The effect of heat treatment on the homogenization of CMSX-4 Single-Crystal Ni-Based Superalloy

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ABSTRACT

Two solution heat treatments were used for the homogenization of as-cast CMSX-4 single crystal Ni-based superalloy and their effects were investigated. The heat treatment temperatures were established using thermodynamic calculations based on the CALPHAD method. The effect of heat treatment on the homogenization degree was evaluated quantitatively using the local chemical composition and partition coefficients, and qualitatively using element distribution maps and backscattered electron images after each cycle of heat treatments. The evolution of porosity and dissolution of the γ/γ′ eutectic pools and coarse γ′ fractions were investigated using the quantitative image analysis. The experimental results showed that the strongly segregated microstructure of the as-cast superalloy homogenize with different rates as a function of temperature. In both cases a low residual level of microsegregation still maintain even after long term exposure at high temperatures. Long holding time at both temperatures generates a notable increase of porosity levels being more accentuated with the increase in temperature.

KEYWORDS: *superalloy, homogenization, heat treatment, porosity*

NOMENCLATURE

SEM - scanning electron microcopy
EDS - energy dispersive X-ray spectrometry
S - S type pores
H - H type pores
TCP - topologically close-packed phases
Ki - partition coefficient
γ' - gamma prime phase
γ - gamma phase
Tγ' - γ' solvus temperature
Ts - solidus temperature

1 INTRODUCTION

Nickel-based superalloys are still the most used materials for manufacturing critical components for the hot sections of gas turbines such as, blades, vanes or disks due to their high strength, oxidation resistance and creep behaviour at elevated temperatures [1]. Besides the advanced coating and cooling systems, the outstanding behaviour of Ni-based superalloys that allowed the increase of the turbine entry temperature (TET) is mainly due to the development of the directional solidification techniques in order to produce columnar or single-crystal structures. To increase the high temperature capabilities the modern single-crystal superalloys (SX) contain a high amount of refractory elements such us Ta, Mo, W and Re that generates highly segregated structures. During the solidification of single crystal superalloys, the refractory elements (mainly W and Re) tend to

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segregate into the dendrites, while the other elements which compose the gamma prime (γ′) phase (Al, Ti, Ta) tend to accumulate in the interdendritic regions and in the eutectic pools [2]. This behaviour generates microstructural and chemical heterogeneity that allow the precipitation of brittle topologically close-packed (TCP) phases that seriously affects the mechanical properties and hence the performances of superalloys at high temperature [1] [3] [4]. To reduce the segregation level and to obtain chemical and microstructure homogeneity, the as-cast alloys undergo solutioning heat treatment.

Despite numerous researches, it is still challenging to design a proper homogenization heat treatment for high segregated as-cast Ni-based superalloys. It is quite difficult to identify the solvus and solidus of as-cast superalloys from Differential Scanning Calorimetry (DSC) profiles because of the interference of the phase transformation temperatures that are influenced by the heating or cooling rate and the degree of homogenization [5]. Other challenges relate to the complete dissolution of γ/γ′ eutectic. The eutectic has a coarse blocky morphology with a low surface area per volume ratio which makes it to dissolve very slowly into the γ matrix during the solution heat treatments [6] and may promote local incipient melting due to a low solidus temperature [3]. The refractory metals (Re, W, Ta, Mo) that provide the solid solution strengthening have slow diffusion rates and decrease the diffusion rate of the other alloying elements during the heat treatment. This leads to different chemical composition between the dendrites and the interdendritic regions and to notable differences even between the primary and secondary dendrite arms. It is well known that Re strongly segregate in dendrites and has a great impact on the properties by causing directional and incompressible Ni-Re bonds that hinder the vacancy migration and whose effects dominates over any differences in the vacancy-solute binding energy and in any influence of the atomic radius on the solute [2]. Huang and Zhu [7] showed that this behaviour is due to the atomic radii of the alloying elements which are very close to that of Ni. A solution to improve the microstructure stability is the addition of Ru to reduce the level of Re segregation and to decrease the content of TCP phases in Re-rich alloys [4, 8].

For these reasons it becomes important to design the heat treatment based on these particularities of the single crystal superalloys in order to better homogenize its local chemical composition and to ensure an advanced dissolution of the γ/γ' eutectic pools and coarse γ', while keeping the porosity level as low as possible.

To establish a suitable homogenization heat treatment for a single-crystal Ni-based superalloy, the experimental methods and/or the analytical calculation generally rely on the global chemical composition of the materials. These methods provide just the information about the global chemical composition and do not take into account the different chemical compositions in the segregated areas. An alternative solution to this approach experimentally verified by several authors [9-11] is to predict the transformations temperatures by thermodynamic calculations based on the CALPHAD method.

The purpose of this paper is to investigate the effect of solution heat treatment on the homogenization of CMSX-4 single-crystal superalloy based on simulation predictions and experimental results.

2 MATERIALS AND PROCEDURES

The experiments were performed using cylindrical rods of 16 mm diameter and 200 mm length cast in CMSX-4 single-crystal Ni-based superalloy with the typical composition listed in Table 1. The single crystal rods were produced using a Bridgman type vacuum induction melting and casting furnace at Giesserei-Institute, RWTH Aachen University. The solidification was performed with a thermal gradient of 3 $K \cdot mm^{-1}$ and a withdrawal rate of 3 $mm \cdot min^{-1}$. Details on the experimental work performed and the results are presented elsewhere [10-11]. Cylindrical samples of 6 mm height cut from the single crystal rods used for heat treatment experiments and microstructural investigation. For porosity measurements the samples were prepared by grinding and polishing and for the eutectic phase fraction analysis and microstructural investigations the samples were metallographically prepared by grinding, polishing and etched with Marble reagent (10g $CuSO_4$, 50ml HCl, 50ml H_2O).

Table 1: Typical chemical composition (wt%) of CMSX-4 Ni-based superalloy

Al	Ti	Cr	Co	Hf	Ta	W	Re	Mo	Ni
5.6	1.0	6.5	9.0	0.10	6.5	6.0	3.0	0.60	balance

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2.1 Heat treatment conditions

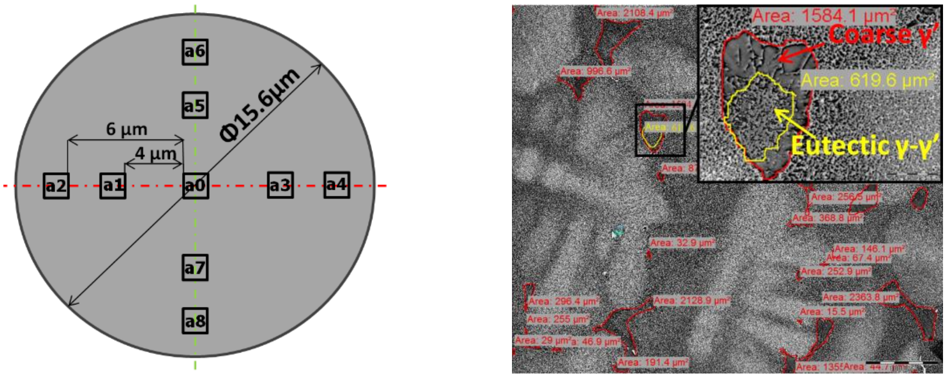
The alloy solidification path and phase transformation temperatures were predicted by thermodynamic calculations using Pandat™ software (registered trademark of Computherm LLC) with PanNi_2017 multi-component thermodynamic database. Within the calculated solution heat treatment window two temperatures were selected for the heat treatment experiments. The samples were subject of homogenization heat treatments at 1300°C and 1310°C, with a heating rate of 15°C/min and holding duration of 4, 8, 12, and 16h, followed by air cooling. After each homogenization heat treatment cycle the samples were metallographically prepared for microstructural investigations.

2.2 Microstructural and micro-compositional analysis

The microstructural and micro-compositional analysis of the investigated CMSX-4 superalloy were performed using a scanning electron microscope FEI Inspect F50 (SEM) equipped with an energy dispersive X-ray spectrometer EDAX. The effect of the heat treatment on the chemical homogenization of the alloy were evaluated qualitatively by using the element distribution maps (EDS mapping) and quantitatively by using the local chemical composition analysis (EDS analysis). To improve the accuracy of the quantitative EDS analyses, the known bulk chemical composition of the superalloy was used as standard (standardless mode). The quantitative chemical composition was performed in the dendrite cores (DC), dendrite arms (DA) and in the interdendritic regions (IR) of four nearby dendrites. The chemical composition measurements were used to determine the Ki partition coefficient which is commonly used to evaluate the degree of segregation. The partition coefficient is defined as the ratio of the concentration of the elements in the dendrite core and in the interdendritic region: $Ki=C_D/C_I$, where C_D is the concentration of the element in the dendrite core and C_I is the concentration of the element in the interdendritic regions.

2.3 Quantitative image analysis

To track the effect of heat treatment on the homogenisation in terms of dissolution of coarse γ′ islands and γ/γ′ eutectic pools, quantitative measurements of phase fractions were performed using the image analysis software Scandium (Fig. 1b). The measurements were carried out on as-cast samples and after each stage of the heat treatment (4-16h) targeting the same 9 areas of the investigated samples as shown in Fig. 1a using the same magnification (x500).



a) b)

Figure 1: Location of quantitative image analysis areas (a) and residual phase fractions measurement results (b)

The evolution of the porosity during the homogenization heat treatment was evaluated on SEM images at a lower magnification (x200) using the same methodology as in the case of the phase fraction measurements. For a clearer assessment of the pores in the investigated samples, which can range from few hundred nanometres to several tens of microns, it was used the binarization technique of SEM images using the image analysis software (Scandium) that associate the pixels in the image with the pores and the rest of material. For each heat treatment stage SEM images were achieved by adjusting the brightness and contrast to highlight the pores. The images were subsequently converted into a 16-bit grayscale format followed by conversion into black and white threshold image. The microareas corresponding to the pores and the rest of the material were obtained by counting the pixels from the black and white regions and the percentage of the porosity area was calculated.

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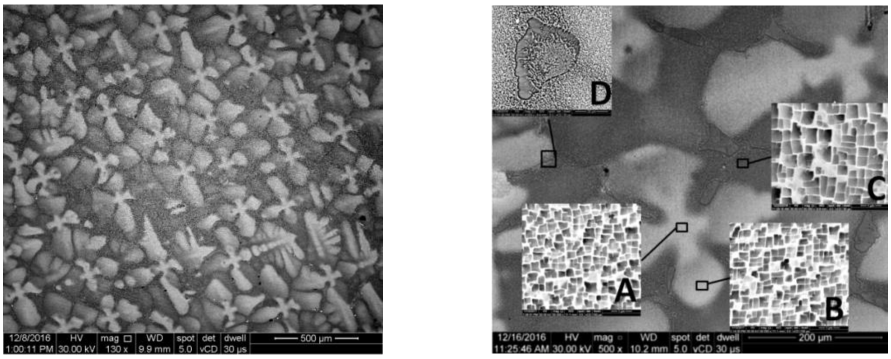
3 RESULTS AND DISCUSSION

The as-cast microstructure of the investigated single-crystal CMSX-4 superalloy in cross section consists of an array of cut dendrite trunks with a fine γ–γ′ structure, interdendritic regions with a coarser γ–γ′ structure, pools of γ/γ′ eutectic and coarse γ′ islands (Fig. 2). Fig. 2b highlights the shape and size of γ' precipitates which are more regular and smaller in the dendrite cores (detail A) than in the dendrite arms (detail B) or in the interdendritic regions (detail C), the γ/γ′ eutectic pools and the coarse γ' islands (detail D). This morphology of γ' precipitates is due to the growth kinetics in correlation with the segregation level of the alloying elements [13], while the eutectic γ/γ' fractions and coarse γ' islands are developing during the solidification in the interdendritic regions.



a) b)

Figure 2: The cross section microstructure of the as-cast single crystal superalloy (a) and the morphology of γ' precipitates, coarse γ' islands and γ/γ′ eutectic pools (b)

The highly segregated microstructure of the as-cast CMSX-4 superalloy was qualitatively assessed by the EDS surface distribution of the relative X-ray intensity of the elements which segregate in the dendrite cores, dendrite arms and in the interdendritic regions. The backscattered electron image and the elements distribution maps presented in Fig. 3 highlights that the high density refractory elements (Re and W) are particularly distributed in the dendrites while those forming the γ' phase (Al, Ti, Ta) are preferential distributed in the interdendritic regions.

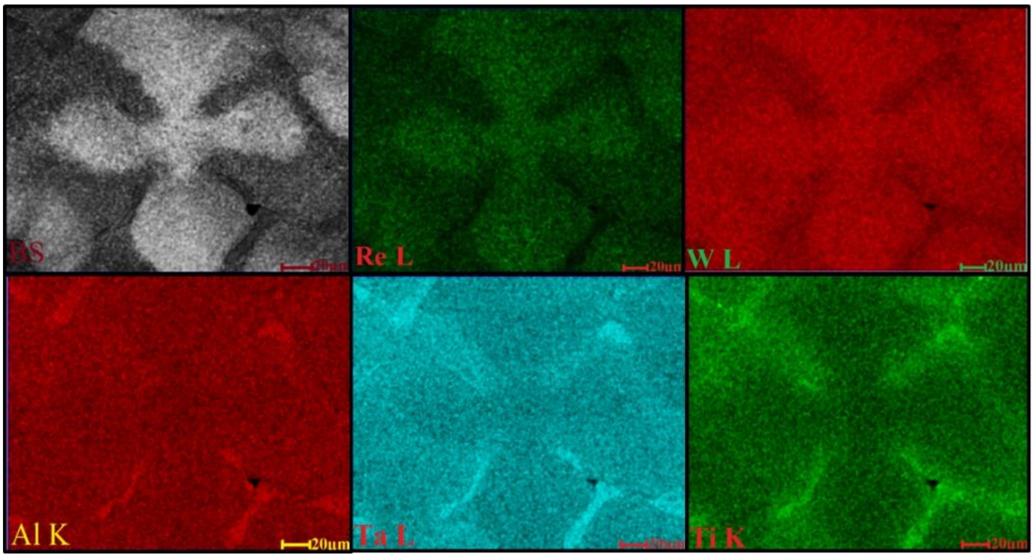


Figure 3: Elements distribution maps of the main elements that segregate in the dendrites (Re and W) and in the interdendritic regions (Al, Ti, Ta)

These qualitative results are confirmed by the EDS quantitative micro-compositional analysis in the dendrite cores, dendrite arms and in the interdendritic regions. The preferential segregation of the alloying elements during solidification causes different chemical compositions in the dendrites and in the interdendritic areas, with considerable differences even between the primary and secondary dendrite arms. Table 2 summarize the chemical composition of the different investigated areas.

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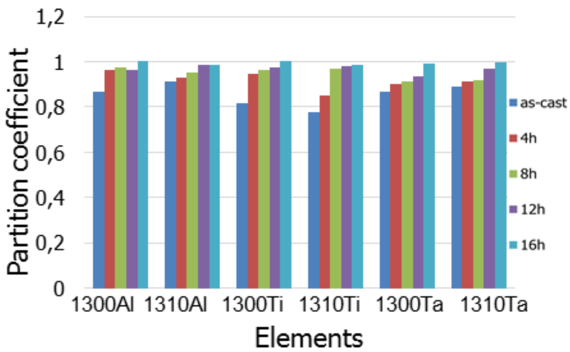
Table 2: EDS chemical composition of the as-cast CMSX-4 superalloy

wt%	Al	Ti	Cr	Co	Ni	Hf	Ta	W	Re	Mo
Bulk composition	5.63	0.92	5.86	8.64	62.77	0.11	7.05	5.7	2.69	0.62
Dendrite cores	5.17	0.87	6.57	9.74	60.67	0.10	5.98	6.65	3.58	0.50
Dendrite arms	5.51	0.88	6.53	9.40	61.46	0.09	6.22	6.16	3.18	0.57
Interdendritic	5.97	1.07	6.54	8.61	62.49	0.10	6.88	5.17	2.62	0.55

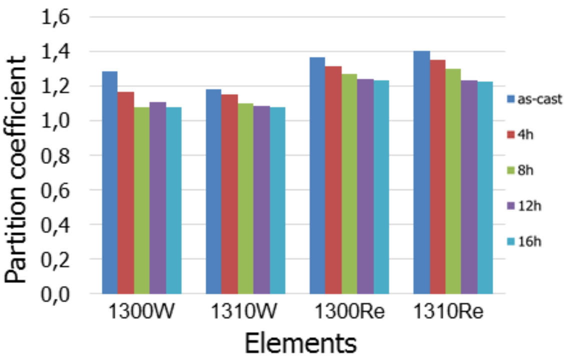
Considering these findings, the superalloys must be subjected of homogenization heat treatments in order to diminish the segregation level. For the chemical homogenization of the of a single-crystal Ni-based superalloy by heat treatment it is necessary to establish a proper temperature between the highest γ' solvus temperature ($T_{γ'}$) to ensure the complete dissolution of γ' phases, and the lowest solidus temperature (T_S), to avoid the incipient melting occurrence. Thermodynamic calculations of the solidification path and phase formation using the commercial Pandat™ software predicted for the typical chemical composition of the investigated alloy a heat treatment window of 81°C, between the predicted γ' solvus temperature (1274°C) and the solidus temperature (1355°C). Considering the segregation tendency that generates different composition between the dendrites and the interdendritic regions as shown in Table 2, the heat treatment range is reduced to 71 °C. Taking into account that the heat treatment temperature should not exceed the melting temperature of the eutectic pools and coarse γ', the temperature range for the homogenization heat treatment shrink to only 41°C, in the range 1281 - 1322°C ($T_{γ'}$-T_S). For experiments two heat treatment temperatures were established. First temperature was set at 1300°C, which is about at the half of the previously determined temperature range, and second temperature 10°C higher.

The effect of the solution heat treatment on the microstructural homogenization was investigated by quantitative and qualitative measurements. The quantitative evaluation of the influence of the heat treatment on the homogenization was made through the partition coefficients Ki calculated from EDS quantitative analysis results, while the qualitative evaluation was performed by using the backscattered electron images for each stage of the heat treatments. The partition coefficients were used to highlight the tendency of the alloying elements to segregate either in the interdendritic regions (Ki<1) or in the dendrites (Ki>1). The partition coefficients were calculated for the five critical elements (Re, W, Al, Ti and Ta) with a strong influence on generating the high temperature properties and behaviour of the CMSX-4 single-crystal superalloy.

Based on EDS results the partition coefficients between the dendrite cores and the interdendritic regions were calculated for the as-cast superalloy and after each homogenization cycle at the two selected heat treatment temperatures. Fig. 4 summarizes the calculated partition coefficients for the critical elements as a function of holding time at the two heat treatment temperatures.



a)



b)

Figure 4: The calculated partition coefficients Ki for the elements that segregate in the interdendritic regions (a) and in dendrite cores (b) after the heat treatment at 1300°C and 1310°C

As shown in Fig. 4 the highest values of Ki in as-cast condition were calculated for the refractory elements Re (1.4) and W (1.2), showing their strongest segregation degree in dendrites. An opposite behaviour is recorded for the elements that segregate in the interdendritic regions (Al, Ti, Ta) having Ki values less than 1. This behaviour is governed by the redistribution of the alloying elements ahead of the solidification front as the solidification progresses and the secondary dendrite arms grow in the interdendritic liquid depleted in refractory elements and enriched in Al, Ti and Ta. This leads to lower

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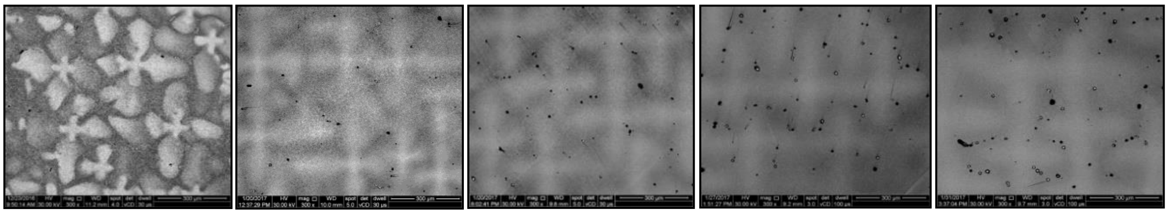
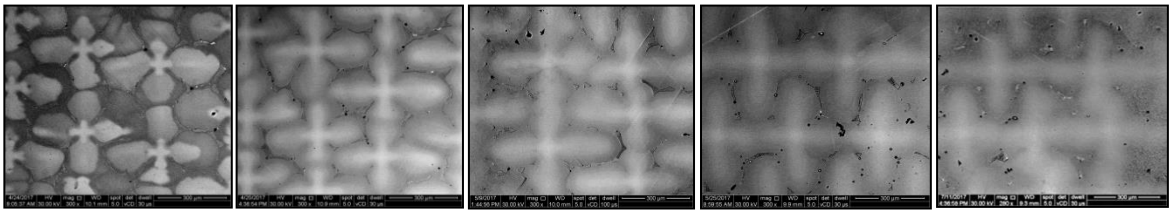
partition coefficients for the refractory elements and partition coefficients less than unity for Al, Ti and Ta. As expected, after the heat treatment the local chemical composition tends to homogenize and all values of Ki tend to a value of 1. After the heat treatment at 1300˚C the experimental results still show a certain level of residual segregation for Al, Ti and W. After the first heat treatment cycle of 4h were recorded considerable changes of the concentration of Re and W, especially in the case of heat treatment at 1300˚C. Excepting small fluctuations of the concentration, considerable changes for both temperatures (1300˚C and 1310˚C) occurred after the first 8h holding duration for the refractory elements that segregate in dendrites (Re and W). The SEM backscattered electron images shown in Fig. 5 and Fig. 6 present the evolution of the local chemical composition homogenization during the solution heat treatments as a function of temperature and holding duration in which contrast reduction shows increased homogenization.



a) b) c) d) e)

Figure 5: SEM backscattered electron images of CMSX-4 in as-cast condition (a) and after each cycle of heat treatment at 1310˚C for 4h (b), 8h (c), 12 h (d), and 16h (e)



a) b) c) d) e)

Figure 6: SEM backscattered electron images of CMSX-4 in as-cast condition (a) and after each cycle of heat treatment at 1300˚C for 4h (b), 8h (c), 12 h (d), and 16h (e)

Fig. 5 and Fig. 6 show that the refractory elements, which exhibit a bright contrast in the backscattered electron images, are strongly segregated in the dendrites, while the other elements that segregate in the interdendritic regions have a dark contrast. The evolution of the chemical composition homogeneity with increasing the holding durations at 1300°C and 1310°C is highlighted by a mitigation of the contrast between the dendrites and interdendritic regions. In the case of the heat treatment at 1310°C this effect is more pronounced that in case of the heat treatment at 1300°C, in very good agreement with the calculated partition coefficients based on the quantitative EDS analysis. The solution heat treatments applied to single-crystal superalloys is followed by the homogenization of the local chemical composition and the dissolution of the eutectic pools. Quantitative analysis using SEM image analysis software were carried out in order to monitor the dissolution of the islands of coarse γ′ and eutectic γ-γ′ fractions during the homogenization heat treatments, as summarized in Table 3.

Table 3: Experimentally measured fractions of the γ/γ′ eutectic pools and coarse γ′

Temp. [°C]	Heat treatment cycle	$A_{islands}$ [%]	$A_{eutectic}$ γ-γ′ [%]	$A_{coarse\ \gamma'}$ [%]
1300	as-cast	6.39	2.20	4.19
	4h	4.41	2.59	1.82
	8h	2.42	0.99	1.43
	12h	1.57	0.73	0.84
	16h	0.89	0.41	0.48
1310	as-cast	5.84	1.56	4.28
	4h	0.11	0.05	0.05
	8h	0.08	0.04	0.04
	12h	0.06	0.02	0.04
	16h	0.03	0.01	0.02

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The results presented in Table 3 show the influence of the heat treatment temperature on the dissolution of the γ/γ′ eutectic pools and coarse γ′ islands fractions. During the heat treatment at 1300°C there is recorded a steady reduction of the γ/γ′ eutectic fraction (to 0.41%) and of the coarse γ′ fraction (to 0.48%). At higher temperature (1310°C) an almost complete dissolution of these phases occurs after only 4h holding time with a further decrease to very low levels after 16h of heat treatment. Even in both cases the residual eutectic and coarse γ′ fractions decrease to less than 1%, it is notable that the solution heat treatment at 1310°C is more efficient in this respect as compared with the lower temperature of 1300°C. During the heat treatment at 1310°C the dissolution is almost complete after just 4h holding time. However, as it has been shown before, after 4h holding time at 1310°C there is still a compositional gradient between the dendrites and the interdendritic regions. The further increase of holding time at 1310°C improve the chemical homogenization but it was found that it is associated with a significant increase of the porosity as compared with the 1300°C heat treatment.

Using the quantitative image analysis, the porosity level of the CMSX-4 superalloy was investigated in as-cast condition and monitored after each heat treatment stage. The measured porosity level of as-cast CMSX-4 superalloy was only 0.09%. After the first heat treatment cycle of 4h holding time the porosity level shows a sharp rise at both temperatures, with different rates. After 4h holding time the porosity level increase with about 200% at 1300°C as compared with the higher temperature that generates a more pronounced increase of porosity with 300%. Fig. 7 presents the evolution of the porosity fraction measured after each heat treatment cycle as a function of holding time at 1300°C and 1310°C.

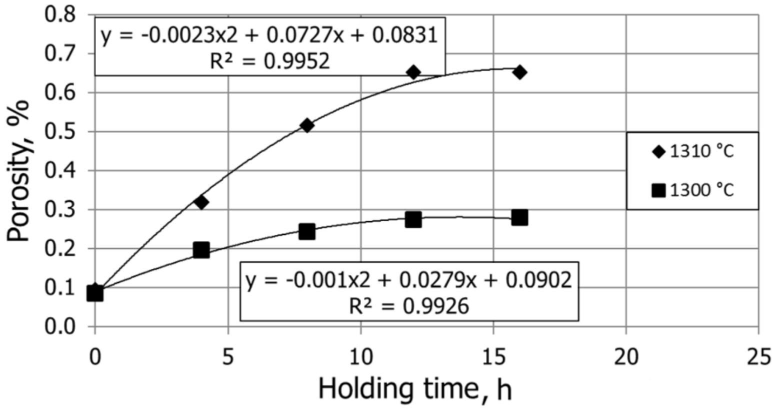

Figure 7: Porosity fraction as a function of holding time

The higher level of the porosity for the heat treatment at 1310°C is obvious for all holding times. It has been observed that for shorter holding time the porosity increases with different rates. Up to 12 hours of holding time the porosity rates are about 0.007%/h at 1300°C/h and 0.027%/h at 1310°C. After 12h holding time the growth rate of porosity considerably reduces in both cases. The mechanism of porosity formation in as-cast superalloy microstructure is governed by the local solidification shrinkage that generates S type pores. During the heat treatment H type pores can independently develop by the coalescence of vacancies (small pores) or they can concentrate on the initial type S pores and increase their size.

The accelerated increase of porosity level during the first stages of the heat treatments can be also influenced by the pores generated by the local melting of the eutectic γ/γ′ pools. Due to the segregation process these pools may have chemical compositions that generate local melting temperatures lower than the heat treatment temperature. During cooling to ambient temperature the molten eutectic islands will solidify and shrink, that generates porosities in a similar manner with the S type pores formation.

These findings show that an increase of heat treatment temperature with only 10°C degrees improve the microstructure homogenization but presents the great drawback of inducing a considerable increase of porosity level. This becomes important in the cases where the superalloy components are not subject to additional operations to reduce porosity such as hot isostatic pressing. When designing the homogenization heat treatment, a balance between the targeted homogenization degree and the porosity level must be considered.

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CONCLUSIONS

In the as-cast CMSX-4 superalloy the refractory elements (especially Re and W) strongly segregate in the dendrite cores while the γ′ forming elements Al, Ta, and Ti partition to the interdendritic regions. During the solution heat treatments, the dendritic and interdendritic regions homogenise at different rates and stages. Towards the end of the heat treatment cycle the main alloying elements tend to have Ki values closed to unity, showing an advanced homogenization. A certain level of inhomogeneity still remains even after long holding times at high temperatures.
The residual eutectic pools and coarse γ′ phases fractions reduce to less than 1% for both selected heat treatment temperatures. A notable decrease is encountered during the heat treatment at 1310°C/4h.
Associated with the homogenization process the high temperature heat treatments induce a substantial increase of the porosity level. The porosity level is temperature dependent being more pronounced at 1310°C heat treatment.

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