Microstructural characterization of plasma nitrided nickel based superalloys: nitriding response of γ matrix and γ' precipitates

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1. INTRODUCTION

Thanks to their good fatigue and creep properties at high temperature, nickel based superalloys are widely used in pressurized water heat exchangers or in the hottest sections of aeroengines or industrial gas turbines. Superalloys typically have a matrix with an austenitic face centered cubic (FCC) crystal structure called γ phase. In addition to the hardening by substitution solid solution of the γ phase, some Ni-based superalloys gain their impressive mechanical properties from the presence of a high fraction of ordered $L1_2$ face-centered cubic γ′ precipitates (Ni_3(Ti,Al,Ta) type). However, increasing their resistance to very aggressive conditions (wear, fretting, oxidation, corrosion, higher temperatures and pressures, higher mechanical solicitations…) is still challenging and plasma nitriding could be a potential efficient surface treatment to enhance the life time and to fulfill the expected conditions of operations of the next generation gas turbines.

In previous studies [1] and [2], plasma assisted nidriding of various Ni-based superalloys, polycrystals (Haynes230, Udimet720Li, N18) and the single crystal MC2, presenting from 100 vol.% to 30 vol.% of γ phase, has been performed at moderate temperature (400°C) to shed light on the specific response of the different phases (γ, γ') under nitriding. Macroscopic characterizations, via glow discharge optical emission spectroscopy (GDOES) and X-ray diffraction (XRD), have evidenced the formation of nitrided layers with ~25-30 at.% N at the surface and thickness varying from ~3 µm to ~7 µm depending on alloys. In all alloys, formation CrN was revealed by XRD. The γ phase was also shown to be nitrided as in austenitic stainless steels to form the expanded austenitic FCC phase γ_N, a nitrogen insertion solid solution, with ~25 at.% N. On the other hand, γ' precipitates was found to exhibit different behaviour depending on alloys: in the studied polycrystals, γ' seem nitrided in similar proportion than the matrix γ, while, in case of MC2, γ' seem not or poorly nitrided. The present work is focused on characterization of the structural and chemical modifications induced by plasma nitriding at the submicrometric/nanometric scales. Characterization by SEM and TEM, coupled with HAADF-STEM, EELS and EDS have thus been performed to confirm the macroscopic results, but also to determine the distribution and the size of the CrN formed and the chemical and structural changes of nitrided γ' precipitates due to nitrogen incorporation. All these results should provide important information especially to explain the different nitriding responses of the Ni based superalloys observed at the macroscopic scale.

2. RESULTS

3.1 Materials and experimental details

Two representative superalloys have been studied: Udimet 720Li and MC2, for which γ′ precipitates are *a-priori* respectively nitrided and not from previous studies. The polycristaline Udimet 720Li superalloy contains a multimodal γ′ distribution with primary, secondary and tertiary precipitates of various sizes (~few µm, ~100 nm and ~10 nm respectively). The MC2 monocristal microstructure consists of cuboidal γ' precipitates of around 400 nm separated by ~40 nm thick γ channels. Nitriding was performed under 8 Pa of 60% vol. N_2 / 40% vol. H_2 during 4 hours at 400°C in a home-fabricated RF plasma assisted thermal nitriding reactor. SEM cross sectional observations have been realized on a JEOL 7001F-TTLS equipped with EDS. TEM plane-view specimens have been prepared by mechanical thinning and double jet electropolishing. TEM observations, HAADF-STEM imaging and EELS were performed with a JEOL 2200FS equipped with an omega energy filter.

3.2 SEM/TEM characterizations and chemical analysis

SEM observations and EDS analysis clearly confirm the different nitriding response of γ' in Udimet 720Li and in MC2 (Figure 1). The micrometric primary γ' precipitates are actually nitrided and semi-quantitative analysis indicates that concentration of nitrogen is as high as in the matrix (~25 at.%). On the contrary, γ' precipitates in MC2 is shown to not incorporate nitrogen. TEM observations and EELS analysis, confirm that nitrogen has been inserted not only in micrometric primary γ' precipitates but also in secondary γ' precipitates

(~100 nm) in Udimet 720Li, resulting in the loss of the ordered $L1_2$ structure and the formation of at least two different phases which are still to be determined. HAADF-STEM imaging (Figure 2) was used to evidence the chemical heterogeneity of the nitrided γ matrix which could be interpreted as a mix of expanded γ_N phase and CrN nitrides. The darker clusters could correspond to CrN precipitates of few nanometers.

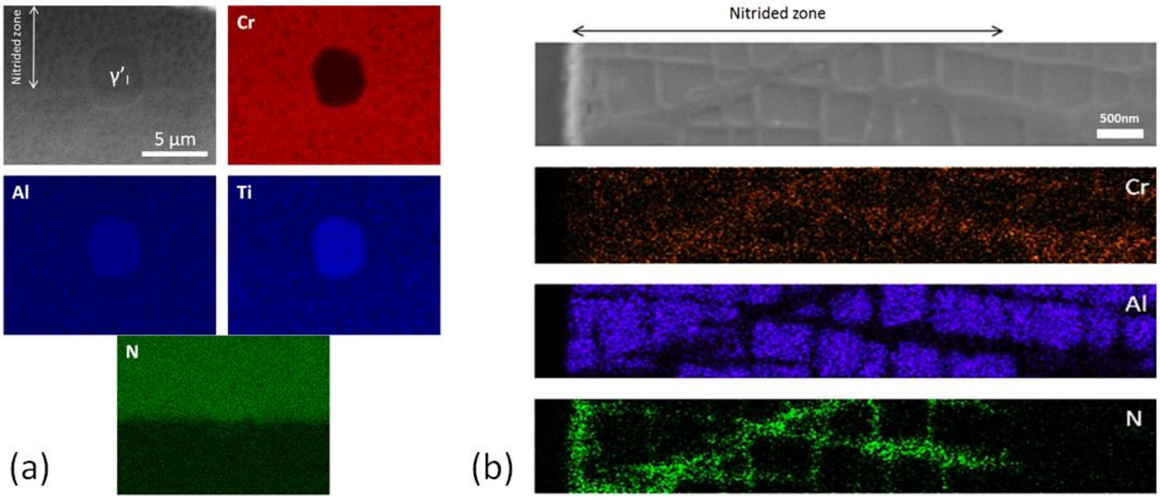

Figure 1. Secondary electrons SEM image and corresponding EDS element maps of (a) nitrided Udimet720Li and (b) nitrided MC2

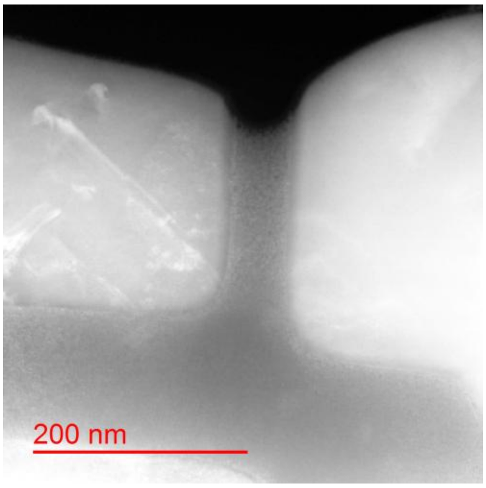

Figure 2. HAADF-STEM image of nitrided MC2

3. CONCLUSION

Structural and chemical characterizations of two plasma nitrided Ni-based superalloys have been performed using different imaging and spectrometry techniques. It has been shown that the γ matrix of both alloys is nitrided with similar N concentration and form expanded austenite and nanometric CrN precipitates. This work has directly confirmed that the nitriding response of γ’ precipitates depends on alloys: γ’ is not nitrided in MC2, while, in the case of Udimet 720Li, γ’ is nitrided with similar N concentration than the surrounding matrix γ_N and form two phases. No evident proof, like formation of new phase at the interphases, acting as diffusion barrier for instance, has been found to explain why γ' precipitates are not nitrided in MC2. However, determination of the nature of the phases formed in the nitrided γ’ in udimet 720Li, via complementary characterizations using EFTEM or EDS in STEM for instance, should help to understand the two different nitriding responses of the γ' precipitates.

REFERENCES

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