Effect of applied chemical heat treatment on the structure and properties of low-alloy Cr-containing iron powders

Desislava Mincheva[1,*], *Plamen* Petrov[1]

[1]Technical University of Varna, Bulgaria

Abstract. The article presents experimental results on the application of thermal oxidation or low temperature gas nitrocarburizing (LTGNC) of Ecosint powders sintered under industrial conditions. Surface hardness HRB and microhardness (HV0.1) were studied. A structural analysis was carried out and the corrosion resistance of the alloys was investigated. Conclusions were made on chemical heat treatment performed on structure and mechanical properties of the investigated alloys.

1 Introduction

Powder metallurgical parts are widely used in various industries. New powders are introduced to meet the requirements for minimal concentration of alloying elements. EcosintC and EcosintHighCrA powders developed by “PometonSpA” are powdered alloys designed to promote sintering [1,2]. Numerous publications have provided data on the behavior of powders during sintering. According to preliminary studies, the combination of alloying (Cqr, Mo, Mn, Ni, Cu) elements results in a significant reduction in the critical cooling rate. It is reported that the hardness achieved after industrial processing is 90HRB for cooling rate of 0.25^{o}C/s and 43HRC after cooling at 1.5^{o}C/s. The microstructure observed under those conditions is fully martensitic [3,4]. Based on their characteristic properties, they are quite widely used in the production of cutting tools, machine parts, small-sized gears, etc., which are subject to requirements for high hardness, wear resistance and corrosion resistance. Previous research by the authors has found out that when these powders are sintered in the industrial conditions of our companies, optimal mechanical properties are not achieved due to the impossibility of meeting all the sintering cycle specifications suitable for Ecosint powders [6]. For this reason, it has been possible to combine the sintering technology with subsequent chemical heat treatment or heat treatment to improve the resulting characteristics of the sintered parts.
Chemical heat treatment technologies, such as carbonitriding, nitriding and nitrocarburizing in gas atmosphere are known to be used for hardening sintered parts. In the field of development and application of these technologies for different types of iron-based sintered alloys, the authors have many years of experience. In many research papers authors report their results about the application of the low temperature gas nitrocarburizing (LTGNC) in NH_3 and CO_2 atmosphere, upon different PM – materials on the basis of Fe-powders [7-9].
This paper aims *at* investigating the influence of low-temperature gas nitrocarburizing (NTCNC) and thermal oxidation at different modes on corrosion behavior, surface hardness and microhardness of powders ECOsint.

2 Materials and experimental procedure

Following commercial” Pometon Powders S.p.A.” pre alloyed iron base powders were used:

- ECOsint C (1.4%Cr, 1%Cu, 1%Ni)
- ECOsintHighCrA (2.0%Cr)

Powders were uniaxially compacted at compacting pressure of 600MPa into 10x10x50mm compacts.
Sintering was performed in industrial conditions in a tube furnace at T=1140ºC, for 40min, in a protective environment of 85%N_2:15%H_2 and furnace cooling.
The sintered specimens were nitrocarburized using low temperature gas nitrocarburizing (LTGNC) method performed at T=560^{o}C (CARBONIT process), for 30 and 60 min., followed by furnace cooling. The process was carried out in a laboratory shaft furnace with a volume of 2 dm^3, in ammonia and carbon dioxide at an HN_3/CO_2=7.5/1 ratio.
The process of thermal oxidation is carried out in furnace at a temperature of T=450°C for 15 and 30 min. The samples are cooled in oil. The corrosion behavior of the chemical heat treated samples was investigated by applying an express method - a "drip sample" with a saturated solution of copper sulphate $CuSO_4$ in water. The microstructure of the alloys after sintering and chemical heat treatments was observed using a metallographic microscope "Neophot-2" and a digital

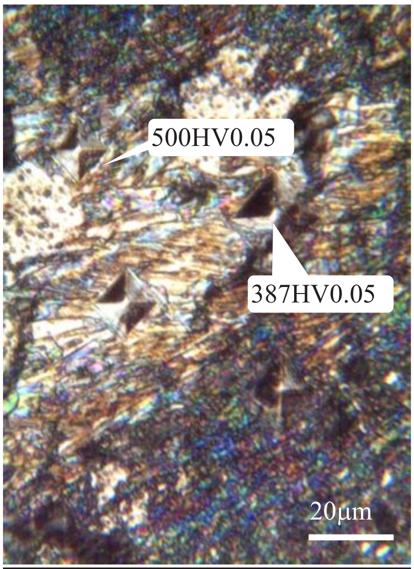
* Corresponding author: mincheva_d@abv.bg

https://doi.org/10.1051/matecconf/201928706004

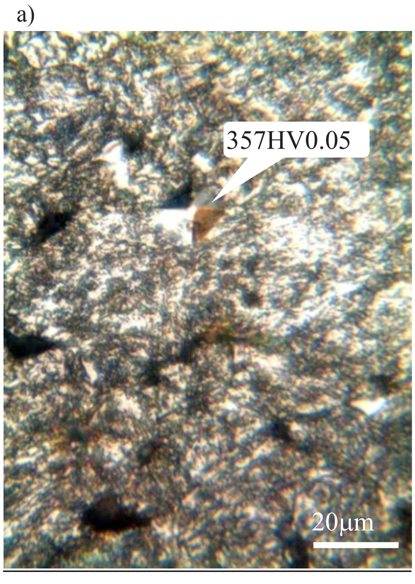
camera specialized for metallographic analyzes "ProgRes CT-3".
To determine the surface hardness of the samples Rockwell hardness Scale B (HRB) and Vickers HV0.1 were used.

3 Results and discussion

In Figs. 1a, b the microstructures of the sintered samples is shown. Microstructures of the surface layers of test bodies from ECOsint C and ECOsintHighCrA after chemical heat treatment are shown in Figs.2, 6, 7, 8.
In Figs. 4, 5 the surface hardness HRB and microhardness HV0.1 after sintering and different modes of heat treatment are shown. The results of the drop samples made to assess the quality of cathodic protection of the surface layers after gas nitrocarburizing and thermal oxidation are shown in Fig. 8.



a)

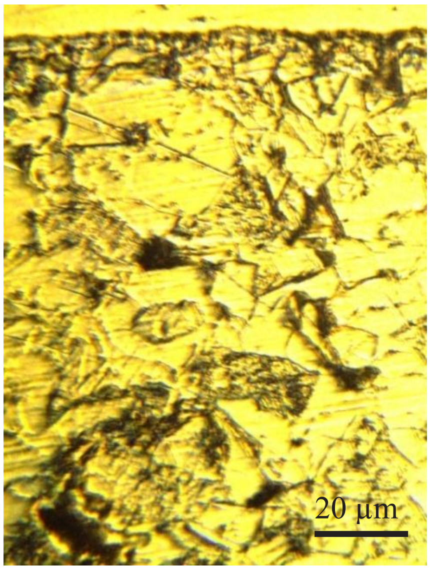


b)

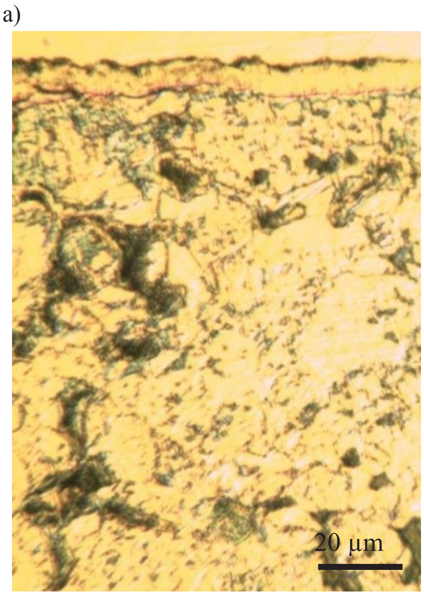
Fig. 1. Microstructures of the sintered samples: a) EcosintC; b) EcosintHighCrA

<u>After nitrocarburizing process</u>

The microstructural analysis of the investigated alloys after low temperature gas nitrocarburization shows that surface layers of ε-nitride and γ'-nitride phases with a thickness of 2-7.7μm are formed. It is observed that with an increase in saturation time, the average layer thickness increases. The average thickness of the carbonitride zone in the lower alloyed sintered EcosintC alloy is greater – 3,5 and 7,7μm, respectively, at a saturation time of 30 and 60 minutes, compared to that of EcosintHighCrA - 2 and 4.6μm (Figures 2, 6). This confirms the assertions of various authors that with a larger quantity of the alloying elements the diffusion of nitrogen and carbon is made difficult and thinner layers are formed [4]. The carbon nitride layers formed are relatively dense, with the results of the drip test with copper sulphate (significant shrinkage with characteristic stains being observed only for the



a)



b)

Fig. 2. Microstructures of samples EcosintC x500: a) LTGNC, 30 min; b) LTGNC, 60 min

 https://doi.org/10.1051/matecconf/201928706004

specimen samples without further chemical heat treatment) suggesting good cathodic protection of the products from slightly aggressive environments. The microstructure in depth of the base material corresponds to that obtained after sintering, with a predominantly fine pearlite-sorbite structure, with lighter, possibly beinitic-martensite zones. Surface micro-hardness after chemical heat treatment is 541 to 725HV0.1 (Fig.5) This corresponds to a 64-70HRC table alignment. These values exceed the quoted data for the investigated alloys cooled by their prescribed cooling rate [2] and are evidence that successful low-temperature gas nitrocarburizing can be used to compensate for the insufficient surface hardness of these alloys after their sintering in industrial furnaces not providing the cooling rate prescribed for the alloy.

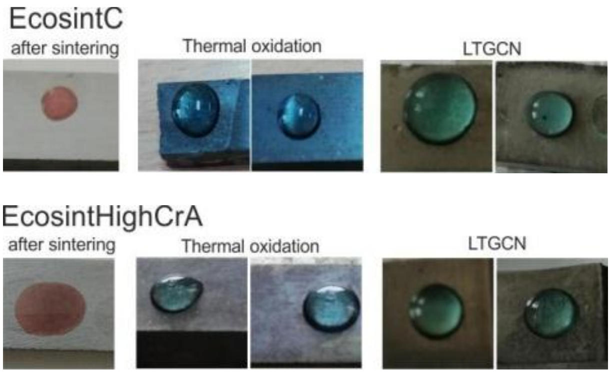


Fig. 3. Results after application of a drop of copper sulphate ($CuSO_4$) on the samples

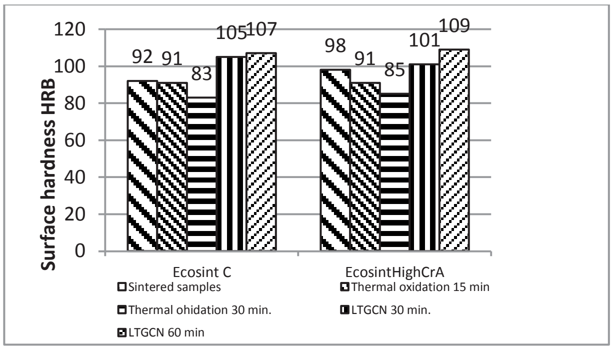
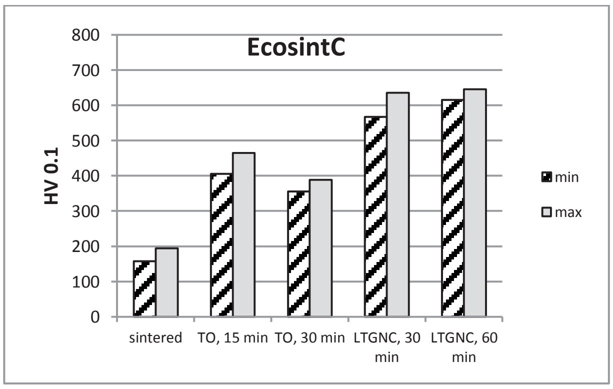
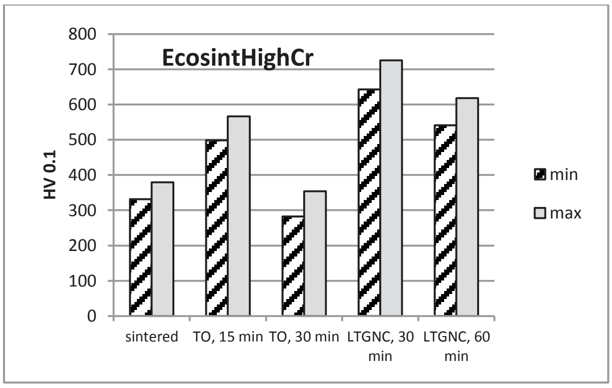


Fig. 4. Surface hardness HRB

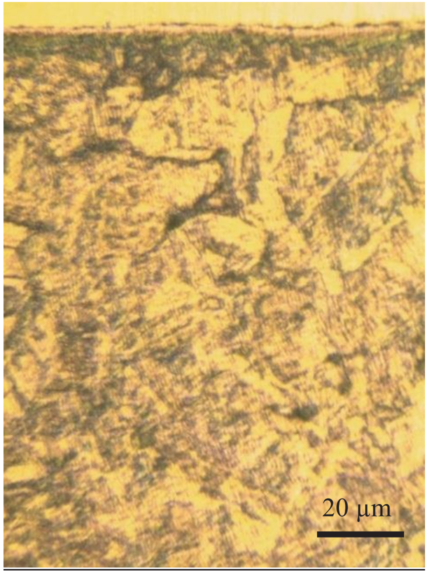


a)

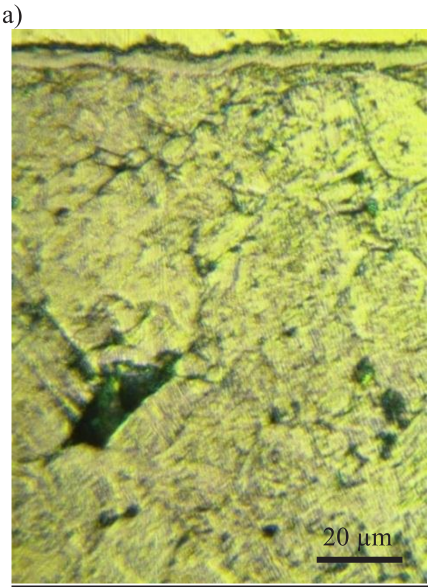


b)

Fig. 5. Microhardness HV0.1



a)

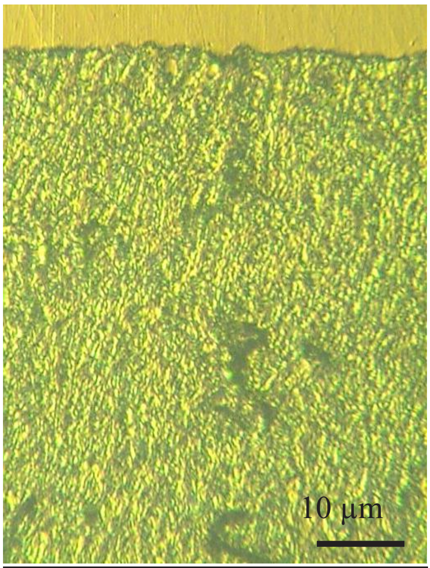


b)

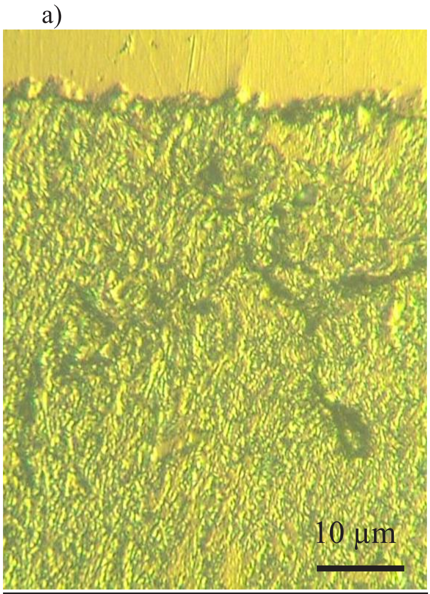
Fig. 6. Microstructures of samples EcosintHighCrA x500: a) LTGNC, 30 min.; b) LTGNC, 60 min.

<u>After thermal oxidation</u>

Through metallographic analysis of the materials thermally oxidized at different times, the formation of thick, continuous oxide coatings was established. It was found out that significantly thicker coatings (2-3μm) were formed on EcosintHighCrA samples, probably due not only to the retention time but also to the alloying elements contained in the metallic powder composition. The measured surface microhardness is in the range of 350-500HV0.1. For both types of materials, the 30-minute TC mode results in a significant reduction in the surface hardness HRB (fig.5). On the other hand, when examining the color change of a drop of CuSO4, a drop on the specimens showed that the formed oxide layers created good cathodic protection against poorly aggressive media.

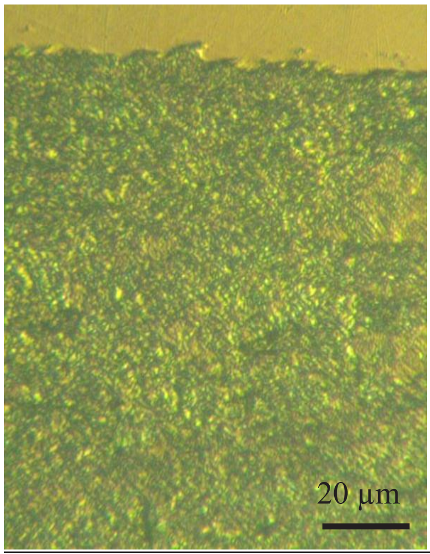


a)

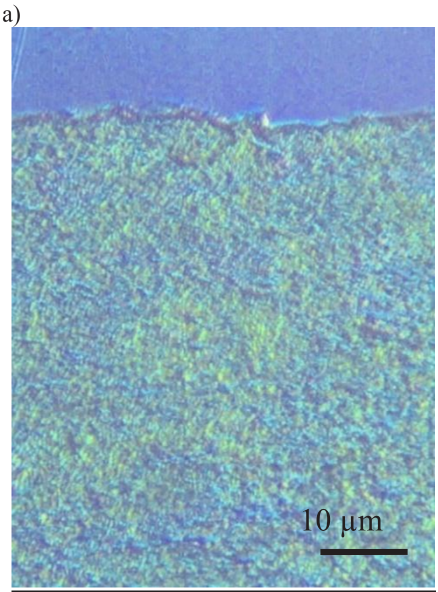


b)

Fig. 7 Microstructures of samples EcosintC
a) thermal oxidation 15 min.; b) thermal oxidation 30 min



a)



b)

Fig. 8 Microstructures of samples EcosintHigh CrA
a) Thermal oxidation 15 min.; b) thermal oxidation 30 min

4 Conclusions

1. Low-temperature nitrocarburizing at 560°C in the CARBONIT process lasting 30 or 60 minutes can be successfully applied to increase the surface hardness and, respectively, wear resistance of sintered alloys of the Ecosint C and EcosintHighCrA type
2. The comparatively thin carbonitride layers combined with a relatively softer base obtained upon cooling after sintering at a lower rate than that prescribed for the alloy suggest the use of this chemical thermal treatment for articles operating at lower contact loads to avoid braking the thin rigid surface layer;
3. When using the chemical heat treatment as a technology for enhancing the corrosion resistance of Ecosint C and EcosintHighCrA alloys, a thermal oxidation or gas nitrocarburizing regime of 30 minutes should

be selected and if we aim for greater surface hardness and wear resistance, a 60 min. gas carbonation regime is preferred.

4. Some advantages of thermal oxidation are lower temperature, shorter saturation times, lower equipment cost and gaseous atmosphere saturation, and it should be recommended as a technology to increase the corrosion resistance of parts in poorly aggressive environments, when there is no requirement for high mechanical strength and abrasion resistance.

References

1. http://www.pometon.com/dettaglioNews_eng.php/id_news=23
2. https://www.pm-review.com/ecosint-the-new-high-performance-steel-powder/
3. S. Bueno, S.Saccarola, A. Karuppannagonder, EUROPM2011, Spain (2011)
4. S.Saccarola, S. Sainz. Adv. In Powder Met & Part Mater **10**, 52 (2009)
5. R.M. German, *Powder metallurgy science: Second edition*, (Princeton, New Jersy, USA, 1994)
6. D. Mincheva, P. Petrov, Annual Journal of TU, Varna, **1,** (2018)
7. S. Charizanova, G. Dimitrov, E. Rousseva, V. Marcov, Journal of Materials Processing Technology **77** (1998)
8. R. Rusev, S. Harizanova, E. Ruseva, Hardening of PM materials on the basis of Fe by chemical heat treatment technologies, Proc. of Deformation and Fracture in structural PM materials, International PM conference, Stara Lesna, **2**.(2002),
9. S. Harizanova, I. Ivanov, Nitrocarburation of ferrocarbonic porous alloys, steel alloyed with Cu and Mn, International Scientific Journal of Acta Universitastis Pontica, Euxinus, **1**, (2002)