Strength of nanoporous Ni-based superalloy membranes

J. Rösler, O. Näth
Technische Universität Braunschweig, Institut für Werkstoffe, Langer Kamp 8, D-38106 Braunschweig, Germany

j.roesler@tu-bs.de

Abstract. Nanoporous Ni-based superalloy membranes are a new material class. They are fabricated from the two phase $\gamma/\gamma'$ base material by thermomechanical processing, followed by selective phase extraction. Compared to other metallic membrane materials, they stand out due to an extremely regular and fine channel-like porosity on the nanoscale. This allows for particularly interesting applications in areas such as particle filtration, catalysis of chemical reactions or heat exchange. However, fundamental understanding of the mechanical behaviour is a prerequisite in all these cases. Thus, the microstructure property correlation of these novel materials is analyzed here, examining a $\gamma'$-membrane (where the $\gamma$-phase is leached out) by tensile testing. It will be demonstrated that nanoporous superalloy membranes are remarkably strong materials, provided the processing parameters are properly selected.

1. Introduction

Porous metals having pore dimensions on the nanoscale are receiving considerable attention as they are of particular interest for functional applications (e.g. phase separation or catalysis of chemical reactions) where small pore dimensions and large specific surface areas are required in combination with metallic properties [1-6]. To date, two processing routes have emerged, allowing to produce cellular metals with porosity on the nanoscale. Dealloying, where a less noble alloying element such as silver is leached from a solid solution strengthened noble metal such as gold, is one potential route [1-3]. The second route, developed by the authors and discussed here, uses two-phase alloys, in particular Ni-based superalloys, containing cube shaped $\gamma'$-precipitates embedded in the Ni-rich $\gamma$-matrix [4-6]. The “trick” is to alter the microstructure by thermomechanical processing such that an interpenetrating network of both phases is formed, whereby each phase is in itself interconnected. Then, one phase can be (electro-)chemically dissolved while the other remains rigid. As a result, a porous and permeable membrane material is obtained, containing channel-like interconnected pores, some hundred nanometers wide, at the location of the dissolved phase.

The described process has been demonstrated successfully in [5,6] on the example of single crystalline Ni-based superalloys, where directional coarsening of the $\gamma'$-particles by uniaxial creep deformation in tension as described, for example, in [9,10] was used to form the required interpenetrating and interconnected microstructure. However, satisfactory mechanical properties are also essential for practical applications. For this reason, we report here on the strength and elastic stiffness of a nanoporous superalloy membrane material, using tensile testing.

2. Material and processing

The single crystalline Ni-based superalloy CMSX-4 was used here as starting material. Its chemical composition (in wt-%) is given by: Ni-6.5Cr-9.6Co-0.6Mo-6.4W-3.0Re-1.0Ti-6.5Ta-0.1Hf. The microstructure of the material after solution and precipitation heat treatment is depicted in fig. 2a. It consists of cube shaped $\gamma'$-particles embedded in the $\gamma$-matrix. The material was subsequently creep deformed in tension, whereby the loading direction was essentially parallel to the crystallographic [001]-orientation. While stress and temperature were set to 170MPa and 1273K, respectively, the creep duration was varied. Typical creep curves are shown in fig. 1, displaying a minimum of the
strain rate at a critical strain $\varepsilon_c$ of about 0.2%. Sheets, about 16mm wide and 140mm long, were then machined from the deformed creep specimen and, after polishing, the $\gamma$-phase was electrochemically dissolved, using the parameters given in [5]. Typically, the final thickness of the sheets was 0.3mm. Their ends were masked so that solid end pieces for easy clamping in the tensile test machine resulted.

Fig. 1: Creep curves (strain rate versus strain) obtained for CMSX-4 at 1000°C / 170MPa. Note the existence of a strain rate minimum at a strain of about 0.2%.

3. Microstructure and mechanical properties

The microstructure of the sheets after creep deformation and selective phase extraction is depicted in fig. 2b-d as a function of the prior creep strain. Channel-like porosity, a few hundred nanometers wide, is clearly visible at the location of the dissolved $\gamma$-phase, while the ligaments are composed of the $\gamma'$-phase. The tensile stress during creep deformation was applied in vertical direction and directional growth of the $\gamma'$-particles in the plain perpendicular to the applied stress is apparent. At the smallest creep strain of about 0.1%, individual $\gamma'$-particles are connected with their neighbors along side faces (see fig. 2b). However, an interconnected network has not yet been established. Consequently, the sample is disintegrating upon handling and mechanical testing is not possible. In fact, this behavior is generally observed when the creep strain $\varepsilon$ is less than $\varepsilon_c$. In contrast, when $\varepsilon$ is larger than $\varepsilon_c$, the samples maintain their integrity upon handling and display significant mechanical strength (see below). This finding suggests that interconnectivity of the prior $\gamma'$-precipitate particles to a rigid, three-dimensional network is established at the point in time when the creep rate minimum is attained, i.e. when the material is at its largest creep resistance. In fact, it is qualitatively understandable why the material reaches it largest flow strength when this particular microstructural state is reached: Beforehand, the $\gamma'$-phase is still existing in the form of isolated precipitates (even though their morphology is no longer cube shaped but elongated) and the imposed deformation of the sample can be accommodated by creep deformation of the softer $\gamma$-phase alone. Once interconnectivity of the $\gamma'$-phase is established, this stronger phase must be deformed as well so that the flow strength increases until interconnectivity is established. Upon further deformation, the microstructure coarsens (compare fig. 2c with 2d), leading to softening of the material. As a result, a creep rate minimum at $\varepsilon = \varepsilon_c$ is obtained.

The ultimate tensile strength $R_m$ and elastic stiffness of the membrane materials, obtained by tensile testing at ambient temperature, is displayed in fig. 3 as a function of the prior creep strain. Hereby, the loading direction was again perpendicular to the $\gamma'$-ligaments. Note that $R_m$ increases initially with the creep strain. This is so because more cross-links between $\gamma'$-ligaments are formed in the course of creep deformation so that the stability of the $\gamma'$-network increases beyond the critical creep strain $\varepsilon_c$. However, the microstructure of the nanoporous material becomes also coarser and less regular at large
prior creep strains (compare fig. 2c with 2d), leading to softening. Consequently, a strength maximum of about 100MPa at about 4% creep strain results. This is a remarkably large value for a porous material and a consequence of (i) the high strength of the base material and (ii) the regularity of the microstructure.

![Microstructures](image)

Fig. 2: Microstructures of the CMSX-4 base material (a) and the membrane materials after creep deformation to a strain of approx. 0.1% (b), 1.5% (c) and 11.5% (d).

The elastic stiffness follows the same trend with the creep strain as the ultimate tensile strength (see fig. 3), which can be explained analogously. Note, however, that the elastic modulus of single crystalline Ni$_3$(Al, Ti) in [001]-direction is 133GPa [7]. Thus, the values obtained here are about one order of magnitude less even though the pore volume fraction is only about 26%. This comes about because perpendicular loading causes substantial shear and bending of the ligaments. In fact, it is shown in [8] that the obtained results can be quantitatively explained when axial, shear and bending displacements are taken into account and it turns out that bending is the most significant contribution, even though the other two contributions cannot be neglected.
Conclusion
Nanoporous superalloy membranes stand out as they combine remarkably fine and regularly arranged porosity on the nanoscale with excellent mechanical strength. The results demonstrate that creep deformation beyond the creep rate minimum is a prerequisite for the fabrication of these membrane materials and that best strength is achieved after creep strains of about 4% as a well interconnected but still very fine and regular microstructure is attained at the same time. The elastic stiffness, which is about one order of magnitude less than that of the bulk material when loading is perpendicular to the γ’-ligaments, is a result of ligament bending and shear.

Acknowledgements
We would like to thank the Deutsche Forschungsgemeinschaft for financial support of this work.

References
[1] Y. Ding and J.J. Erlebacher, Am. Cem. Soc. 125 (2003) 7772.
[2] R. Li and K. Sieradzki, Phys. Rev. Lett. 68 (1992) 1168.
[3] J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov and K. Sieradzki, Nature 410 (2001) 450.
[4] J. Rösler and D. Mukherji, German Patent (2008) 10231577.
[5] J. Rösler, O. Näth, S. Jäger, F. Schmitz and D. Mukherji, Acta Mater. 53 (2005) 1397.
[6] J. Rösler and D. Mukherji, Adv. Eng. Mater. 5 (2003) 916.
[7] H. Yasuda, T. Takasugi and M. Koiwa, Acta Metall. Mater. 40 (1992) 381.
[8] J. Rösler and O. Näth, Acta Mater. 58 (2010) 1815.
[9] R.A. MacKay and L.J. Ebert, Metall. Trans. 16A (1985) 1969.
[10] H.-A. Kuhn, H. Bierrmann, T. Ungar, H. Mughrabi, Acta Metall. Mater. 39 (1991) 2783.