

A study of the effects of alloying additions on TCP phase formation in 4th generation nickel-base single-crystal superalloys

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Abstract. The demand for higher engine operating temperatures to improve aeroengine efficiency has meant that increasing levels of alloying additions are being added to single-crystal nickel-base superalloys for turbine blades applications. Whilst better mechanical and environmental performance may be obtained with these alloying additions, they also destabilise the alloys forming topologically closed-packed (TCP) phases. In this study, the formation of TCP phases has been studied in a series of four alloys designated LDSX1-4 which have a systematic variation in the levels of Co, Mo and W. The alloys were exposed to elevated temperatures between 900-1100°C for up to 1000 hours. This was followed by detailed analysis of the microstructures in the SEM. Identification of the TCP phases in selected alloys was also carried out. The effects of each alloying addition on TCP phase formation is discussed in light of these results.

Introduction

Nickel-base superalloys have been continuously developed over the last few decades fuelled by the demands of higher engine operating temperatures to improve aeroengine efficiency. The addition of dense refractory elements has given rise to significant improvement in the mechanical and environmental performance of these alloys, leading to greater high temperature capabilities. However, associated with increasing additions of these dense refractory elements, a progressive reduction in alloy stability was observed due to the precipitation of topologically closed-packed (TCP) phases after prolonged exposure at elevated temperatures. TCP phases are detrimental to the alloys as they are brittle and may therefore act as crack initiation sites. In addition, the formation of these TCP phases depletes the microstructure of refractory elements critical for high temperature performance.

There is hence a need to understand the effects of alloying additions on alloy stability and TCP phase formation, and several studies have been carried out, principally concentrating on a single alloy composition [1,2]. These studies are key to enable newer alloys to be safely employed in commercial service, but in addition, the understanding of the complex interactions between the alloying elements could be used to drive further improvements. The current study adds to the existing understanding by investigating the effects of alloying addition on TCP phase formation in 4th generation nickel-base superalloys, specifically focusing on the effects of Co, Mo and W additions.

Material

The materials used were four alloys designated LDSX1-4 developed under the DARP SRR400 alloy development program [3]. These alloys were chosen as they possess a systematic variation in the Co, Mo and W contents as shown in Table 1. Single crystal test bars with a longitudinal axis close to <001> were supplied by Rolls-Royce plc in fully heat-treated condition.

Table 1: Alloy composition in %wt of material used in the study, balance nickel

Alloy	Al	Ti	Cr	Co	Mo	Hf	Ta	W	Ru	Re
LDSX1	6	0.25	3	3	2.5	0.1	6.5	2.9	3.5	6.2
LDSX2	6	0.25	3	8	5	0.1	6.5	2.9	3.5	6.2
LDSX3	6	0.25	3	3	5	0.1	6.5	4.8	3.5	6.2
LDSX4	6	0.25	3	8	2.5	0.1	6.5	4.8	3.5	6.2

The solution heat treatment conditions used on the alloys were 1355°C/10hr for LDSX1, 1340°C/10hr for LDSX2 and 4, and 1340°C/20hr for LDSX3. All alloys were subsequently primary aged at 1150°C/4hr and secondary aged at 870°C/16hr. The fully heat-treated microstructures of these alloys consist of γ' precipitates with average sizes of approximately 500 nm. After the heat treatment, TCP precipitates were already observed in the dendrite cores of the LDSX3 alloy.

Experimental

Alloy samples for annealing were prepared from 5 mm transverse sections of the fully heat-treated test bars. Annealing was carried out at 900°C, 1000°C and 1100°C with exposure times of up to 1000 hours. The annealing temperatures were chosen to replicate the temperatures experienced at various areas of the turbine blade during service, while the maximum annealing time was chosen to represent the approximate 'hot time' life of the turbine blades. The annealing was carried out in Carbolite laboratory chamber furnaces in an air environment; after annealing the samples were removed from the furnace and left to cool in laboratory air. The samples were then prepared by polishing to finish with colloidal silica for examination in a Camscan MX2600 FEG-SEM operating at an accelerating voltage of 20kV in back-scattered electron imaging mode.

Selected samples were also deep-etched electrolytically in order to reveal the TCP phases in greater detail. The samples were polished to ¼ micron diamond finish and deep-etched using an electrolyte composed of 10% HCl and 1% tartaric acid in methanol. Samples were etched with an anodic current density of 2 mA/mm² for approximately 5 minutes and subsequently examined in a JEOL 5800LV SEM operating at an accelerating voltage of 20kV in secondary electron imaging mode.

Identification of the TCP phases was carried out by analysing the SADP (selected area diffraction pattern) in the JEOL 200CX TEM operating at an accelerating voltage of 200kV. Specimens for the TEM were electropolished using a 10% perchloric acid in methanol solution at -5°C temperature and 20V potential difference. Samples were sectioned near the {011} plane, this way both the {111} and {001} planes are within reach using a double-tilt TEM sample holder and therefore the SADP associated with these planes could also be analysed.

Results

The TCP phases formed after 1000 hours exposure at 900°C, 1000°C and 1100°C are shown in Fig. 1. The TCP phases are shown in greater detail in the deep-etched samples of the alloys exposed to 1000°C for 1000 hours in Fig. 2. With higher exposure temperature, the severity of TCP phase precipitation increases in all the alloys. At all exposure temperatures, LDSX1 and 4 show greater stability with significantly lower amounts of TCP precipitates observed compared to LDSX2 and 3. The TCP precipitates in LDSX1 and 4 (Figs. 1-2) are found predominantly at the dendrite cores in all conditions. LDSX1 shows greater stability compared to LDSX4, where in LDSX1 only very low amounts of TCP precipitates was observed at 1000°C and this diminishes as the exposure temperature is raised to 1100°C. LDSX4 shows significantly greater TCP phase precipitation after 1000 hours exposure at both 1000°C and 1100°C. After 1000°C exposure, LDSX1 and 4 exhibit two distinct types of TCP phases consisting of thin sheets and fine platelets, whilst after 1100°C exposure, the TCP phase in LDSX4 consists only of thicker sheets as shown in Fig. 1. The thin sheet TCP phases observed in both LDSX1 and 4 are thought to be the σ phase; work to identify these TCP phases is still underway.

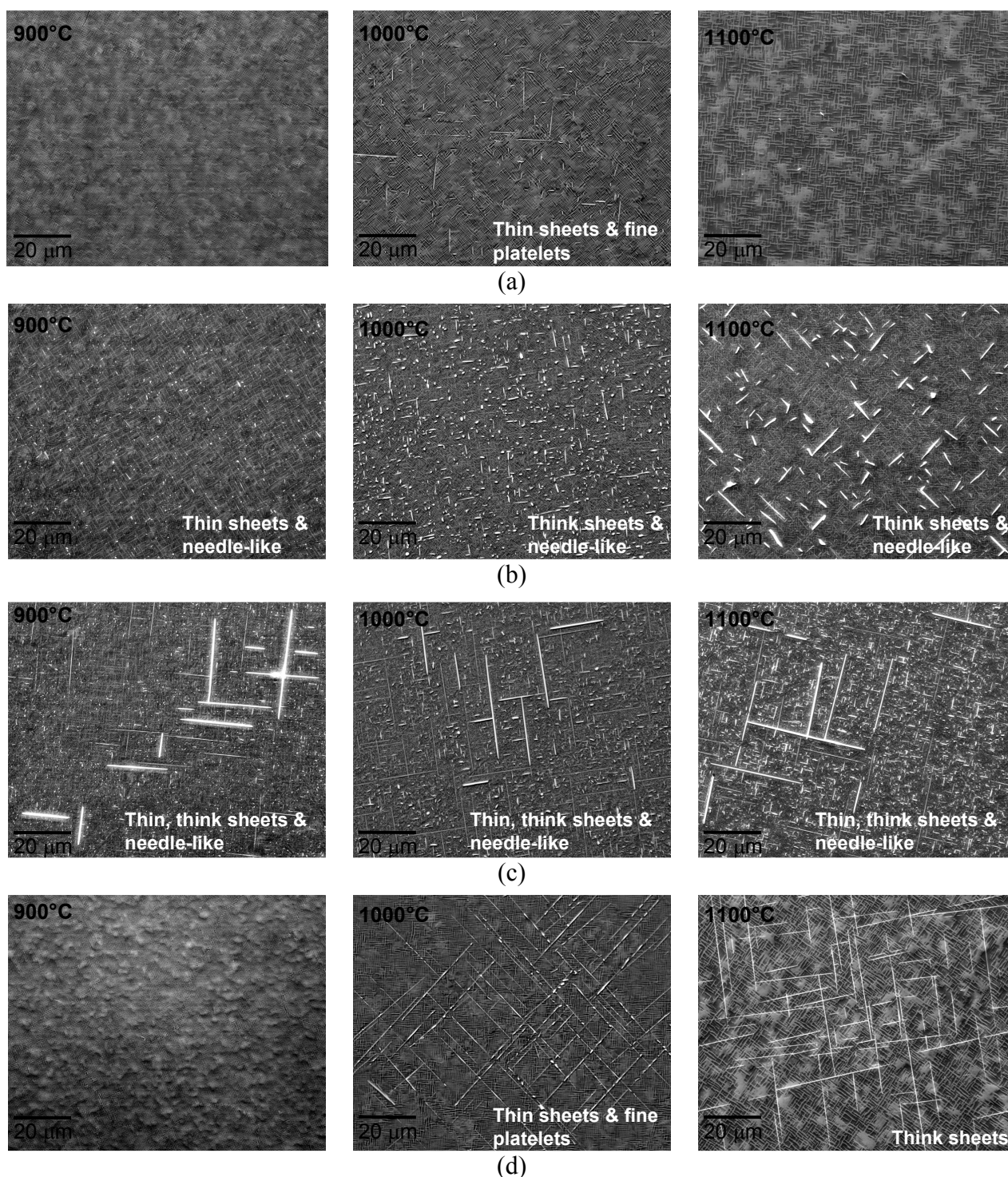


Fig. 1: SEM micrographs of TCP phases after 1000 hours exposure at various temperatures
(a) LDSX1, (b) LDSX2, (c) LDSX3 and (d) LDSX4

In contrast, both the dendritic and interdendritic areas of LDSX2 and 3 are swamped by TCP precipitates, with the occurrence of TCP phases being more pronounced in the dendritic core areas. For both LDSX2 and 3, the morphology of the TCP phases precipitated appear to be relatively similar, both showing sheet precipitates parallel to $\{111\}$ planes and additionally needle-like precipitates. In both LDSX2 and 3, thin sheet TCP phases are seen at all the exposure temperatures, but the size and amount of the needle-like TCP increases with increasing exposure temperature. The propensity to TCP phase formation in LDSX3 is marginally more severe than in LDSX2, indeed in LDSX3 some precipitates form during the heat treatment and lead to the thicker sheet precipitates visible in all samples. At a given exposure temperature, the thin sheet TCP phases of LDSX3 are more distinct and thicker c.f. to those observed in LDSX2.

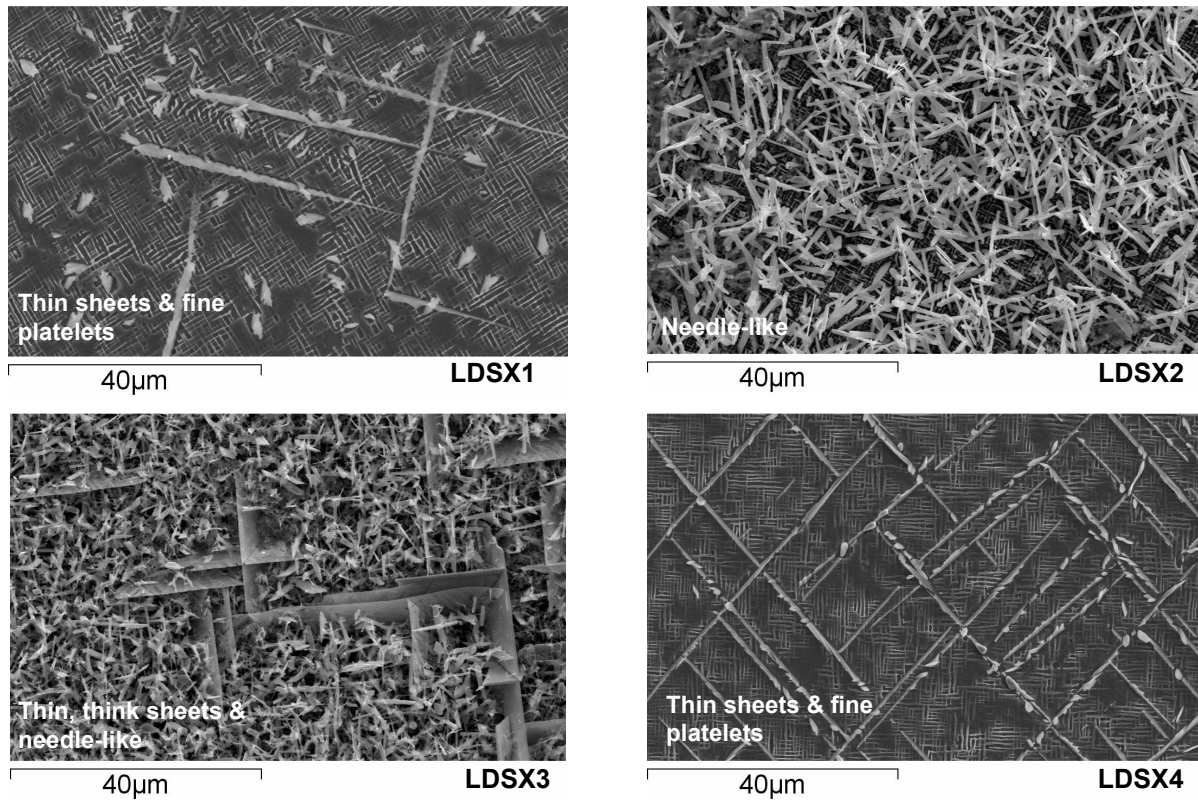


Fig. 2: SEM micrographs of TCP phases after deep-etching; 1000°C/1000hr exposure

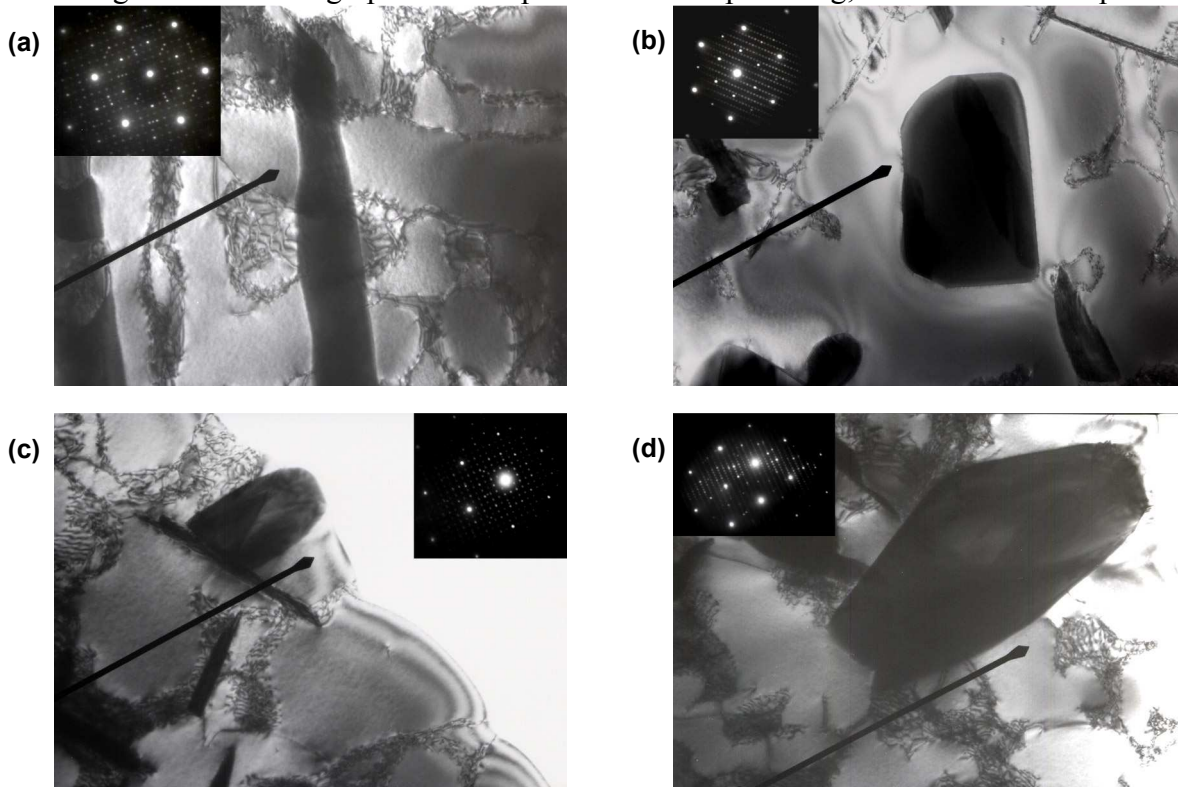


Fig. 3: TCP phases observed in the TEM after 1000°C/1000hr exposure, diffraction pattern inset
(a) LDSX2 σ phase, (b) LDSX2 P phase, (c) LDSX3 σ phase and (d) LDSX3 P phase

TEM images of the TCP phases observed in LDSX2 and 3 are shown in Fig. 3 with the diffraction pattern inset. From these the thin sheet precipitates were identified as σ phase and the needle-like phase as P phase. The σ phase has an orientation relationship of $(111)_{\gamma} // (001)_{\sigma}$ and $[\bar{1}10]_{\gamma} // [\bar{1}10]_{\sigma}$ while the P phase needles has an orientation relationship of $(111)_{\gamma} // (001)_P$ and $[20\bar{2}]_{\gamma} // [201]_P$. In LDSX3 the $(001)_P$ of the P phase shows a minor misorientation off the $(111)_{\gamma}$ of the γ phase.

Discussion

TCP phases have been shown to consist predominantly of refractory elements such as Ni, Co, Cr, Mo, Re and W [4,5], therefore greater addition of the critical refractory elements and / or strong segregation of these elements in the microstructure are expected to promote TCP phase precipitation. In a study on the effects of Mo on creep properties of a series of non Re-containing experimental alloys, excessive Mo content of 4 wt% was found to cause precipitation of TCP phases after creep testing at 800°C and 1010°C which was not observed if the Mo content was reduced to either 1 wt% or 2wt% [6]. However, detailed compositions of the alloys were not given and a comprehensive analysis of the TCP phases observed was not carried out in the particular study to allow substantial conclusion to be made. In another study utilising Re-containing alloys, increasing the W content at the expense of Mo was found to decrease the overall TCP precipitation and to increase in the σ volume fraction at the expense of P phase precipitates, i.e. Mo appear to stabilise the P phase [5].

While cobalt is one of the constituents of the TCP phase and therefore higher Co addition is expected to increase the propensity to TCP phase formation, the opposite effect has been found in various studies [7]. In a study by Wang et al. investigating the effects of Co and Re on TCP phase formation in a series of Re-containing alloys, it was found that addition of 3 wt% Co suppresses TCP phase formation after 1000 hours at 1050°C and the addition of 12wt% Co suppresses TCP phase precipitation after 2000 hours at 1050°C. Without the cobalt addition, TCP phase formation was observed after 500 hours exposure at 1050°C. The authors argued that cobalt accelerates the diffusion of other elements including the TCP forming elements, thus reducing the segregation of these elements and thereby retarding TCP phase formation [7]. In another study investigating TCP phase formation in Re-containing alloys, doubling the cobalt content at the expense of nickel was also found to significantly reduce the amount the σ phase precipitated [5]. It was thought that cobalt additions i) decrease the thermodynamic stability of the σ phase, ii) suppress μ phase nucleation due to reduced σ phase precipitation or iii) reduce the γ' volume fraction which in turn reduces the super-saturation of TCP formers in the γ matrix; all the above factors reduce the propensity of TCP phase formation.

Table 2: Relative stability of alloys investigated in the current study

Relative stability	Alloy	Mo	W	Co	Mo at%	W at%	Co at%
1	LDSX1	2.5	2.9	3	1.62	0.98	3.17
2	LDSX4	2.5	4.8	8	1.64	1.65	8.56
3	LDSX2	5	2.9	8	3.28	0.99	8.53
4	LDSX3	5	4.8	3	3.32	1.66	3.24

The relative stability of the alloys investigated the current study is briefly summarised in Table 2, where lower relative stability numbers represent greater alloy stability. The stability of alloys LDSX1 and 4 are relatively similar and both are significantly more stable than LDSX2 and 3. Referring to Table 2, the strongest distinction between the stability of the LDSX1 and 4 compared to LDSX2 and 3 can be attributed to the lower Mo content of the former pair. Next, comparing alloys of a given Mo content, the subtle difference in the relative stabilities of LDSX2 compared to 3, and 1 compared to 4 are correlated to the lower W content in LDSX1 and 2. Any effect of higher cobalt content stabilising the alloy is lowest of all and no clear trend is seen in these alloys.

In the current study, a high density of the needle P phase was observed in LDSX2 and 3 and it is driven by the high Mo content, consistent with a previous study [5]. The higher TCP phase formation propensity of LDSX3 compared to LDSX2 can be attributed to the higher W content exacerbated by the low Co content of only 3 wt% in LDSX3. In fact, the composition of LDSX3 is so highly susceptible to TCP phase formation that TCP phases are observed after solution heat

treatment, this precipitation is likely to be exacerbated by the residual segregation of the TCP formers such as Re and W to the dendrite core during solidification. In the present study, the contents of Mo, W and Co are varied at the expense of the Ni content in the alloys. As this was part of a 'design of experiment' series with varying compositions, no adjustment was made for other generic parameters such as γ' volume fraction or overall refractory metal content. The addition of Mo and W in particular have been shown to have a strong effect on the overall stability of the alloys. It is very clear that the increase in Mo has a much greater destabilising effect than W, although the lower atomic mass of Mo means that the increase in atomic percentage of Mo is rather greater (Mo increases by ~1.6 at% and W by 0.6 at%).

Further work is underway to gain a more detailed understanding of the effects of alloying addition on these alloys including the effect of Ru additions.

Summary and Conclusions

The effects of alloying additions on the TCP phase formation in 4th generation nickel-base single crystal superalloys have been investigated. Four alloys designated LDSX1-4 which has a systematic variation in the levels of Co, Mo and W were chosen for the study. The alloys were annealed at elevated temperatures between 900-1100°C for up to 1000 hours after which detailed microstructural analysis were carried out. The TCP phases observed in LDSX1 and 4 were mainly concentrated in dendritic cores and both alloys were found to be significantly more stable compared to LDSX2 and 3 where TCP phases were observed throughout the dendritic and interdendritic areas. The TCP phases found in the four alloys generally have thin sheets and needle-like structures. The TCP phases in LDSX2 and 3 were identified as σ and P phases. The results of this study indicates that the propensity of TCP phase formation increasing with higher Mo contents. For a given Mo content, greater W content also appear to increase TCP phase formation susceptibility. Higher Co addition has the effect of reducing the TCP phase formation but this effect is less pronounced compared to the detrimental effects of high Mo and W additions.

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References

- [1] J.X. Yang, Q. Zheng, X.F. Sun, H.R. Guan, Z.Q. Hu: Mat. Sci. Eng. A Vol. 465 (2007), p. 100
- [2] M.V. Acharya, G.E. Fuchs : Mat. Sci. Eng. A Vol.381 (2004), p. 143
- [3] R.A. Hobbs, G.J. Brewster, C.M.F. Rae, S. Tin, in *Superalloys 2008*, TMS (2008), p. 171
- [4] Y.H. Kong, Q.Z. Chen: Mat. Sci. Eng. A Vol. 366 (2004), p. 135
- [5] C.M.F. Rae, R.C. Reed: Acta Mater. Vol 49 (2001), p. 4113
- [6] J. Zhang, J. Li, T. Jin. X.F. Sun, Z.Q. Hu: Mat. Sci. Eng. A Vol. 527 (2010), p. 3051
- [7] W.Z. Wang, T. Jin, J.L. Liu, X.F. Sun, H.R. Guan, Z.Q. Hu: Mat. Sci. Eng. A Vol. 479 (2008), p. 148