Ni-Base Superalloys

Subjects: Metallurgy & Metallurgical Engineering
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Ni-base superalloys are materials largely used in aero-space and energy production sectors, in particular for manufacturing engine parts (e.g. blades, rotors, turbine disks etc.) of aircrafts and aerospace vehicles and parts of power plants (e.g. extraction of oil and gas, nuclear reactors, etc.). At high temperature they exhibit an exceptional combination of high mechanical strength and excellent corrosion resistance. Ni-base superalloys are considered materials of strategic importance and a lot of metallurgical research has been devoted for optimizing their microstructure and improving mechanical properties so that they can operate at ever higher temperature in conditions of safety and reliability. Ni-base superalloys are strengthened by the precipitation of the ordered γ' phase, L12 Ni3(Al,Ti), crystallographically coherent to the f.c.c. γ matrix and their unique mechanical properties at high temperature result from the great microstructure stability. The volume fraction of γ' phase varies from 25% to 50% in polycrystalline superalloys and reaches about 70% in the most modern single crystal superalloys used for the first stage of aeronautical turbine blades. In order to reduce as much as possible the strain misfit between coherent γ and γ' phases (less than 0.4%) they are designed by an accurate tailoring of the chemical composition and a strict control of the process parameters; the resulting interface energy (20-30 mJ/m2) guarantees an excellent stability of the microstructure at high temperature. Other phases such as carbides, borides, γ'', η, δ, σ, μ and Laves phases may be also present with various effects on the mechanical properties; for instance, the topological closed-packed (TCP) σ, μ and Laves phases are undesirable because reduce the ductility. In spite of the fact that Ni-base superalloys cost from 3 to 5 times the Fe-base ones, their use is expanding especially in gas turbine components for the production of energy because higher temperature of the thermal cycle guarantees greater efficiency and reduction of polluting emission. The demand of Ni-base superalloys is expected to expand also for the energy production through conventional steam turbine plants for achieving super-critical conditions with a predicted increase of efficiency to ~ 60% and reduction of CO2 to about 0.7 ton/kWatth while current sub-critical power plants have an efficiency of ~ 35% and produce 1.2 ton/kWatth of CO2. Of course, higher operating temperature involves more severe degradation of mechanical properties owing to these factors: (i) microstructure evolution including formation of undesired phases, coalescence of γ' precipitates, degeneration of carbides due to fatigue and creep exposure etc.; ii) the formation of cracks. Three topics of great industrial relevance will be discussed hereinafter: (i) microstructural stability; (ii) manufacturing parts of complex geometry; (iii) welding of superalloys.

Keywords: Ni-base superalloys ; Microstructural stability ; Manufacturing ; Welding

1. Microstructural Stability

The microstructural and mechanical stability is one of the most stringent requirements for materials operating at high temperature.

In general, coarsening of the ordered γ' phase and changes in its morphology (rafting) due to creep are the most relevant phenomena leading to the degradation of mechanical performances of Ni-base superalloys at high temperature. A large lattice misfit between the γ and γ' phases promotes the coarsening of γ' phase with detriment of the structural stability [1]. As shown in **Figure 1**, at high temperature and under an applied stress, the γ' particles, which usually have a cuboidal shape (a), tend to coalesce, forming layers known as rafts (b). At very high temperatures (above ~1050 °C), rafting takes place during the initial part (1–3%) of creep while at lower temperature (~900 °C) it only completely develops during the tertiary creep.

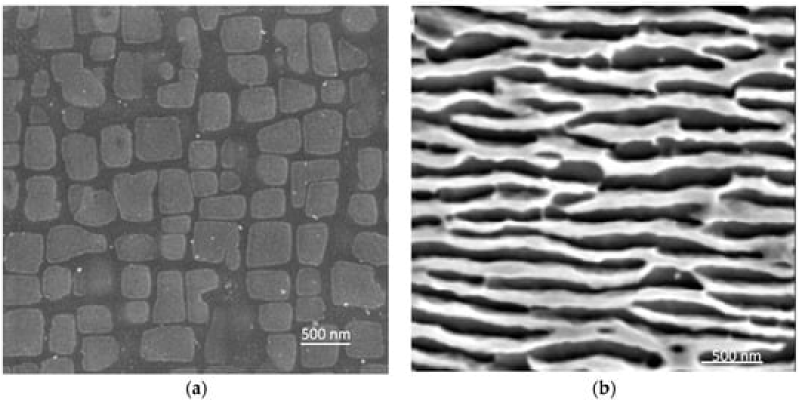

Figure 1. The typical morphology of the γ' phase in Ni-base superalloys (**a**) results changed by rafting (**b**).

At the beginning of creep, dislocations are forced to bow in the narrow matrix channels where all the plastic strain occurs, while γ' phase deforms elastically [2][3]. The progressive increase of plastic deformation in the γ phase enhances internal stresses, leading to dislocation shearing of γ' particles during the tertiary creep. Of course, γ' particle coarsening involves the degradation of creep properties.

Refractory elements, such as Re, Ta, Ru, Nb, Mo and W, are today added to Ni-base superalloys to improve their high temperature properties [4][5][6][7][8]. These elements provide good creep strength because their low atomic mobility retards dislocation climb in both γ and γ' phases. Re concentrates mostly in the γ matrix, forming nanometric atomic clusters with short-range order, which reduce rafting during creep and hinder dislocation movement. The partition of refractory metals between γ and γ' phases occurs depending on their relative contents in the alloy composition. For instance, the amount of Re in the γ' phase increases by increasing W content in the alloy. Furthermore, as Nb and Cr are major formers of η and σ phases respectively, the concentration of these solutes in the g matrix likely serves as the primary driving force for the precipitation of secondary phases. Nb has a very limited solubility in the σ phase while Cr has limited solubility in the η phase. Therefore, the ratio of Cr to Nb atoms in the γ matrix can serve as a good indicator of the phase stability and determines the probability of η -Ni_6AlNb or σ forming [9].

In general, these alloys have more than seven alloying elements in their composition, and the addition of further elements may strongly alter segregation profiles in casting, thus solidification has been extensively investigated by focusing the attention on the partition of elements in solid and liquid during cooling [10][11][12][13]. Guan et al. [11] reported that liquidus and solidus decrease by increasing Cr in Re-containing alloys, and changes of these critical lines induced by Ru, were observed by Zheng et al. [14].

The addition of B and N to superalloys containing refractory metals affects solidification defects. For instance, N has been proved to increase the micro-porosity [15], while B retards grain boundary cracking and reduces the size of carbides with consequent improvement in mechanical properties [16].

Some of present authors evidenced also an early stage of microstructural instability in both single crystal (PWA1482) [17] [18] and directionally solidified (IN792 DS) [19] Ni-based superalloys, connected to the re-arrangement of dislocation structures induced by heating to moderate temperature (~500 °C).

Dislocation cells present in the precipitate free (PF) zones of the matrix (**Figure 2**) grow to form cells of larger size; the process proceeds by steps modifying dislocation density and average distance of pinning points; finally the growth stops when cells reach a size comparable to that of the corresponding PF zone.

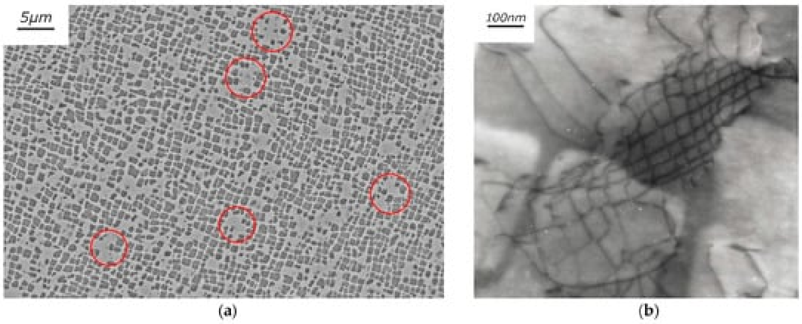

Figure 2. PWA 1483 superalloy. Precipitate free zones (PFZ) are indicated by red circles (**a**). The TEM micrograph in (**b**) displays a network of dislocations inside a PFZ. Figure is taken from [18].

Today, grain boundary engineering (GBE) represents an interesting field of research that could contribute to the reduction of inter-crystalline damage in superalloys and, in general, to the improvement of their mechanical properties [20]. Annealing twin boundaries are very important for GBE owing to their low energy. Jin et al. [21] reported an interesting result about the correlation of the annealing twin density in Inconel 718 with grain size and annealing temperature. These investigators showed that twin density mainly depends on the original one in the growing grains, but not on the temperature at which they grow, namely no new twin boundaries form during the grain growth process.

2. Manufacturing Parts of Complex Geometry

An aspect of relevant importance for these materials is the possibility of manufacturing aeronautic components of complex geometry. Owing to their high hardness and poor thermal conductivity, the machining of superalloys is challenging and novel techniques (e.g. see [22][23][24][25][26][27][28]) have been investigated. For example, laser drilling and electrical discharge machining are used to produce effusion cooling holes in turbines blades and nozzle guide vanes [22]. Recently, there is an increasing interest of aeronautic industry in the use of Additive Manufacturing (AM) for the production of Ni-base high-temperature components. Among the different AM technologies selective laser melting (SLM) and selective electron beam melting (SEBM) are the most used and investigated because enable the preparation of almost fully dense metal parts of complex shape, starting from a computer-aided design (CAD) model [29][30][31][32][33][34][35][36][37].

Components manufactured through SLM exhibit excellent mechanical properties and a strong anisotropy. The directional heat flow during the process leads to the growth of columnar grains with a strong crystalline texture, which especially affects creep resistance and fatigue life [38][39][40][41][42][43]. The (001) crystallographic direction has the lowest stiffness involving better creep resistance and longer fatigue life, thus it is optimal for the upward direction in gas turbine blades.

Experiments of Popovich et al. [42] on Inconel 718 demonstrated that suitable SLM process parameters and laser sources allow to control the material anisotropy with great design freedom. The same approach can be also applied to design functional gradients with selected properties and/or heterogeneous composition depending on the specific application.

SEBM is characterized by very high solidification rates and thermal gradients, leading to relevant microstructure refinement with primary dendrite arm spacings two orders of magnitude smaller than as-cast single crystals. A drawback is represented by internal stresses arising from high cooling rates which can cause crack formation, as observed by Parsa et al. [44] in the CMSX-4 superalloy.

3. Welding of Superalloys

Cracks may form in Ni-base superalloys during both production process and service life under severe conditions of high temperature and stress in an extremely aggressive environment. Such defects are generally repaired through welding [45], with significant economic saving.

Welding should preserve, as far as possible, the original microstructure without relevant residual stresses in the molten (MZ) and heat affected (HAZ) zones, and chemical segregation changing the composition of γ and γ' phases. During the solidification the microstructure of the MZ is affected by dendritic growth and solute partitioning, with the consequent formation of metallic compounds such as carbides, borides etc. Another critical aspect is connected to the presence of low melting compounds which could lead to micro-cracks after post-welding heat treatments (PWHTs) [46] and local residual stresses in the MZ [47][48].

Some welding technologies are already mature, such as Transient Liquid Phase (TLP) bonding, developed by Pratt & Whitney Aircraft and based on Ni-Cr-B or Ni-Cr-B-Si fillers; Activated Diffusion Bonding (ADB) developed by General Electric with fillers of composition close to that of the reference superalloy and with the addition of B and/or B+Si; Brazing Diffusion Re-metalling (BDR) developed by SNEMECA with fillers with two components: one of a composition close to that of the alloy, and the other, in small quantities, containing elements such as B and Si which lower the melting point. The advantage of BDR is the slow isothermal solidification that makes easier the interdiffusion of the elements and guarantees a composition of the joint similar to that of the superalloy. Unfortunately, the costs of the above techniques are very high.

In recent years, research has been focused on high energy density welding techniques such as Laser Welding (LW) [49][50][51][52] and Electron Beam Welding (EBW) [53][54][55][56][57], which provide greater penetration depth, reduced HAZ and minimal distortion, if carried out with a high pass speed. These techniques represent simpler and cheaper solutions for repairing cracks in Ni-base superalloys. Thanks to a reduced thermal input, high energy density welding techniques enable to prepare joints with narrower seams and HAZ. Through LW and EBW the superalloy microstructure is changed at little extent, so that residual stresses, micro-cracks, porosity and other defects in the junction are limited. In spite of that some microstructural modifications always occur in MZ of the welded joints. An example of microstructural changes occurring in the MZ is given in Figure 3 [57]. The directionally solidified IN792 superalloy has been EB welded and in the MZ round γ' particles of very small size from 20 to 40 nm can be observed. After solidification these particles nucleate below solvus (~1120 °C) and, because of the rapid cooling to room temperature, have short time to grow.

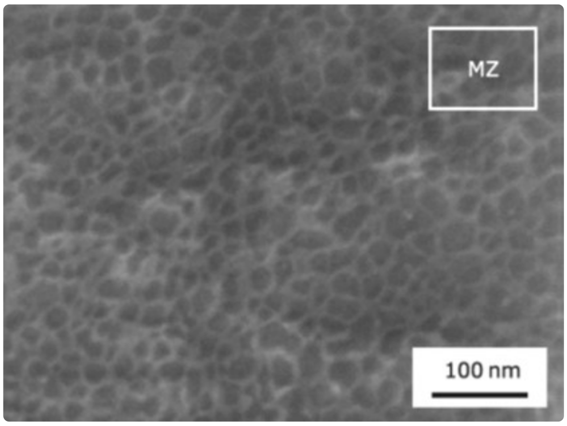

Figure 3. EBW joint in IN792 superalloy: round γ' particles with size in the range 20-40 nm are observed in the MZ. The micrograph has been taken from ref. [57].

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