 ml HCl (37%), and 20 ml HNO_3 (65%) at 70°C.

Creep testing was carried out in proprietary creep testing devices [21,22] under vacuum ($<10^{-5}$ mbar) at a temperature of 980°C and stresses of 30, 50 and 75 MPa. Details of the temperature measurement procedure are described in [23].

Atomprobe tomography of the rhenium distribution

The highest rhenium-containing alloy, MSX Re9, was examined by APT to detect possible rhenium clusters. This alloy has an advantage over the previous investigated binary and two phase alloys [13] as it contains all alloying elements which are included in the matrix of superalloys and no other phases such as γ' are present. The measurement was performed with the local electrode atom probe (LEAP[®] 4000X HR) instrument at Oak Ridge National Laboratory. The LEAP was operated in voltage-pulsed mode with a pulse repetition rate of 100 kHz, a pulse ratio of 0.2, an ion detection rate of 0.5% ions per pulse, and a specimen temperature of 40 K. The detection efficiency of the instrument was ~37%. The dataset

contains more than 30,000 detected rhenium atoms. The data were analyzed with the highly sophisticated method described in detail by Mottura et al. [13] in which the random clusters in solid solution alloys were taken into account.

3. Results

Orientation of cast single crystals

All seven matrix alloys were successfully produced as single crystals. The deviations Φ of the cylindrical axis from the $\langle 001 \rangle$ crystallographic direction were in all cases $< 9^\circ$, as shown in table 1. These small deviation influence only slightly influences the creep results of single crystal matrix alloys [24]. No other phases, apart from the γ matrix, were detected by secondary electron microscopy (SEM).

Creep behaviour of matrix alloys

All alloys were tested at a temperature of 980°C and stresses of 30, 50 and 75 MPa resulting in more than 20 creep tests on 7 single crystal alloys. All creep curves looked similar and the rupture strain was in all cases above 30%. Representative creep curves for the matrix alloy MSX W14 are shown in Fig. 1a. The creep rate-strain curves show an increase of the strain rate in the primary creep stage, which is called inverse creep behavior. In this case, no minimum creep rate can be found and the transition creep rate $\dot{\epsilon}_t$ is taken. $\dot{\epsilon}_t$ is the point of intersection of two lines which are fitted in the primary and the secondary creep stage (see Fig.1b).

The Norton plots with the transition creep rates for all alloys are shown in Fig. 2. The influence of the solid solution hardening elements, i.e., Re, W, and Mo, can be seen qualitatively. As expected, the creep resistance increases strongly with increasing solute

contents of rhenium, tungsten or molybdenum. The resulting Norton exponents are given in table 1. All Norton exponents lie in the region 5.3 ± 0.8 .

Results of atom probe tomography measurement

The experimental results from APT data analysis using the maximum separation method [13] for the number of clusters observed for different Re cluster sizes in MSX Re9 are compared with the randomized data in Fig. 3. No Re clusters were observed having eight or more atoms. An excellent agreement between the two curves in Fig. 3 is observed, indicating that no clusters are present other than the ones expected from a random solid solution for the maximum Re content (9 wt.%). One small deviation was observed for a cluster size of five Re atoms. In the experimental dataset, a total of 12 clusters were found compared to six in the randomized data, i.e., involving a total of 60 detected atoms instead of the expected 30 atoms. This small difference is not evidence for systematic clustering, because the deviation is caused by only 30 atoms compared to about 30,000 of detected Re atoms.

4. Discussion

4.1 Creep Behavior

The determined Norton exponent for all matrix alloy single crystals (see table 1) is close to 5. This value is characteristic for alloys that exhibit Class M behavior [25], i.e., the creep deformation is climb controlled as in pure metals. On the contrary, inverse creep behavior (see Fig. 1), which was also found by Siebörger [24] for the matrix of CMSX-4 at 850°C and 50 MPa, is typical for glide-controlled creep behavior [26]. In this case, inverse creep occurs due to strong solid solution hardening. As Heilmaier et al. [27] showed for the single phase Ni-based alloy Nimonic 75, the inverse creep behavior can change to normal creep behavior at higher stresses.

By analyzing the creep properties of matrix alloys with different contents of rhenium, tungsten and molybdenum, the solid solution hardening potential can be determined. Therefore, the assumption is made that the solid solution hardening effect from Co (in the range of 9.2 - 18.8 wt.%) and Cr (in the range of 13.9 - 28.8 wt.%) can be neglected.

According to Pelloux and Grant [28], and Monma [29,30], Cr has a much lower effect on creep properties compared to Mo and W. Cobalt improves the creep resistance of pure Ni [31], but in alloys with a high alloying element content, as in this investigation, the effect is low [32].

The γ' -forming elements Al, Ta, und Ti are also strong solid solution hardening elements [33], but the overall element content is low and comparable for all the investigated matrix alloys, so the influence on creep resistance does not affect the results for the refractory elements.

Three of the investigated alloys only show a different Re content (MSX Re0, MSX Re4.5 and MSX Re9). The transition creep rate at 980°C and 50 MPa versus Re content is shown in Fig. 4.

A linear relationship between the transition creep rate $\dot{\varepsilon}_t$ plotted on a logarithmic axis and the Re content in wt.% is clearly observed, which can be described by the following equation

$$\frac{\dot{\varepsilon}_t}{\dot{\varepsilon}_{t,0}} = 10^{-\eta_{Re} \cdot c_{Re}} \quad (1)$$

where $\dot{\varepsilon}_t$ is the transition creep rate of the Re containing alloy, $\dot{\varepsilon}_{t,0}$ is the transition creep rate of the Re free alloy, η_{Re} is a factor which describes the solid solution hardening efficiency of Re, and c_{Re} is the Re content in wt.%. From Fig.4, η_{Re} is determined to be -0.16 (wt.%⁻¹) indicating that 6.3 wt.% Re in the matrix alloy is necessary to reduce the creep rate by one order of magnitude. The logarithmic relationship between alloying element concentration and creep resistance was also observed by Monma [29,30].

In the other investigated alloys, the Re content was 0% and the W and Mo were simultaneously varied (see table 1). The solid solution hardening efficiency factors η_W and η_{Mo} can be determined by solving the over-determined system of equations (equation 2), which can be set up by the five investigated Re-free alloys:

$$\eta_W \cdot \Delta c_{W,i} + \eta_{Mo} \cdot \Delta c_{Mo,i} = \Delta \log \dot{\varepsilon}_{t,i} \quad (2)$$

where $\Delta c_{W,i}$ and $\Delta c_{Mo,i}$ are the differences in W or Mo content (in wt.%) between alloy i and MSX Re0, $\Delta \log \dot{\varepsilon}_{t,i}$ is the difference of the logarithm of the creep rate of alloy i and MSX Re0. The resulting efficiency of the different solid solution hardening elements are summarized in table 2.

A comparison of the results indicates that Re is 1.6 times more effective by weight ratio for strengthening than W or Mo. This result confirms that Re is by far the strongest solid solution hardening element.

By comparing MSX W14 and MSX Re4.5, it is found that increasing the W content by 5.7 wt.% or the Mo content by 2.2 wt.% have almost the same effect on the creep behavior at 980°C as alloying with 4.5 wt.% Re. If W and Mo could be increased in the matrix without changing overall W and Mo content, i.e., by changing the distribution of refractory elements between matrix and γ' precipitates, similar creep behavior in a rhenium-free compared to a rhenium containing alloy is expected.

4.2 Reasons for solid solution strengthening

The often discussed ‘rhenium clusters’ as the possible reason for the strong effect of rhenium could be excluded by APT measurements of the alloy MSX Re9. No clusters were detected that were larger than eight atoms due to the statistical distribution of Re.

According to [34], the reasons for the improved creep resistance by solid solution strengthening are the reductions of diffusivity and stacking fault energy, and an increase in the elastic modulus. This can be described by equation 3, where A is a constant, γ_{SF} the stacking fault energy, D the diffusion coefficient, σ the applied stress, E the elastic modulus, and n the Norton exponent of the fcc metal.

$$\dot{\epsilon}_{min} = A \cdot \gamma_{SF}^{3.5} \cdot D \cdot \left(\frac{\sigma}{E}\right)^n \quad (3)$$

The effective diffusivity of a binary alloy $\tilde{D}_{bin}$, which exhibits Class M behavior, can be estimated by a simple lever rule according to Herring [36], see equation 4, where D_A and D_B are the diffusion coefficients and x_A and x_B the concentration (in at.%) of the alloy components A and B,

$$\tilde{D}_{bin} = \frac{D_A \cdot D_B}{x_B \cdot D_A + x_A \cdot D_B} \quad (4)$$

The determination of the effective diffusivity $\tilde{D}$ in multi component alloys can be estimated with equation 5, which is an extension of equation 4 [37]

$$\tilde{D} = \frac{1}{\sum_i x_i / D_i} \quad (5)$$

where x_i is the concentration in at.%, and D_i is the diffusion coefficient of the alloying element i in Ni.

Some authors [35,38-42] have indicated that the stacking fault energy is strongly influenced by alloying. In table 3, the measured values of stacking fault energy and the composition of different nickel alloys and pure nickel are listed.

Carter and Holmes [38] gave an overview of the stacking fault energies of Ni, which were measured by different authors and different methods, and found that their values ranged between 120-130 mJ/m². In nickel alloys, the stacking fault energy is much lower compared to that of pure nickel, leading to lower ε'_{min} and higher creep strength. Under the assumption that the stacking fault energy is lowered with increasing content of Co, Cr and heavy elements, they can be interpolated for the matrix alloys in this investigation.

The third variable from equation 3, which is influenced by alloying, is the elastic modulus. Siebörger et. al found for the matrix of CMSX-4 (comparable to MSX Re9) a Young's modulus in (001)-direction of 78 GPa at 1000°C [24]. Fährmann et. al measured it to be 74 GPa at 1000°C for a matrix alloy with a low refractory element content (comparable to MSX Re0) [43]. Assuming that the modulus is increased with increasing content of Mo, W and Re content the elastic modulus $E_{<001>}$ of the different matrix alloys can be estimated according to the content of these elements. The calculated diffusivity $\tilde{D}$ and the interpolated stacking fault energy γ_F and elastic modulus $E_{<001>}$ of the matrix alloys are summarized in fig. 5.

Fig. 6 shows the measured creep rate as a function of $\gamma_{SF}^{3.5} \cdot D \cdot E^{-5.3}$, which was calculated using the values from fig. 5. The error was determined using the law of error propagation. According to equation 3 the minimum creep rate should be proportional to $\gamma_{SF}^{3.5} \cdot D \cdot E^{-5.3}$. Even though a rough estimation for the stacking fault energy and elastic modulus was used, this is in excellent agreement to fig. 6. Nevertheless, further investigations of the stacking fault energies and elastic moduli should be carried out to confirm the trend.

Zacherl et. al [44] used ab initio calculations of elastic properties, stacking fault energies and diffusivities in binary Ni alloys to compare the influence of alloying elements on creep resistance. They found that rhenium (in at.%) at 0 K is about twice as effective as tungsten and 3.4 times as effective as molybdenum. These results are in very good agreement with the experimentally determined results of this investigation, with rhenium is about twice as effective (in at.%) compared to tungsten and 2.4 times as effective as molybdenum.

4.3 Effect on two-phase superalloys

The effect of the solid solution hardening element rhenium on creep properties increases in two phase γ' -strengthened alloys compared to W and Mo, because Re segregates more strongly to the γ matrix. This is described by the partitioning coefficient, which is defined as

$$k^{\gamma/\gamma'} = \frac{c_{matrix}}{c_{\gamma'}} \quad (6)$$

The partitioning coefficients $k^{\gamma/\gamma'}$ for the refractory elements in different commercially used first and second generation superalloys are shown in table 4. Rhenium exhibits, by far, the highest partitioning coefficient.

If a γ' volume fraction of 70% is assumed, which is typical in modern single crystal alloys, the efficiency of the refractory elements on solid solution hardening in two-phase superalloys can be calculated from the partitioning coefficient and the values in table 2. To reduce the creep rate by a factor of 10, only 2.3 wt.% rhenium must be added, whereas

9.8 wt.% tungsten or 4.5 wt.% molybdenum are necessary. Therefore, in Ni-based superalloys, rhenium (in wt.%) is 2.2 times as effective as molybdenum and 4.3 times as effective as tungsten. This clearly explains the rhenium effect which led to the classification in different superalloy generations.

5. Conclusions

Seven alloys with the composition of the γ matrix of nickel-based superalloys with different rhenium, tungsten and molybdenum contents were cast as single-phase single crystals. The alloys were tested in creep at a temperature of 980°C and stresses in-between 30 and 75 MPa. The use of single crystalline material resulted in very clean creep data because no grain boundary or particle strengthening effects interfere with the solid solution hardening. This made the quantification of the solid solution hardening efficiency of Re, W and Mo possible. The matrix alloy MSX Re9, which corresponds to the matrix of CMSX-4, was characterized by atom probe tomography to establish the presence or absence of the controversially discussed rhenium clusters.

The following conclusions can be drawn:

- All matrix alloys show a Norton exponent of $n = 5.3 \pm 0.8$, supporting an inverse creep behavior (Class-M creep behavior with strong solid solution hardening).
- To replace 1 wt.% rhenium as a solid solution hardening element in the matrix of single crystal superalloys, 1.6 wt.% tungsten or molybdenum are necessary.
- If the partitioning coefficient, which describes the distribution of alloying elements in-between γ matrix and γ' phase in two-phase superalloys, and the effectiveness of the refractory elements for solid solution strengthening are taken into account, the strengthening efficiency of the elements can be calculated for two phase superalloys: 2.2 wt.% molybdenum or 4.3 wt.% tungsten must be added in order to replace 1 wt.% rhenium in single crystal superalloys resulting in same creep rates.

- Rhenium clusters do not exist in matrix alloys, and therefore Re clusters are not the reason for the rhenium effect in nickel-based superalloys.
- The rhenium effect in nickel-based superalloys can be explained by:
 - strongest solid solution hardening efficiency in matrix by reduction of stacking fault energy and increase of elastic modulus and diffusivity
 - highest partitioning coefficient to the matrix

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6. References

- [1] R.C. Reed: The Superalloys - Fundamentals and Applications, Cambridge University Press, Cambridge, 2006.
- [2] C.T. Sims, N.S. Stoloff, W.C. Hagel (Eds.), Superalloys II: High Temperature Materials for Aerospace and Industrial Power, second. ed., WileyBlackwell, New York, 1987.
- [3] M.V. Nathal, Met. Trans. A 18 (1987) 1961-1970.
- [4] T. Murakumo, T. Kobayashi, Y. Koizumi, H. Harada, Acta Mater. 52 (2004) 3737-3744.
- [5] A.D. Cetel, D.N. Duhl, Second-Generation Nickel-Base Single Crystal Superalloy, in: S. Reichman, D.N. Duhl, G. Maurer, S. Antolovich, C. Lund (Eds.), Superalloys 1988, TMS, Warrendale, 1988, pp. 235-244.
- [6] K. Kawagishi, H. Harada, A. Sato, A. Sato, T. Kobayashi, JOM 58 (2006) 43-46.
- [7] C.M.F. Rae, R.C. Reed, Acta mater. 49 (2001) 4113-4125.
- [8] P.J. Fink, J.L. Miller, D.G. Konitzer, JOM 62 (2010) 55-57.
- [9] J.B. Wahl, K. Harris, in: E.S. Huron, R.C. Reed, M.C. Hardy, M.J. Mills, R.E. Montero, P.D. Portella, J. Telesman (Eds.), Superalloys 2012, TMS, Warrendale, 2012, pp. 179-188.
- [10] N. Wanderka, U. Glatzel, Mater. Sci. Eng. A 203 (1995) 69-74.
- [11] D. Blavette, P. Caron, T. Khan, Scr. Metall. 20 (1986) 1395-1400.
- [12] A. Mottura, R.T. Wu, M.W. Finnis, R.C. Reed, Acta Mater. 56 (2008) 2669-2675.
- [13] A. Mottura, N. Warnken, M.K. Miller, M.W. Finnis, R.C. Reed, Acta Mater. 58 (2010) 931-942.
- [14] B. Sundman, B. Jansson, J.-O. Andersson, CALPHAD 9 (1985) 153-190.

- [15] N. Saunders, M. Fahrman, C.J. Small, in: T.M. Pollock, R.D. Kissinger, R.R. Bowman, K.A. Green, M. McLean, S. Olson, J.J. Schirra (Eds.), *Superalloys 2000*, TMS, Warrendale, 2000, pp. 803-811.
- [16] D. Blavette, A. Buchon, S. Chamberland, in: H.E. Exner, V. Schumacher (Eds.), *Proceedings of the First European Conference on Advanced Materials and Processes EUROMAT'89*, DGM, Oberursel, 1990, pp. 419-424.
- [17] C.H. Konrad, M. Brunner, K. Kyrgyzbaev, R. Völkl, U. Glatzel, *J. Mater. Process. Technol.* 211 (2011) 181-186.
- [18] M. Bensch, E. Fleischmann, C. Konrad, R. Völkl, C.M.F. Rae, U. Glatzel, in: E.S. Huron, R.C. Reed, M.C. Hardy, M.J. Mills, R.E. Montero, P.D. Portella, J. Telesman (Eds.), *Superalloys 2012*, TMS, Warrendale, 2012, pp. 387-394.
- [19] C. Schulze, M. Feller-Kniepmeier, *Mater. Sci. Eng. A* 281 (2000) 204-212.
- [20] M. Brunner, M. Bensch, R. Völkl, E. Affeldt, U. Glatzel, *Mater. Sci. Eng. A* 550 (2012) 254-262.
- [21] R. Völkl, D. Freund, B. Fischer, *J. Test. Eval.* 31 (2003) 35-43.
- [22] R. Völkl, B. Fischer, *Exp. Mech.* 44(2) (2004) 121-128.
- [23] M. Brunner, R. Hüttner, M.-C. Bölit, R. Völkl, D. Mukherji, J. Rösler, T. Depka, C. Somsen, G. Eggeler, U. Glatzel, *Mater. Sci. Eng. A* 528 (2010) 650-656.
- [24] D. Siebörger, U. Glatzel, *Acta Mater.* 47 (1999) 397-406.
- [25] F.A. Mohamed, T.G. Langdon, *Acta Metall.* 22 (1974) 779-788.
- [26] W.D. Nix, B. Ilshner, *Strength of metals and alloys - Proceedings of the 5th International Conference (ICSMA5)*, Aachen, Germany, 1980, pp. 1503-1530.
- [27] M. Heilmaier, K. Wetzel, B. Reppich, *Strength of metals and alloys - Proceedings of the 10th International Conference (ICSMA10)*, Sendai, Japan, 1994, pp. 563-566.
- [28] R.M.N. Pelloux, N.J. Grant, *Trans. TMS-AIME* 218 (1960) 232-236

- [29] K. Monma, H. Suto, H. Oikawa, J.Jpn. Inst. Met. 28 (1964) 253-258.
- [30] K. Monma, H. Suto, H. Oikawa, J. Jpn. Inst. Met. 28 (1964) 304-307.
- [31] C.K.L. Davies, P.W. Davies, B. Wilshire, Philos. Mag. 12 (1965) 827-839.
- [32] M.V. Nathal, J.O. Diaz, R.V. Miner, MRS Symp. Proc. 133 (1989) 269-274.
- [33] A.K. Jena, M.C. Chaturvedi, J. Mater. Sci. 19 (1984) 3121-3139.
- [34] C.R. Barrett, O.D. Sherby, Trans. TMS-AIME 233 (1965) 1116-1119.
- [35] M. Benyoucef, B. Decamps, A. Coujou, N. Clement, Philos. Mag. A 71 (1995) 907-923.
- [36] C. Herring, J. Appl. Phys. 21 (1950) 437-445.
- [37] A. Heckl, S. Neumeier, M. Göken, R.F. Singer, Mater. Sci. Eng. A 528 (2011) 3435-3444.
- [38] C.B. Carter, S.M. Holmes, Philos. Mag. 35 (1977) 1161-1172.
- [39] N. Clément, P. Coulomb, Philos. Mag. 30 (1974) 663-672.
- [40] E.H. Köster, A.R. Tholen, A. Howie, Philos. Mag. 10 (1964) 1093-1095.
- [41] B. Décamps, A.J. Morton, M. Condat, Philos. Mag. A 64 (1991) 641-668.
- [42] F. Pettinari, J. Douin, G. Saada, P. Caron, A. Coujou, N. Clément, Mater. Sci. Eng. A 325 (2002) 511-519.
- [43] M. Fährmann, W. Herman, E. Fährmann, A. Boegli, T.M. Pollock, H.G. Sockel, Mater. Sci. Eng. A 260 (1999) 212-221.
- [44] C.L. Zacherl, S.L. Shang, D.E. Kim, Y. Wang, Z.K. Liu, in: E.S. Huron, R.C. Reed, M.C. Hardy, M.J. Mills, R.E. Montero, P.D. Portella, J. Telesman (Eds.), Superalloys 2012, TMS, Warrendale, 2012, pp. 455-461.
- [45] T.M. Pollock, Mater. Sci. Eng. B 32 (1995) 255-266.

- [46] T.M. Pollock, R.D. Field. Dislocations and High-Temperature Plastic Deformation of Superalloy Single Crystals, in: F.R.N. Nabarro, M.S. Duesbery (Eds.). Dislocations in Solids, Vol. 11. Amsterdam: Elsevier; 2002.

Table 1: Nominal composition, deviation Φ between the crystallographic $\langle 001 \rangle$ direction and the applied stress in creep test and Norton exponent n of single crystal matrix alloys at 980°C, of tested matrix alloys and corresponding two-phase superalloys. Measured compositions of matrix alloys are listed for comparison, but they were not tested.

alloy	matrix of	nominal composition (wt.%)									Φ ($^{\circ}$)	n
		Al	Co	Cr	Mo	Re	Ta	Ti	W	Ni		
MSX W5	model alloy	1.4	17.0	28.8	3.5	-	0.1	0.1	5.4	43.7	2	5.2
MSX W11	MC2	1.3	9.2	19.2	4.4	-	0.6	0.1	11.4	53.8	5	4.8
	measured [16]	1.2	8.6	21.6	4.2	-	0.9	0.2	12.0	51.2		
MSX W14	model alloy	0.9	11.1	23.1	3.6	-	-	-	14	47.3	6	5.3
MSX W16	model alloy	1.1	17.0	13.9	3.5	-	1.1	0.1	16.3	47.0	6	5.2
MSX Re0	model alloy	1.4	19.8	18.4	1.4	-	0.2	0.1	9.1	49.6	9	6.1
MSX Re4.5	model alloy	1.4	18.8	17.5	1.4	4.5	0.2	0.1	8.7	47.4	6	5.0
MSX Re9	CMSX-4	1.4	18	16.7	1.3	9	0.2	0.1	8.3	45.0	2	5.6
	measured [10]	0.8	17.4	16.4	1.6	9.4	0.6	0.1	8.2	45.5		

Table 2: Solid solution hardening efficiency η_i (wt.%⁻¹) for solid solution hardening elements Re, W and Mo and concentration in matrix alloy, which is necessary to reduce creep rate by a factor of 10.

element i	η_i (wt.% ⁻¹)	i addition to reduce ϵ_i to 1/10 (wt.%)
Re	0.16	6.3
W	0.10	10
Mo	0.10	10

Table 3: Stacking fault energies and composition of different Ni alloys and pure Ni taken from the literature [35, 38-42].

Alloy	composition in wt.%										stacking fault energy γ_{SF} (mJ/m ²)	reference
	Al	Co	Cr	Mo	Re	Ru	Ta	Ti	W	Ni		
Ni	-	-	-	-	-	-	-	-	-	100	120-130	[38]
Ni-Cr	-	-	20	-	-	-	-	-	-	80	77	[39]
Ni-Cr-Co		10	30							70	56	[40]
γ -MC2	1.2	8.6	21.6	4.2	-	-	0.9	0.2	12.0	51.2	21	[35]
γ -AM3	1.6	12.0	24.0	4.7	-	-	1.2	0.3	4.7	51.8	20-30	[41]
γ -MCre	-	-	20.8	3.0	11.9	-	-	-	5.6	58.8	27±3	[42]
γ -MCRu	-	-	21.9	3.2	-	6.6	-	-	5.9	62.5	25±3	[42]

Table 4: Partitioning coefficient $k_i^{\gamma/\gamma'}$ for Re, W and Mo according to [10,16,45,46] for different commercially used first and second generation Ni-Based superalloys and addition of element i to improve creep resistance by a factor of 10.

	partitioning coefficient $k^{\gamma/\gamma'}$ (wt. %/wt. %)					i addition to reduce ϵ_t to 1/10 (wt. %)
	CMSX-3 [45]	CMSX-4 [10]	MC2 [16]	René N5 [46]	average	
Re	-	15.7	-	15.2	15.5	2.3
W	1.3	1.4	1.3	1.3	1.3	9.8
Mo	3	2.7	4.3	3.4	3.4	4.5

- Fig. 1:** a) Creep curves of MSX Re0 at 980°C. b) Determination of transition creep rate between primary and secondary stage.
- Fig. 2:** Norton plot of single crystal matrix alloys. The Norton exponent is determined to 5.3 ± 0.8 .
- Fig. 3:** Experimental results of atom probe tomography data for alloy MSX Re9 in comparison with randomized data.
- Fig. 4:** Change in transition creep rate at 980°C and 50 MPa by Re additions. The slope of the fitted line corresponds to the factor η_{Re} , which describes the efficiency of Re as a solid solution hardening element in the matrix alloy.
- Fig. 5:** Measured transition creep rates at 980°C and 50 MPa as a function of a) calculated effective diffusivity $\tilde{D}$ and interpolated b) stacking fault energy γ_{SF} and c) elastic modulus $E_{\langle 001 \rangle}$ of matrix alloys.
- Fig. 6:** Measured transition creep rates at 980°C and 50 MPa as a function of $\gamma_{SF}^{3.5} \cdot D \cdot E^{-5.3}$. Error margins were determined from the error of the variables using the law of error propagation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6