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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 10. 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

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 Ni-based superalloys, as these 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 $L1_2$-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 $d_{\gamma'} = 0.45$ μm, a γ′ volume fraction $f_{\gamma'} = 70\%$, and a misfit of matrix and γ′ lattice parameter of $\delta = -(1\text{–}3) \times 10^{-3}$, where $\delta = 2(a_{\gamma'} - a_{\gamma})/(a_{\gamma'} + a_{\gamma})$ [3,4]. These values are often achieved 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 great interest to further enhance the mechanical properties. Re, W and Mo are the most effective solid-solution hardening elements, with Re being the strongest, resulting in the development of further generations of superalloys [5]. However, several problems arise with increasing 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 subject to large price fluctuations [8], leading to potentially high alloy costs. Currently, huge development efforts are being undertaken to identify single-crystal superalloys without Re that offer 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 Re 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 Re, W and

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Mo, were cast as single crystals and tested in creep. For the first time single-phase single-crystalline materials with systematically varied heavy element contents were tested in creep. The results provide very clean data for the solid-solution strengthening potential, which are not affected 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 element needed for strengthening of two-phase superalloys can be calculated.

The influence of alloying elements on diffusivity and stacking fault energy is discussed as possible reasons for solid-solution hardening. Another possible explanation for the large effect of Re on the creep rate is the formation of Re clusters in the matrix. These clusters act as obstacles against dislocation movement. The existence of these clusters remains controversial: Re clusters were claimed by several researchers [10,11] and were identified using 1-D 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 contain possible clusters.

2. Materials and methods

2.1. 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 MSX (matrix single crystal) Re or W content. The corresponding two-phase alloys are either different commercial alloys (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, i.e. Re, W and Mo, is represented: the Re content varies from 0 to 9 wt.% (the upper limit corresponds to the matrix content of the second-generation Ni-based superalloy CMSX-4), the W content varies from 5.4 to 16.3 wt.%, and the Mo from 1.3 to 4.4 wt.%. All values are typical for first- and second-generation Ni-based superalloys.

2.2. Single-crystal 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^{-1} and a withdrawal rate of 3 mm min^{-1}. 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 homogeneous distribution of Re and W, which strongly segregate to the dendrite cores [19].

2.3. Creep testing

Flat creep specimens (for geometry, see Ref. [20]) were cut from the single-crystal rods by wire electrodischarge machining, and then ground flat to a surface roughness of $R_a < 0.2$ µm. 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 ⟨001⟩ 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 Ref. [23].

2.4. Atom probe tomography of the rhenium distribution

The highest Re-content alloy, MSX Re9, was examined by atom probe tomography (APT) to detect possible Re 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

Table 1. Nominal composition, deviation Φ between the crystallographic ⟨001⟩ direction and the applied stress in creep test, and the 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 were not tested.

Alloy	Matrix of	Nominal composition (wt.%)									Φ (°)	*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		