Thermochemical Treatments of Alloys 16NiCrMo13 and 23MnCrMo5 : the roles of carbon and nitrogen on metallurgical response to carbonitriding

W. Dal'Maz Silva [1,2] J. Dulcy [1] G. Michel [2] S. Thibault [3]
P. Lamesle [2] T. Belmonte [1]

[1] Institut Jean Lamour, Nancy, France

[2] Institut de Recherche Technologique M2P, Metz, France

[3] Safran Group, Paris, France

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The source material for this presentation has already been authorized by the partners for publication.

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Partners

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Introduction

The need of materials combining core toughness and both fatigue and wear resistances has lead to the development of several surface treatment techniques.

Although carbonitriding has been known for most of the last century, the role of nitrogen on mechanical properties of treated parts remains still unclear.

The present work seeks for better understanding on the role of this element as well the one of carbon in the metallurgical responses of alloys 16NiCrMo13 and 23MnCrMo5.

Source: Safran Group.

Speech: The need to combine both toughness and fatigue and wear resistances led to the development of several surface modification processes, including carbonitriding. This process has been known for long time but still some points regarding the role of nitrogen keep unclear. This work aims to provide a segregate approach in order to investigate the behavior of two low alloy steels when submitted to carbonitriding: 16NiCrMo13 and 23MnCrMo5. Here in the right we have some examples of power transmission components requiring proper surface treatment for operation.

Experimental conditions

Treatments for alloys 16NiCrMo13 and 23MnCrMo5:

Process		Steps (hours) at 1173 K.		
		Carburizing $CO + H_2$	Diffusion $N_2 + H_2$	Nitriding $NH_3 + N_2 + H_2$
Carburizing	**C0**	2	4 (16NiCrMo13) 3 (23MnCrMo5)	-
Nitriding	**N0**	-	-	3
Carbonitriding	**CN**	2	1 (16NiCrMo13) 0 (23MnCrMo5)	3

Treatments were followed by room temperature oil quench which was continued in liquid nitrogen.

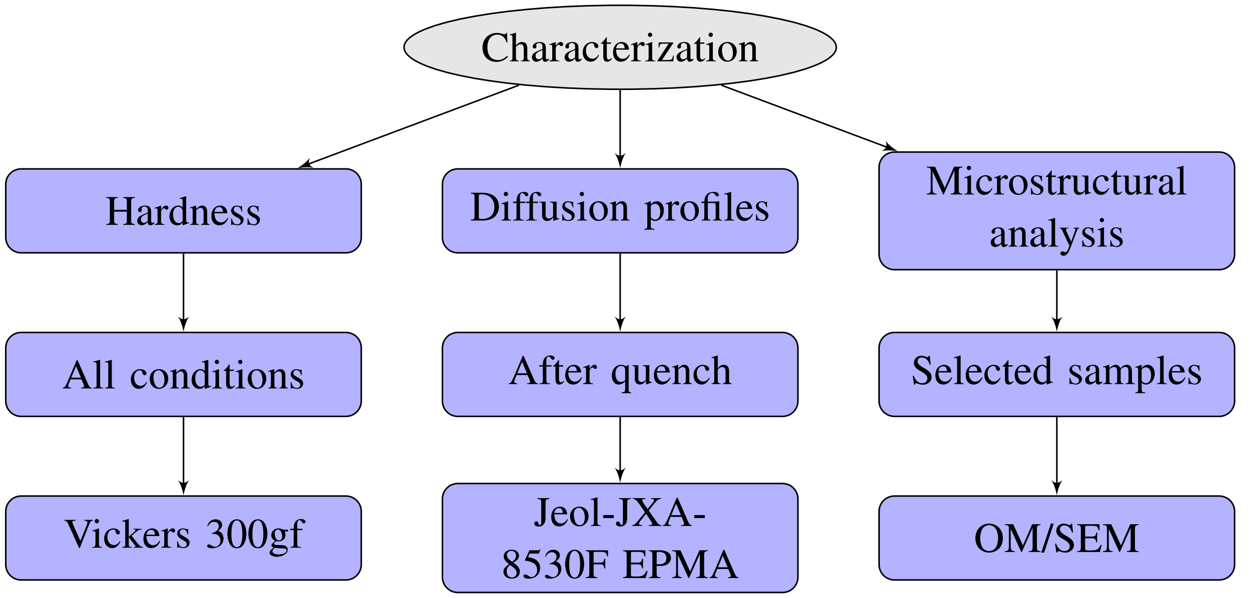
Tempering was carried during 70 hours at 453 K and also 18 hours at 573 K.

Speech: The comportment of these alloys has been studied from the standpoint of three thermochemical treatments in the austenitic field at 1173K: carburizing, nitriding and carbonitriding. Along this presentation we will note carburizing for C0, nitriding for N0 and carbonitriding for CN. The total diffusion time for each interstitial element has been kept constant in order to allow comparisons of the obtained diffusion profiles between treatments. Carbonitriding, apart from the common atmospheric pressure industrial practice, is carried out as a sequence of carburizing and nitriding steps.

All treatments were followed by room temperature oil quench with additional cryogenic treatment in order to minimize retained austenite fractions.

Two different tempering treatments were employed in the study, as presented on screen.

Materials characterization

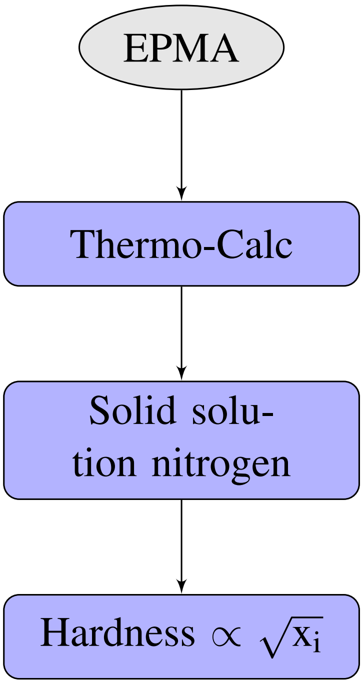


Speech: Regarding characterization, mechanical properties were assessed through Vickers micro-hardness measurement, which was carried for samples of all types of thermochemical treatment and post-treatment condition, it means, after oil quench, cryogenic treatment, first and second tempering conditions.

Diffusion profiles of carbon and nitrogen were obtained by electron probe micro-analyses and compared to the response of submission to different treatment conditions.

In order to explain the mechanical behavior of some samples, optical and scanning electron microscopy investigations were conducted.

Response to quench: effect of interstitials



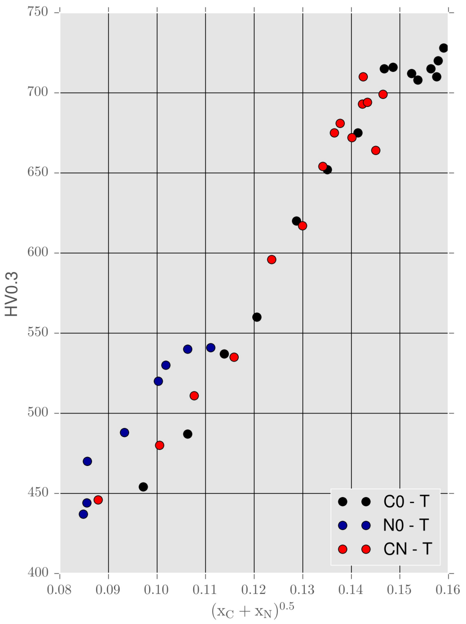
- Thermo-Calc™ was used in order to make an estimation ot the solid solution nitrogen in austenite before quenching.
- Linear dependence of hardness after quench with the square root of the mole fraction of interstitial elements in solid solution.
- Hardness plateau mainly linked to non-transformed austenite (even after liquid nitrogen quenching).

Speech: Diffusion profiles obtained by micro-analyses were used as input for local equilibrium computations along the depth in the condition that samples were just before quenching.

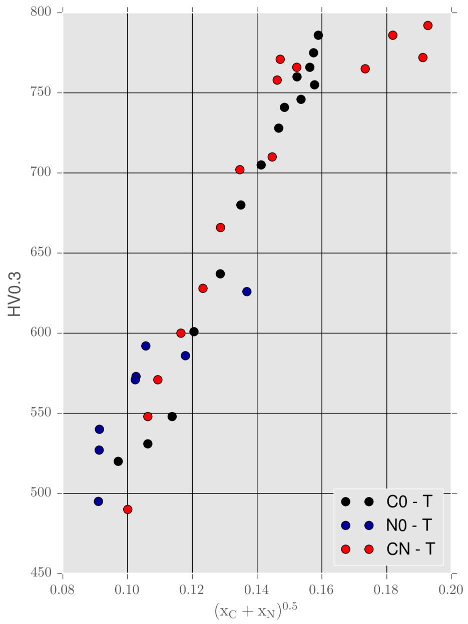
From this equilibrium we estimate the consumption of solid solution chromium (mainly, but also Mn and Mo) due to the precipitation of MN nitrides and thus obtain the chemical composition of the quenched austenite. Since these nitrides are rather stable at low temperature, further analyses will neglect their decomposition due to kinetics of dissolution in solid state and this remaining impoverished austenite with limited nitrogen content is assumed to form the martensitic/bainitic structure.

Using the total residual content of interstitials, hardening is analyzed and shows a quite good linear dependence on the square root of this quantity. After this well behave region, a hardness plateau is formed, which is mainly due to residual austenite.

Alloy 16NiCrMo13



Alloy 23MnCrMo5



Speech: In these figures we have the hardness after quench and cryogenic treatment as a function of the square root of the total interstitial content (comprising carbon and free nitrogen). As we may now evidence, a reasonable linear behavior is observed, regardless the slight microstructural gradient. showing a major martensite hardening control. In richer zones (to the right) limited hardening linked to residual austenite is put into evidence.

Tempering effects: role of carbon and microstructure

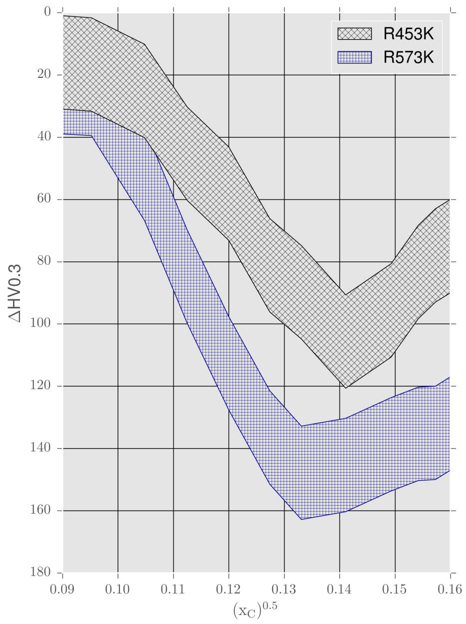
$$\boxed{\text{As-quenched hardness}} \rightarrow \boxed{\text{Temper hardness}} \rightarrow \boxed{\Delta\mathrm{HV} \text{ vs. } \sqrt{x_i}}$$

- Alloy 16NiCrMo13: retained austenite decomposes into ferrite + carbides which leads to a maximum hardness loss below surface.
- Contributions of both microstructure and composition are taken into account, although plots are obtained in function of composition.

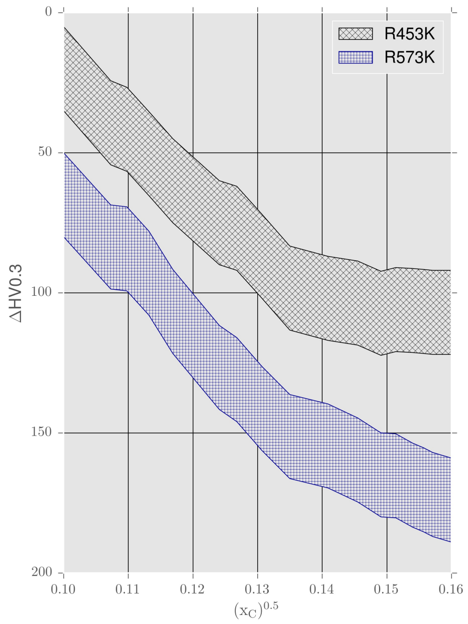
Speech: Hardness losses after tempering were also investigated from the standpoint of composition or microstructural gradient. In this case the local morphology plays an important role and cannot be neglected.

Tempering effects: role of carbon and microstructure

Alloy 16NiCrMo13



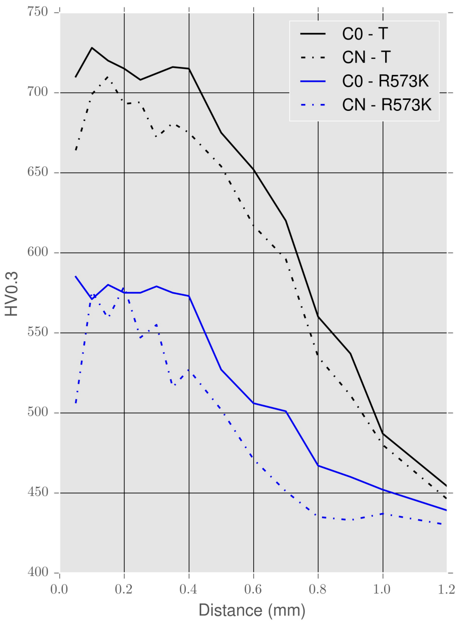
Alloy 23MnCrMo5



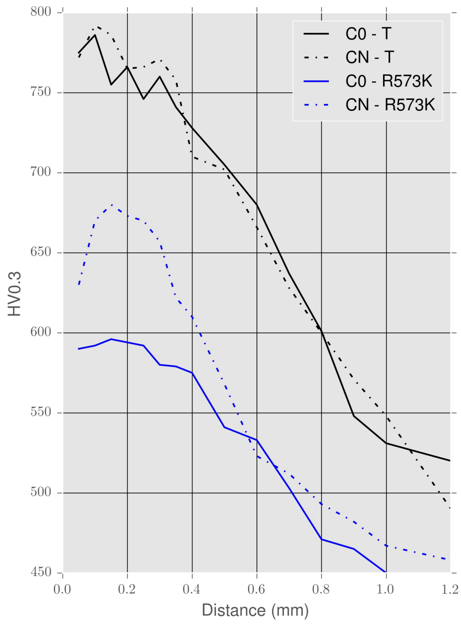
Speech: Hardness drop as a function of chemical composition and position has also been investigated. Results show that alloy 16NiCrMo13 which possesses higher tendency to retain austenite after quench (even after liquid nitrogen) also show highest hardness loss below surface. This is linked to the fact that the decomposition of retained austenite produces a higher hardness microstructure composed of ferrite and carbides. For alloy 23MnCrMo5 hardness loss is proportional to original martensite hardness, as expected.

Carburizing vs. Carbonitriding

Alloy 16NiCrMo13

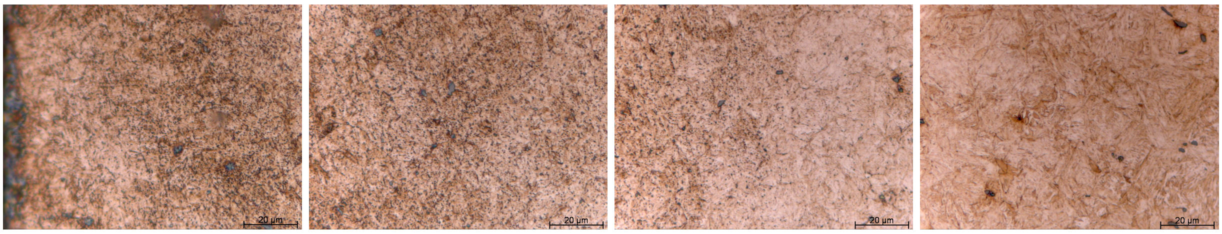


Alloy 23MnCrMo5



Speech: Now we compare the hardness losses for carburizing and carbonitriding. Alloy 16NiCrMo13 show similar behavior to both thermochemical treatments, the difference been the lower carbon content obtained close to the core for carbonitriding. By the other hand, alloy 23MnCrMo5 shows better retained surface hardness when carbonitrided than when carburized. At this point it must be said that this alloy has been treated to high levels of surface nitrogen, up to 0.9%wt which lead to a strong consumption of chromium and formation of high temperature nitrides. Although typically these nitrides are said to play no role in hardening due to their size and misfit with the matrix, at such high density a composite hardness, that of matrix and nitrides, is measured in reality.

Carbonitriding: behavior of alloy 23MnCrMo5

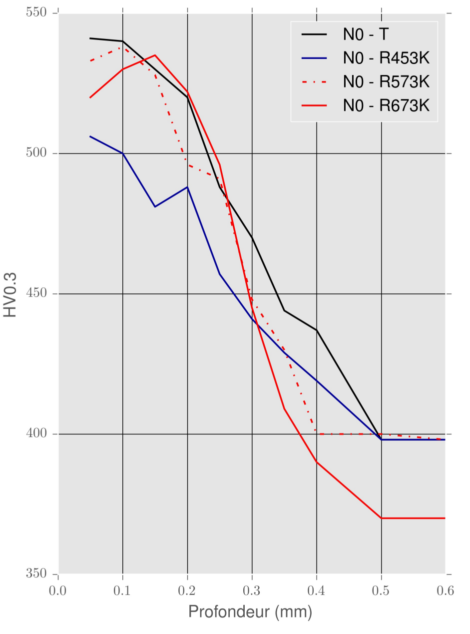


0.05 mm	0.15 mm	0.25 mm	0.45 mm
0.90 % wt N	0.75 % wt N	0.37 % wt N	0.05 % wt N

Speech: This composite hardness may be justified by this sequence of micrographs showing a high density of precipitates close to the surface with decreasing quantity toward the core. For information local nitrogen content is also given.

Secondary precipitation: nitriding of alloy 16NiCrMo13

- Hardness drops when tempering is conducted at 453 K for long duration (70 hours) but at 573 K, as-quenched hardness is almost preserved in surface after 18 hours of tempering, although decreases steeper to the core.
- Even at 673 K (hold during 18 hours) surface hardness is kept, although important core hardness decrease is measured.



Speech: Aiming to investigate the role of nitrogen alloy 16NiCrMo13 has been nitrided in the austenitic field, quenched and tempered. At 453K tempering reduces hardness in the whole treated depth. Increasing tempering temperature to 573K lead to the same surface hardness as the quenched sample with steeper hardness decrease toward the core, showing that it was tempered while the outermost surface had a secondary precipitation. Even at 673K surface hardness was conserved with even higher hardness drop in the core, confirming the secondary precipitation proposed.

Conclusion and perspectives

Hardening responses as a function of total **interstitial content** lead to the critical amount of these elements implying in **non-transformed austenite** in alloy 16NiCrMo13 even after cryogenic treatment. Working below these levels is suggested as a means to possibly achieve better fatigue performance.

Alloy **23MnCrMo5 shows higher remaining hardening after temper** when highly enriched with nitrogen. The mechanism which lead to this performance needs further investigation.

Although the effect of nitrogen could not be directly identified from carbonitriding, **nitriding** results suggest that TEM analyses may allow the identification of **secondary precipitation** leading to better understanding of carbonitriding for the studied alloys.

Speech: This work has shown the validity of Norstrom approach to as-quenched martensite hardness even when extended to nitrogen. It also made it possible to determine the fraction of interstitials above which non-transformed austenite is kept even after cryogenic treatment. Alloy 23MnCrMo5 showed better hardness when highly enriched in nitrogen due to a composite hardness produced by a high density of MN nitrides. Nitriding of alloy 16NiCrMo13 showed that a secondary tempering precipitation needs to be investigated in order to provide better understanding of the role of nitrogen in carbonitriding.

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PENSER LES MATÉRIAUX DE DEMAIN

Thank you for your attention!