

SPONTANEOUS RAFTING IN SINGLE CRYSTAL Ni-BASE SUPERALLOY DURING LONG-TERM AGEING

Marek GEBURA, Juraj LAPIN

Authors: **Marek Gebura, Juraj Lapin**
Workplace: **Institute of Materials & Machine Mechanics, Slovak Academy of Sciences**
Address: **Račianska 75, 831 02 Bratislava, Slovak Republic**
E-mail: **ummsgebu@savba.sk, ummslapi@savba.sk**

Abstract

Morphological changes of γ' precipitates in nickel based single crystal superalloy CMSX-4 were studied during long-term ageing at four temperatures of 900, 925, 950 and 1000°C and various ageing times up to 4000 h. The precipitates were extracted from the γ (Ni based solid solution) matrix into thin carbon extraction replicas and then studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Using quantitative metallography, emphasis was set on real three-dimensional shape of such extracted γ' precipitates. It was found out that long-term ageing leads to a change of some cuboidal shaped precipitates to precipitates with so called spontaneous rafted morphology. At a temperature of 950 °C, spontaneous rafted precipitates were found after 3000 h of isothermal ageing. The temperature of 1000 °C was used to accelerate this type of degradation process and to increase occurrence of spontaneously rafted precipitates in the microstructure for their better observation and analysis. Eventual physical based aspects of spontaneously rafted γ' precipitates occurrence are discussed in this paper.

Key words

nickel based superalloy, degradation, ageing, microstructure, spontaneous rafting

INTRODUCTION

Single crystal nickel base superalloys contain significant additions of refractory elements such as Mo, W, Ta and Re which improve creep strength and microstructure stability at high temperatures [1-3]. On the other hand, these refractory elements in general lead to higher microsegregation during directional solidification [4] and increased precipitation of hard topologically close packed (TCP) phases during exposure to high temperatures and stresses [5-7]. Due to microsegregation, dendrites have particularly different chemical composition in comparison with interdendritic region. This fact leads to difference (misfit) between lattice parameters of γ (Ni base solid solution) matrix and γ' ($\text{Ni}_3(\text{Al,Ti})$) precipitates in these two regions [8-11]. When single crystal superalloy is exposed to a high temperature for a sufficiently long time, the size of the γ' precipitates changes. The coarsening mechanisms are generally involved with two microscopic kinetic steps: diffusion and interface reaction,

which occur simultaneously. In aged superalloy with a coarsened γ/γ' microstructure, the internal coherency stresses can be reduced by the formation of interfacial dislocations on the γ/γ' interfaces [12]. Only few authors [1,13,14] have reported morphological changes of γ/γ' microstructure of single crystal nickel base superalloys during long-term ageing without presence of external stress. It is clear, that after a long-term ageing there is not only cuboidal morphology of the γ' embedded in the γ matrix, but there are also highly morphologically changed γ' particles [1,13,14].

The aim of this paper is to study morphological changes of cuboidal γ' precipitates in single crystal superalloy CMSX-4 during long-term ageing at various temperatures. Special attention is paid to determine a real three-dimensional shape of the γ' precipitates after ageing.

EXPERIMENTAL MATERIAL AND PROCEDURE

As-cast ingot of nickel base superalloy CMSX-4 with diameter of 80 mm, length of 250 mm and chemical composition Ni-6.5Cr-9.0Co-0.6Mo-6.0W-6.5Ta-3.0Re-5.6Al-1.0Ti-0.1Hf (wt.%) was supplied by Canon-Muskegon (USA). The ingot was cut to smaller rectangular rods by electro-spark machining and lathe-turned to cylindrical rods with a diameter of 8 mm and length of 120 mm. Single crystals with [001] crystallographic orientation were prepared by seeding in a modified Bridgman type apparatus described elsewhere [15]. Crystallographic orientation of directionally solidified rods was controlled by Laue X-ray diffraction technique. Maximum deviation from $\langle 001 \rangle$ crystallographic direction was determined to be 7 degrees. Then the single crystal rods were exposed to seven step solution annealing in high purity argon atmosphere (99.9995%) and rapidly cooled in flowing argon. Finally, the ingots were subjected to two steps precipitation annealing at 1140 °C for 2 h and 870 °C for 20 h in air followed by gas fan cooling to room temperature.

The ageing experiments were performed on the samples with a thickness of 5 mm and diameter of 8 mm at temperatures ranging from 900 to 1000 °C for different times from 100 to 4000 h in air. As was shown elsewhere [16], CMSX-4 superalloy exhibits an excellent high temperature oxidation resistance and no special surface protection is required up to 1000 °C.

After ageing the samples were wet grinded, polished and electrolytically etched in the solution of 35.6 ml H₂SO₄, 37.5 ml HNO₃ and 9.4 ml H₃PO₄ at voltage 7 V for 120 s. For dissolving γ phase, sample polarity was negative. On the other hand, for dissolving γ' phase, sample polarity was set to positive. For preparing extraction replicas, samples were polished down to 1 μ m, than electrolytically etched in the same etching agent for 60 s and consequently covered by thin carbon layer. Carbon layer was sliced to squares of about 3 x 3 mm and than electrolytically etched until separation of the replica from the sample surface. Microstructure was investigated by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

Directional solidification and heat treatments

Fig. 1 shows the typical example of a rod after directional solidification (DS) in the [001] crystallographic direction. It is clear that the seed is melted only partially (Fig. 1a) and there was an excellent junction between the seed and the remaining part of the rod. The microstructure after the DS consists of dendrites and interdendritic regions (Fig. 1b). The dendrites are light-grey colored and the interdendritic region is dark-grey (Fig. 1c). The

average primary dendrite arm spacing was measured to be 230 μm . Due to different partition coefficients k of the alloying elements the elements with $k > 1$ such as Re, Mo, Co, Cr and W segregate mainly in dendrite cores and elements with $k < 1$ such Al, Ti and Ta generally into interdendritic regions [4]. The microsegregation leads to a large chemical heterogeneity between the dendrites and interdendritic region.

Solution annealing followed by ageing decreased the degree of microsegregation in comparison with the microstructure after the DS, as shown in Fig. 2. The fact that there is still a certain degree of chemical heterogeneity after the solutioning and ageing was confirmed by both SEM (Fig. 2a) and BSE (Fig. 2b). Light color areas in Fig. 2b represent increased quantity of Re, Mo, Co, Cr and W and grey areas belong to regions with higher content of Al, Ti and Ta.

Fig. 3a shows the typical γ/γ' microstructure within the dendrites and interdendritic region. The mean size of the γ' precipitate characterized by the length of γ' cube edge a was measured to be 313 nm. The distribution curve for precipitates size after the standard heat treatments is illustrated in Fig. 3b. The average volume fraction of precipitates was measured to be (69 ± 2.4) vol.%.

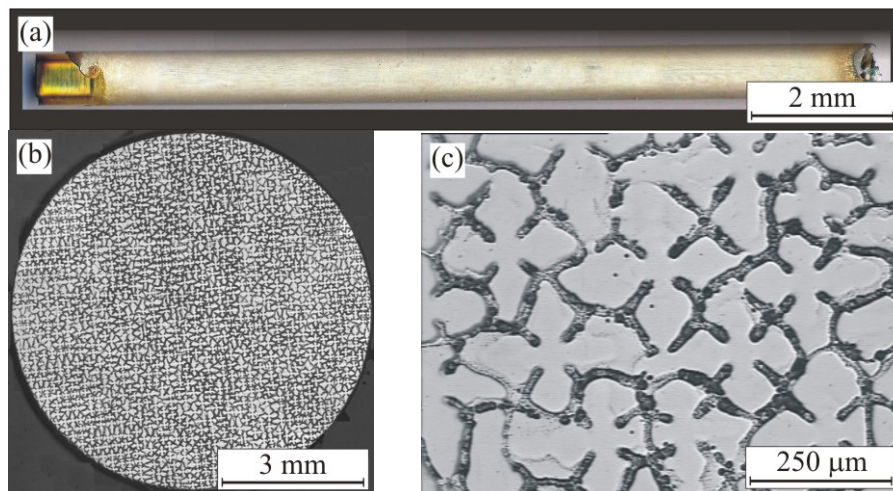


Fig. 1. (a) Single crystal rod after DS, (b) and (c) Optical micrographs showing the typical dendritic microstructure and morphology of dendrites after DS

Microstructure characterization after long-term ageing

Matrix-precipitates type of structure in whole material

Microstructure in the whole material is γ matrix/ γ' precipitates type (cuboidal precipitates embedded in the matrix). When the γ/γ' microstructure is exposed to thermal exposure, coarsening process of precipitates occurs. Early stages of the γ' coarsening process are Ostwald type [17-19], e.g. the growth of precipitates is controlled by diffusion and precipitates do not change their cuboidal shape because the larger precipitates grow at the expense of smaller ones. In the case of the studied alloy the Ostwald type ripening is represented by following ageing regimes: 900 $^{\circ}\text{C}$ up to 3000 h, 925 $^{\circ}\text{C}$ up to 2000 h, 950 $^{\circ}\text{C}$ up to 2000 h and 1000 $^{\circ}\text{C}$ up to 500 h. Fig. 4 shows extracted cuboidal shaped γ' precipitates from the γ matrix.

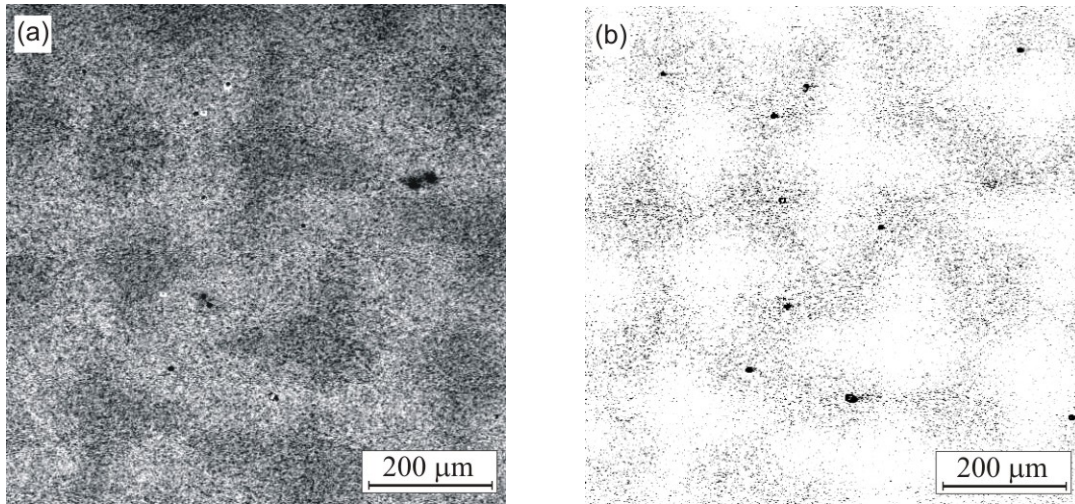


Fig. 2. Microstructure after the standard solution heat treatment followed by precipitation annealing. (a) SEM micrograph and (b) BSE micrograph taken from the same sample area

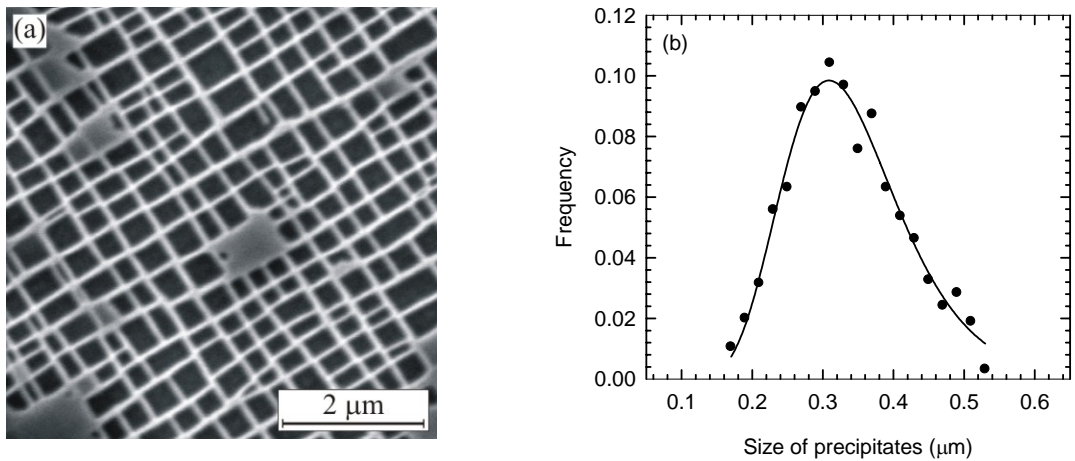


Fig. 3. (a) The typical γ/γ' microstructure inside the dendrites and interdendritic regions after standard solution heat treatment followed by precipitation annealing. (b) Distribution curve for size of the γ' precipitates

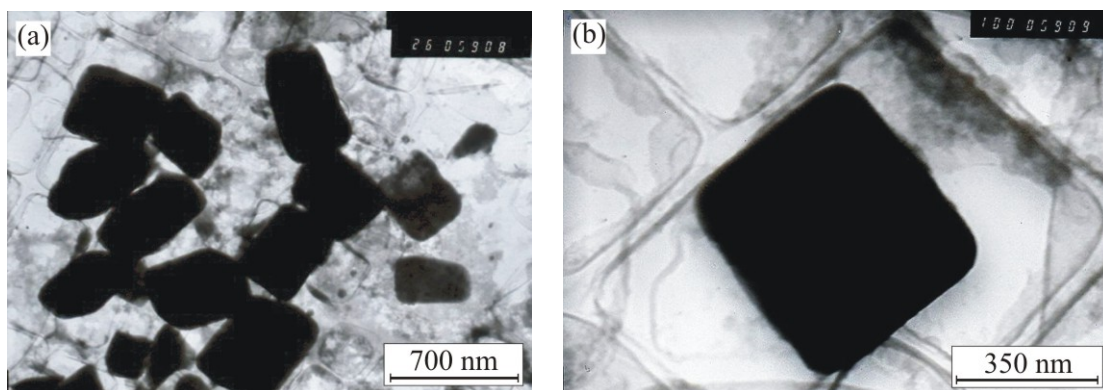


Fig. 4. (a) TEM micrograph showing extracted γ' precipitates from the γ matrix after ageing at 925°C for 500 h, (b) Detail showing the cuboidal shape of the γ' precipitate

Microstructure with matrix-matrix and matrix-precipitates type of structure

After sufficient long time of ageing at high temperature (e.g. 1500 h at 1000°C) the process of γ' coarsening is rather different in comparison with that at shorter ageing time [1,13,14]. The γ and γ' phases are interlacing each other so structure seems like moistener – they are creating so-called spontaneous rafts. Therefore, microstructure after long-term thermal exposure can be divided morphologically into two types: matrix-precipitates and matrix-matrix type (γ' phase is not more in a form of embedded cuboidal precipitates). Fig. 5 shows micrographs taken from the sample after ageing for 2000 h at 1000°C. The microstructure within the dendrites (D) is different when compared with that within the interdendritic region (I), as seen in Fig. 5a and 5b. In addition, formation of topologically close-packed phases (TCP) is observed within the dendrites, as shown in Fig. 5c [5-7]. Within the interdendritic region, there are regions with cuboidal γ' precipitates (Fig. 5d) and also with spontaneous rafted γ/γ' microstructure (Figs. 5e and 5i). The dendritic areas are characterized by spontaneous rafts (Figs. 5f, 5g and 5h).

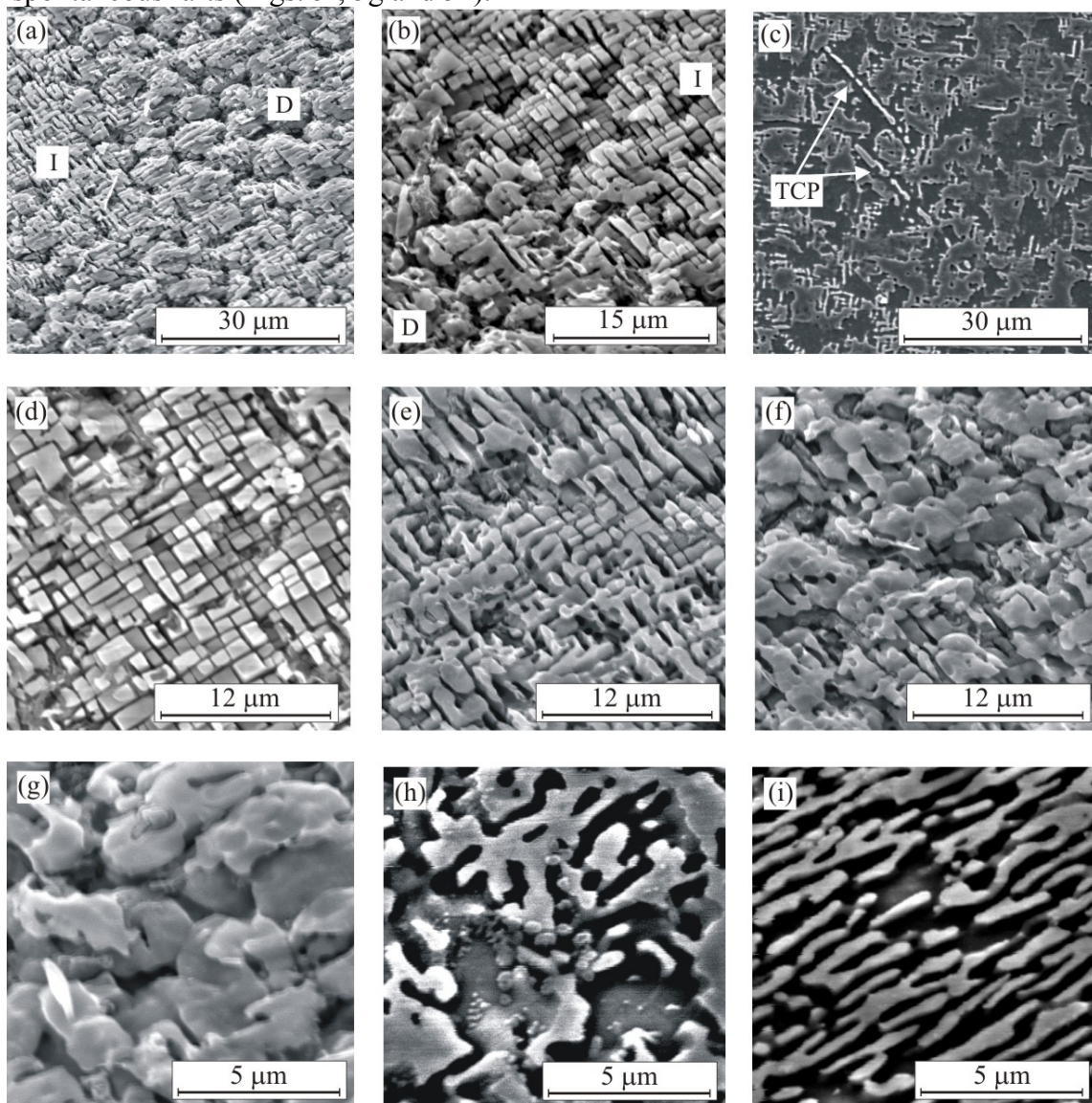


Fig. 5. SEM micrographs showing the morphology of γ and γ' phases in CMSX-4 superalloy after long-term ageing. Scanned planes are (001). (a), (b) Difference between dendrite (D) and interdendritic region (I), (c) Microstructure within the dendrite with TCP phases, (d) Cuboidal γ' precipitates within I, (e) Rafted structure within I, (f) Rafted structure within D, (g) Detail of the γ' rafts within D, (h) Detail of the γ rafts within D, (i) γ rafts within I

The formation of spontaneous rafting is possible to explain by the difference between lattice parameters of the γ and γ' phases (so called misfit) and internal stresses in the alloy caused by the dendritic microstructure. According to Brückner et al. [9], the difference between lattice parameters in the superalloy CMSX-4 is the largest in the dendrites and the lowest in the interdendritic region. It is possible to assume that if the difference between the lattice parameters of the matrix and coherent precipitate is higher, then the stresses at their interfaces will be higher. These stresses in combination with the internal stresses can result in directional diffuse flow of softer matrix, thus directional coarsening of the γ' precipitates - spontaneous rafting.

Sample analysis showed that the primary and secondary dendrite arms contain areas with microstructure with the rafts oriented only perpendicularly to the [001] growth direction. On the other hand, the interdendritic region with spontaneously rafted areas contained rafts oriented perpendicularly to the [100] and [010] crystallographic directions. This phenomenon can be explained by microsegregation. Chemical composition of the dendrites is different from the composition of the interdendritic region [4], so dendrites have slightly different value of thermal expansion coefficient from that of the interdendritic region. During ageing the dendrites are subjected to tensile stresses and interdendritic regions to compressive stresses along the crystallographic direction [001]. Therefore, such internal stresses result in formation and orientation of spontaneous rafts during long-term ageing without applied load with a manner similar to creep loading conditions.

CONCLUSIONS

The investigation of the effect of long-term ageing on the coarsening and morphological changes of the γ' precipitates in single crystal nickel base superalloy CMSX-4 suggests following conclusions:

1. The cylindrical rods prepared from the seeds by directional solidification were single crystals oriented in a crystallographic direction [001]. The applied heat treatments resulted in a partial chemical homogenization of the rods and led to the microstructure composed of the γ matrix and cuboidal γ' precipitates.
2. After long-term ageing, two types of microstructure were identified: (i) cuboidal γ' precipitates embedded in the γ matrix and (ii) spontaneously rafted microstructure composed of the γ' and γ rafts. The internal stresses in the rods and stresses resulting from γ/γ' misfit are assumed to be thermodynamic driving forces for spontaneous rafting. These stresses cause different orientation of spontaneous rafts in the rods.

Acknowledgment

This work was financially supported by the Slovak Grant Agency for Science under the contract VEGA 2/7085/27. The authors would like to acknowledge help of Dr. K. Harris from Canon-Muskegon (USA) for providing the experimental CMSX-4 superalloy.

References

- [1] WANG, W.Z. et al. Role of Re and Co on microstructures and γ' coarsening in single crystal superalloys. In *Mater. Sci. Eng. A*, article in press, 2007.
- [2] RAE, C.M.F., REED, R.C. The precipitation of topologically close-packed phases in rhenium-containing superalloys. In *Acta Mater.* 49, 2001, pp. 4113-4125.

- [3] FUCHS, G.E. Solution heat treatment response of a third generation single crystal Ni-base superalloy. In *Mater. Sci. Eng. A* 300, 2001, pp. 52-60.
- [4] KEARSEY, R.M., BEDDOES, J.C., JONES, P., AU, P. Compositional design considerations for microsegregation in single crystal superalloy systems. In *Intermetallics* 12, 2004, pp. 903-910.
- [5] YANG, J.X., ZHENG, Q., SUN, X.F., GUAN, H.R., HU, Z.Q. Topologically close-packed phase precipitation in a nickel base superalloy during thermal exposure. In *Mater. Sci. Eng. A* 465, 2007, pp. 100-108.
- [6] MOUSAVI ANIJAN, S.H.,BAHRAMI, A. A new method in prediction of TCP phases formation in superalloys. In *Mater. Sci. Eng. A* 396, 2005, pp. 138-142.
- [7] FENG, Q., NANDY, T.K., POLLOCK, T.M. Observation of a Ru-rich Heusler phase in a multicomponent Ni-base superalloy. In *Scripta Mater.* 50, 2004, pp. 849-854.
- [8] BRÜCKNER, U., EPISHIN, A., LINK, T. Local X-Ray diffraction analysis of the structure of dendrites in single-crystal nickel-base superalloys. In *Acta Mater. Vol. 45, No. 12*, 1997, pp. 5223-5231.
- [9] VOLK, R., GLATZEL, U., FELLER-KNIEPMEIER, M. Measurement of the lattice misfit in the single crystal nickel based superalloys CMSX-4, SRR99 and SC16 by convergent beam electron diffraction. In *Acta Mater. Vol. 46*, 1998, pp. 4395-4404.
- [10] PYCZAK, F., DEVRIENT, B., NEUNER, F.C., MUGHRABI, H. The influence of different alloying elements on the development of the γ/γ' microstructure of nickel-base superalloys during high-temperature annealing and deformation. In *Acta Mater.* 53, 2005, pp. 3879-3891.
- [11] BRÜCKNER, U., EPISHIN, A., LINK, T., DRESSEL, K. The influence of the dendritic structure on the γ/γ' -lattice misfit in the single-crystal nickel-base superalloy CMSX-4. In *Mater. Sci. Eng. A* 247, 1998, pp. 23-31.
- [12] GROSSMANN, B., BIERMANN, H., TETZLAFF, U., PYCZAK, F., MUGHRABI, H. Measurement of local elastic strains in aged monocrystalline nickel-base superalloys by CBED. In *Scripta Mater.* 43, 2000, pp. 859-864.
- [13] LIU, L.R. et al. Microstructural evolution of a single crystal nickel-base superalloy during thermal exposure. In *Materials Letters* 57, 2003, pp. 4540-4546.
- [14] ACHARYA, M.V., FUCHS, G.E. The effect of long-term thermal exposures on the microstructure and properties of CMSX-10 single crystal Ni-base superalloys. In *Mater. Sci. Eng. A* 381, 2004, pp. 143-153.
- [15] LAPIN, J., ONDRÚŠ, L., NAZMY, M. Directional solidification of intermetallic Ti-46Al-2W-0.5Si alloy in alumina moulds. In *Intermetallics* 10, 2002, pp. 1019-1031.
- [16] LAPIN, J., PELACHOVÁ, T., MAREČEK, J. Directionally solidified multiphase Ni₃Al-based intermetallics for high-temperature applications. In *8th Liège Conference on Materials for Advanced Power Engineering*.
- [17] BALDAN, A. Progress in Ostwald ripening theories and their applications to the γ' precipitates in nickel-base superalloys – Part II / Nickel-base superalloy. In *Journal of Material Science* 37, 2002, pp. 2379-2405.
- [18] <http://www.msm.cam.ac.uk/phase-trans/2003/Superalloys/superalloys.html>.
- [19] NABARRO, F.R.N. Rafting in superalloys. In *Metall. Trans.* 27A, 1996, pp. 513-530.