INFLUENCE OF POROSITY ON LOW PRESSURE CARBURIZING OF LOW ALLOY SINTERED STEELS

E. Santuliana, A. Molinari, C. Menapace

Abstract

The effect of low pressure carburizing on two low alloyed sintered steels having different amounts of interconnected porosity was investigated. To prevent overcarburizing, both warm compaction and surface densification by shot peening were experimented. Overcarburizing causes precipitation of the grain boundary carbides in 0.8% Cr-0.4% Mn steel and the formation of retained austenite in the 0.9% Ni-0.9% Mo one. In the presence of mostly closed porosity, as well as a densified surface, low pressure carburizing forms a homogeneous case, which is slightly harder and thinner in the Cr free steel.

Impact toughness of the surface densified steels is quite similar (10-12 J), whilst the warm compacted Cr steel has a higher toughness than the Ni-Mo one, because of the more ductile fracture behavior provided by the microstructure.

Keywords: sintered steel, low pressure carburizing, overcarburizing, tempering and solution annealing treatment

INTRODUCTION

Low pressure carburizing (LPC) is a consolidated technology for the surface treatment of wrought steel [1-3]. The dissociation at high temperature (900-1000°C) and in vacuum (15 mbar) of either acetylene or propane produces a carburizing gas made of carbon and hydrogen (acetylene) or carbon, hydrogen and methane (propane), which does not contain oxidizing agents. This gas prevents oxidation of steel parts upon heating [4] and during isothermal soaking at the carburizing temperature [5]. Moreover, the use of gas quenching instead of oil quenching reduces the risk of distortion of pieces and may improve the case depth homogeneity [3,6].

Low pressure carburizing might be particularly suitable for sintered steels for two main reasons:
1. porosity increases the surface exchange area, thus enhancing the risk of oxidation of the Cr and Cr-Mn steels when treated in the conventional carburizing atmospheres;
2. quenching oil remains entrapped in the open porosity, and has to be eliminated before tempering for environmental reasons.

However the very high carburizing potential of low pressure carburizing causes overcarburizing of sintered steels with interconnected porosity, promoting the precipitation of grain boundary carbides and the formation of retained austenite in the case [7-9]. This problem can be solved by eliminating the surface porosity by rolling [8,9]. After surface densification, the microstructure of the carburized layers becomes homogeneously martensitic, in particular using propane instead of acetylene as carbon carrier gas [9].

Elena Santuliana, Alberto Molinari, Cinzia Menapace, Department of Materials Engineering, University of Trento, Italy

The influence of the chemical composition of the steel and of the carburizing temperature on the microstructure of the case was investigated by Bengtsson and Marcu [9]. In this study a 1.5% Cr-0.2% Mo steel and a 1.5% Mo steel were carburized at different temperatures, and the influence of chromium on the precipitation of grain boundary carbides was clearly demonstrated.

In a previous work, the authors of the present investigation studied the influence of the interconnected porosity on low pressure carburizing of two sintered steels having the following composition: 1.5% Cr-0.2% Mo (Astaloy CrL) and 0.9% Ni-0.9% Mo-2% Cu [10]. The two steels were processed according to three different routes, to obtain a different porosity: fully interconnected by means of cold compaction, mostly closed by means of warm compaction, no porosity after surface densification by shot peening. Shot peening was used instead of rolling, because of its better flexibility. The results of that work confirm the role of chromium on enhancing the precipitation of carbides and show the possibility of avoiding overcarburizing not only by surface densification, but even by increasing density through warm compaction.

In this work, the same investigation was carried out on two other steels, having a different composition to evaluate the possibility to reduce the effects of overcarburizing. In particular, chromium steels with a lower Cr content, and one Mo-Ni steel without any copper addition were used. The lower chromium content and the absence of copper are expected to reduce the precipitation of grain boundary carbides and the formation of retained austenite, respectively.

Again, three different microstructural conditions were considered: the fully interconnected porosity, the mostly closed porosity and the densified surface by shot peening.

EXPERIMENTAL PROCEDURE

The nominal composition of the powders (Höganäs AB, Sweden) used for the preparation of the specimens is reported in Table 1. A 0.2% graphite was added and the mixture was either cold or warm compacted. Charpy bars (55x10x10 mm) were produced and sintered at 1120°C with 45 minutes isothermal holding in a N_2/H_2 atmosphere.

Tab.1. Nominal composition (wt.%) of the base prealloyed powders.

Material	%Cr	%Mn	%Mo	%Ni
AD4	0.8	0.4	-	-
ALH	-	-	0.9	0.9

Density and porosity were determined according to ISO 2738 and are reported in Table 2.

Tab.2. Density (ρ), total porosity (ε) and open porosity (ε_{open}) of the investigated materials.

Material	ρ [g/cm^3]	ε [%]	ε_{open} [%]
AD4 cold compacted	6.83 ± 0.04	12.9	12.2
AD4 warm compacted	7.38 ± 0.03	6.1	0.5
ALH cold compacted	6.84 ± 0.01	13.0	12.5
ALH warm compacted	7.37 ± 0.07	6.5	1.6

The cold compacted and sintered specimens were shot peened to densify the surface layers. Shot peening was carried out at an intensity of 12 Almen, with 100% coverage, using hardened steel shots (55-62 HRc) with 0.4 mm diameter. Almen intensity is established by measuring the deformation on the Almen strip that is in the shot peening operation. As the strip reaches a 10% deformation, the Almen strip is hit with the same intensity for twice the amount of time. If the strip deforms another 10%, then one obtains the intensity of the blast stream.

Two different low pressure carburizing cycles were carried out in an industrial furnace, at 945°C with acetylene as carburizing gas. Quenching was carried out with a nitrogen flux at 6 bar. Tempering was carried out at 180°C for 2 hours. The two treatments are described in Table 3.

Tab.3.Low pressure carburizing treatments.

treatment	Boost + diffusion time (minutes)				
	I	II	III	IV	V
LPC1	2 + 15	1 + 1	1 + 4		
LPC2	2 + 10	1 + 15	1 + 19	1 + 27	1 + 4

The microstructural investigation of the samples was carried out by the light optical microscope after the metallographic preparation and etching (Nital-Picral).

The carbon pick-up after carburizing was measured by LECO, by analyzing the average content of a 500 μm thick surface slice of the Charpy bar.

The HV0.1 microhardness profile was measured on all the specimens. Impact tests were carried out on three specimens of each material.

Solution annealing at 1150°C for 20 minutes and tempering at 250°C for 2 hours in air were carried out on AD4.

Tempering treatment was carried out on ALH at 300°C for 1 h in air.
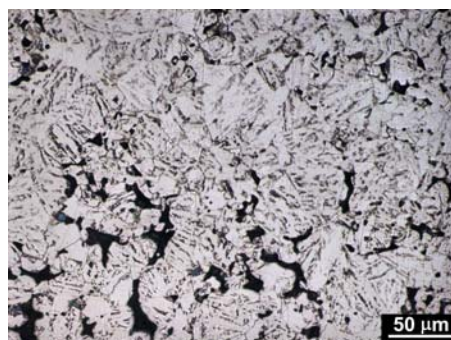
RESULT AND DISCUSSION

As sintered microstructure

Figure 1 shows the ferritic-pearlitic as sintered microstructure of cold compacted AD4 (Fig.1a) and the ferritic-bainitic one of cold compacted ALH (Fig.1b).
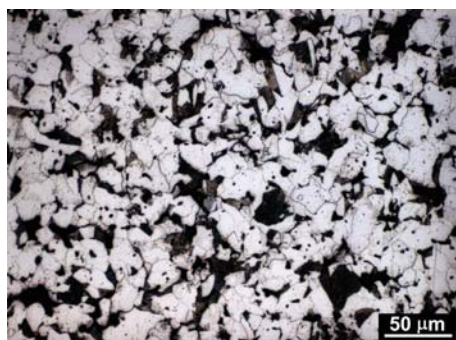
a) cold compacted AD4   b) cold compacted ALH

Fig.1. Sintered microstructure of cold compacted AD4 and ALH.

Shot peening causes an extensive plastic deformation of the surface which results in the formation of a fully dense layer, as shown in Fig.2. The thickness of this layer is around 80 μm in both of the steels.
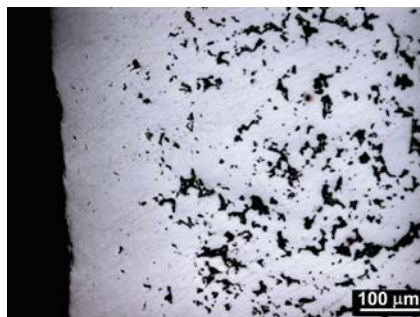

Fig.2. Microstructure of the shot peened AD4 with the surface densified layer.
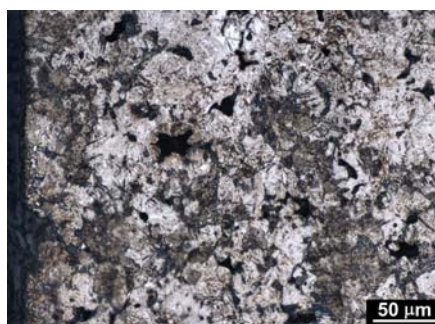
Plastic deformation worsens the flatness of the peened surface, as shown by the irregular profile in Fig.2. In the case of practical application, shot peening must be optimized to avoid such a phenomenon.

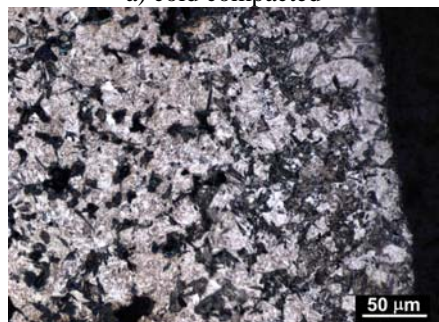**Low pressure carburizing of AD4 steel**
Figure 3 shows the microstructure and the microhardness profiles of AD4 after the LPC1 treatment.
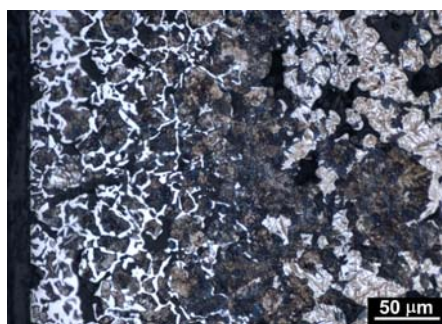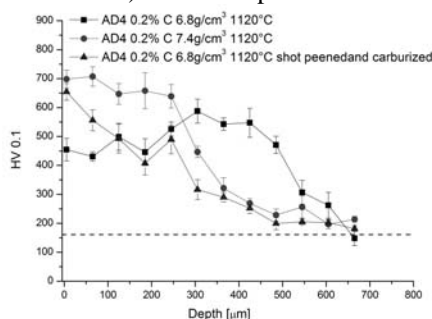

a) cold compacted

b) warm compacted

c) cold compacted and shot peened

d) microhardness profiles

Fig.3. Microstructure of 0.2% C AD4 after LPC1 and microhardness profiles.

The cold compacted material shows an extensive precipitation of carbides at the prior austenitic grain boundary (Kremel et al. [7]), due to overcarburizing. Precipitation propagates in depth up to 200 μm. The microhardness profile shows a low microhardness within this layer and it increases at around 200 μm, reaching the maximum value of 600 HV0.1 at a depth of 300 μm. Grain boundary precipitation does not contribute to hardening. The warm compacted material does not show the grain boundary precipitation and the microhardness is high even on the surface layers. It reaches 700 HV0.1, and the case depth, calculated as the distance at which 550 HV0.1 is measured (d_{550}), is 280 μm. The very low open porosity (Tab.2) in the warm compacted material prevents overcarburizing. As expected, grain boundary precipitation does not occur in the shot peened material, as well, but the microhardness profile shows a poor hardening in comparison to the warm compacted material: the surface microhardness is 650 HV0.1 and case depth is 70 μm. This is attributed to a lower carbon pick-up, which is confirmed by the presence of lower bainite at the grain boundary in the carburized layer, different from the warm compacted material.

Because of the overcarburizing of the cold compacted material, LPC2 treatment was carried out on the warm compacted and the shot peened specimens only. Figure 4 shows the microstructure and the microhardness profiles.

a) warm compacted   b) cold compacted and shot peened
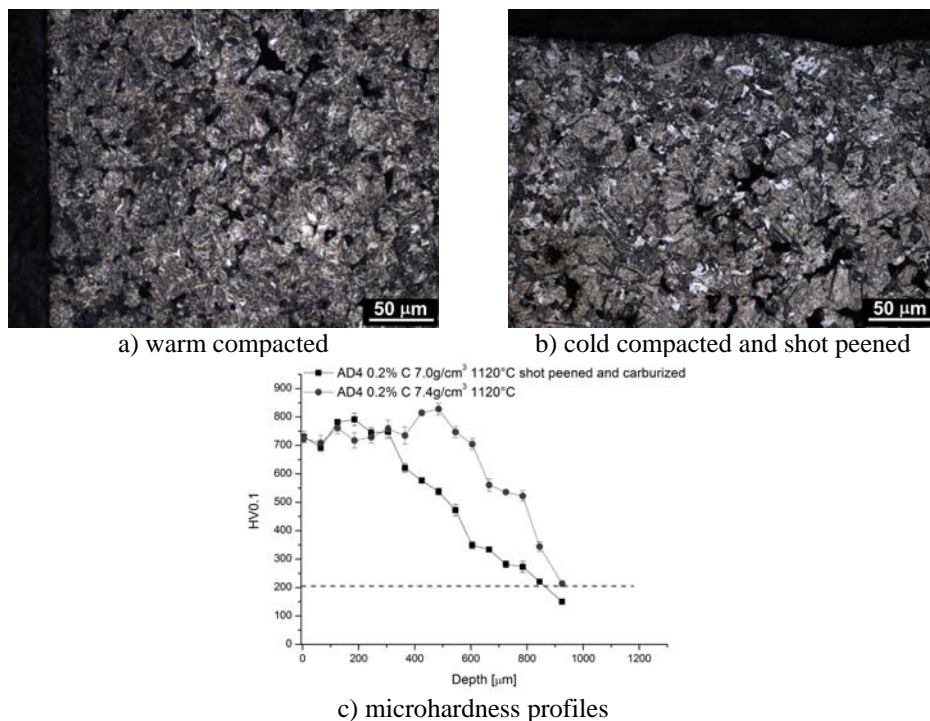

c) microhardness profiles

Fig.4. Microstructure of 0.2% C AD4 after LPC2 and microhardness profiles.

In both cases no overcarburizing is observed, despite of the more intense treatment. The main effects of the prolonged carburizing are the absence of bainite in the case of shot peened material and the more effective hardening than in the case of LPC1 treatment, represented by both a higher surface microhardness and a deeper penetration. Again, both

microhardness and case depth are higher in the warm compacted material than in the shot peened one.

The higher carbon pick-up in the warm compacted material is due to the residual open porosity that increases the exchange surface area of the specimens. Shot peening eliminates completely all the surface pores. The average carbon content was analyzed by LECO, obtaining 0.51% and 0.49% in the warm compacted and the shot peened materials, respectively. The difference is negligible and therefore the one effect of the residual open porosity is that of promoting a deeper penetration of carbon, as the microhardness profiles demonstrates.

Low pressure carburizing of ALH steel

Figure 5 shows the microstructure and the microhardness profile of ALH material after LPC1 treatment.

a) cold compacted

b) warm compacted

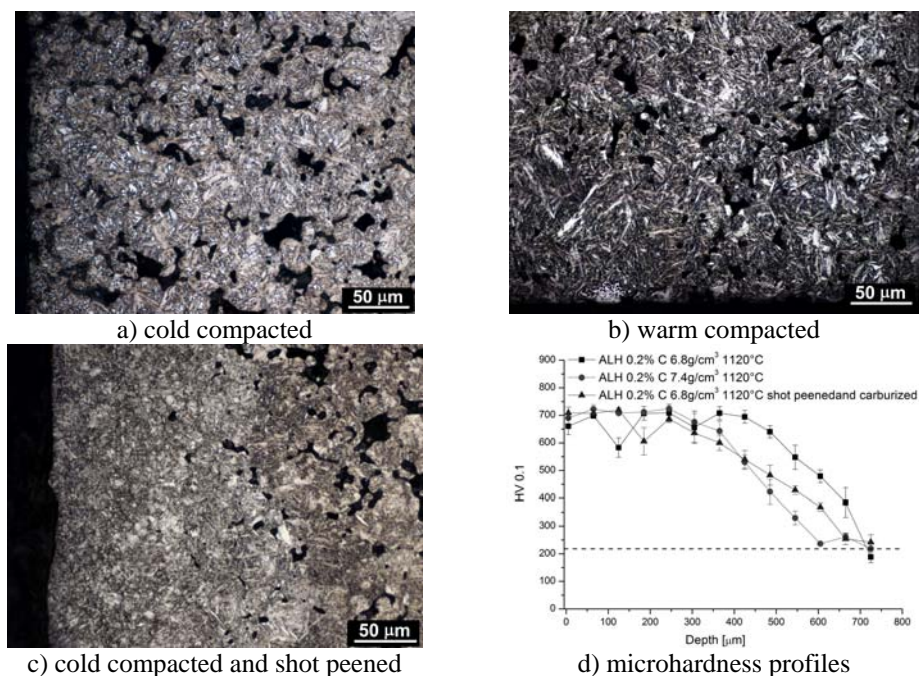c) cold compacted and shot peened

d) microhardness profiles

Fig.5. Microstructure of 0.2% C ALH after LPC1 and microhardness profiles.

The cold compacted material shows a martensitic microstructure with some retained austenite. Unlike the previous material, the absence of carbide forming elements avoids the grain boundary precipitation. In this case, carbon is completely dissolved in austenite, decreasing the martensite finish temperature below room temperature. The microhardness profile is quite flat up to a distance of 400 μm from the external surface, indicating that retained austenite does not decrease hardness significantly, because of its low amount. The maximum microhardness is 700 HV0.1 and case depth is 550 μm. The warm compacted material has a martensitic microstructure, and no retained austenite is observed with the light optical microscope. The microhardness profile is very regular, with a maximum microhardness of 700 HV0.1 and a case depth of 420 μm. The shot peened material is very similar to the warm compacted one: martensitic microstructure and almost the same microhardness profile. Even for ALH, LPC2 treatment was experimented on the

warm compacted and the shot peened materials only. Figure 6 shows the microstructure and the microhardness profile of the two materials after LPC2 treatment.

a) warm compacted   b) cold compacted and shot peened
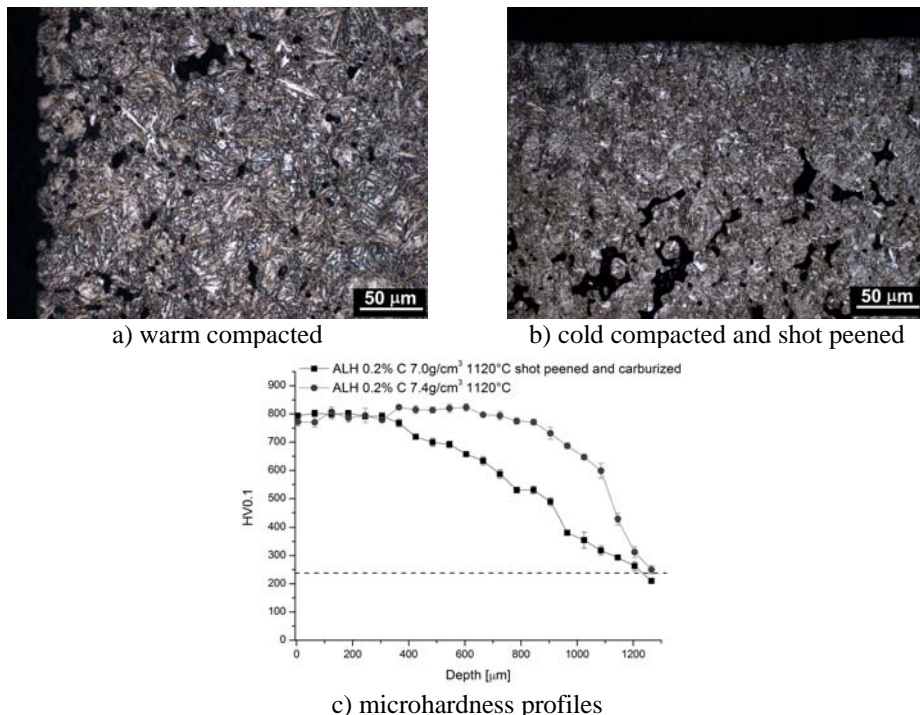

c) microhardness profiles

Fig.6. Microstructure of 0.2% C ALH after LPC2 and microhardness profiles.

The case microstructure of the warm compacted material is still martensitic with traces of retained austenite, due to the greater carbon pick-up than in LPC1 treatment. The microhardness profile shows slightly lower microhardness in the outer part of the case than in the inner (770 HV0.1 versus 830 HV0.1) and case depth is 1.1 mm. The shot peened material does not show any retained austenite, and then the microhardness is flat in the outer part of the case (800 HV0.1) and case depth in around 0.8 mm. The average carbon content was analyzed by LECO, obtaining 0.69% and 0.39% in the warm compacted and the shot peened materials, respectively. The significantly higher carbon content in the warm compacted material is due to the residual open porosity, which is 1.6% (on a total residual porosity of 6.5%).

Warm compaction vs. surface densification and the effect of the base material

Overcarburizing is completely prevented by surface densification in both the steels investigated, and even by warm compaction in AD4. However, in the warm compacted ALH overcarburizing is quite slight, since only a small amount of retained austenite is formed after LPC2 treatment. From this viewpoint, the two alternative solutions to oppose overcarburizing are equivalent.

With reference to previous work [10], it can be concluded that, in the presence of an interconnected porosity (cold compaction):

• the grain boundary precipitation in 0.8% Cr-0.4% Mn steel is less pronounced than in the Astaloy CrL (1.5% Cr-0.2% Mo) steel;

- the content of retained austenite in the case of the 0.9% Ni-0.9% Mo steel is lower than in a 0.9% Ni-0.9% Mo-2% Cu steel.

      In the case of either mainly closed porosity or surface densification:
- the higher chromium content enhances both surface microhardness and case depth;
- the presence of copper in the Ni-Mo steel tends to slightly increase the amount of retained austenite, without any appreciable effect on surface hardening.

      The parameters significant for the microhardness profiles in the two investigated materials are reported in Table 4: the surface microhardness ($HV1_{surf}$), the maximum microhardness ($HV1_{max}$) and the case depth (d_{550}).

Tab.4. Significant parameters of the microhardness profile.

Material	LPC1			LPC2		
	$HV1_{surf}$	$HV1_{max}$	d_{550} [µm]	$HV1_{surf}$	$HV1_{max}$	d_{550} [µm]
AD4 warm compacted	700	710	280	730	850	700
AD4 shot peened	630	630	80	730	800	500
ALH warm compacted	700	730	420	770	830	1100
ALH shot peened	700	710	230	800	800	800

      The main difference between the two materials is the case depth, which is greater in ALH because of its higher hardenability. The LPC2 treatment increases the surface hardening and case depth. In principle, LPC2 treatment is quite well designed for AD4, whilst an intermediate treatment between LPC1 and LPC2, should be preferable for ALH, whose case depth is too thin in LPC1 treatment and too thick in the LPC2 one.

      Charpy impact tests were carried out to evaluate the embrittlement provided by LPC2 treatment. Results are reported in Table 5.

Tab.5. Charpy impact properties of as sintered and carburized materials.

Material	Processing route	Impact energy [J]			
		as sintered	carburized	as sintered	carburized
AD4	warm compaction	74	18	-	-
	cold compaction and shot peening	-	-	16	10
ALH	warm compaction	59	12	-	-
	cold compaction and shot peening	-	-	13	12

      The as sintered impact toughness of the warm compacted materials is quite high, thanks to the low and mainly closed residual porosity, which enhances the load bearing section. After carburizing, it decreases significantly but AD4 maintains a higher toughness than ALH because of the better inherent toughness of core microstructure [11].

      As far as the shot peened specimens are concerned, the as sintered toughness is already quite low, as could be expected from the moderate density. Again, the ferritic-pearlitic microstructure of AD4 provides a higher toughness than the mainly bainitic one of ALH [11]. After carburizing the toughness slightly decreases.

      The comparison between the four carburized materials shows that warm compacted AD4 has the better impact toughness resulting from the combination of a ductile core microstructure and a controlled surface hardening.

Microstructural modification of overcarburized steels

       The microstructural inhomogeneity of the materials having fully interconnected porosity can be eliminated by heat treatments. In the Cr steel, all the grain boundary carbides can be dissolved in austenite by means of a solution annealing treatment in the austenite field, and their precipitation can be avoided by means of a fast cooling from the solution annealing temperature. Solution annealing treatment was carried out on AD4 at 1150°C for 20 minutes with a cooling rate of 8 K/s, followed by tempering at 250°C for 2 hours. The microstructure and the microhardness profile are shown in Fig.7. Grain boundary carbides are effectively dissolved, their further precipitation upon cooling is avoided but the case microstructure is bainitic-martensitic. Therefore, the resulting microhardness is too low, because of the poor hardenability of the base steel.
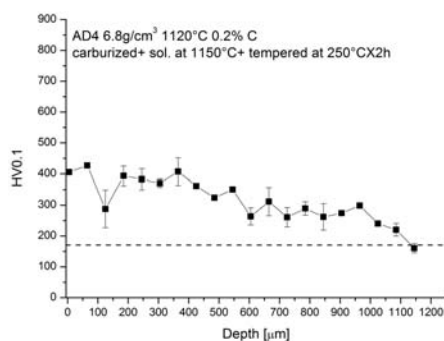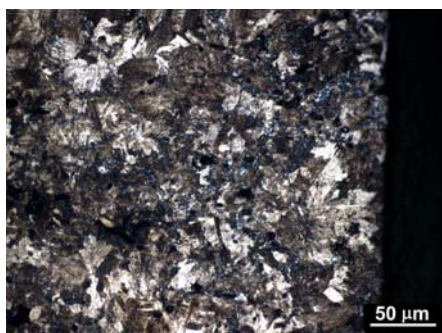

Fig.7. 6.8 g/cm^3 AD4 solution annealed and tempered at 250°C for 2 hours: a) microstructure and b) microhardness profile.

       Retained austenite in ALH can be transformed by tempering. As well known, retained austenite of as quenched steels transforms in ferrite and submicroscopic carbides during the second stage of tempering [12]. The treatment was carried out at 300°C for 1 hour and microstructure and microhardness profile are reported in Fig.8. Microhardness is slightly lower than that of the as carburized steel, and case depth is correspondingly reduced, but the surface layer is still satisfactorily hardened.
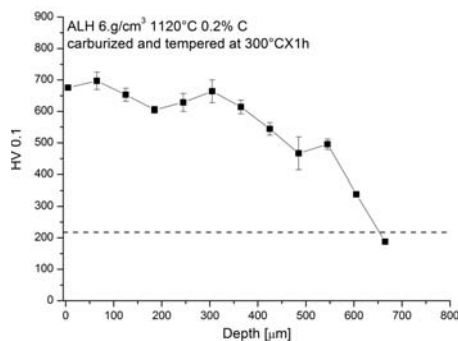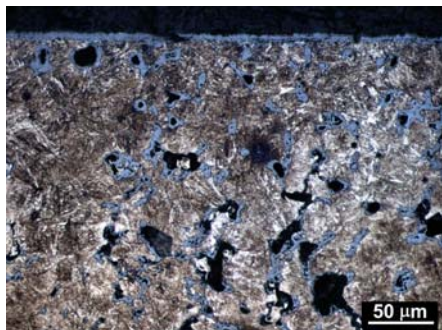

Fig.8. 6.8 g/cm^3 ALH tempered at 300°C for 1 hour: a) microstructure and b) microhardness profile.

The heat treatment of the Cr containing steel to improve its microstructure does not result in appreciable properties, but it might be expected that much more interesting results could be obtained, with the same approach, on a highly alloyed steel. Contrarily, heat treatment of the Ni-Mo steel effectively improves the case microstructure and could be proposed as a practical solution to overcome the effects of overcarburizing.

CONCLUSIONS

The effects of low pressure carburizing treatments on two low alloyed sintered steels processed were investigated.

In the presence of an open porosity all the materials are overcarburized. The microstructure contains grain boundary carbides in the Cr containing material, and retained austenite in the Cr free. In the presence of a densified surface, low pressure carburizing forms a homogeneous case, which is slightly harder and thinner in the Cr free steel.

The two materials processed by warm compaction give different results, since they develop a significantly different porosity after sintering. The Cr containing material has a partially closed porosity, which prevents overcarburizing, whilst the other one still has some open porosity which induces the formation of some residual austenite.

In principle, the effect of overcarburizing on the Cr containing steel is very similar to that observed on similar steel containing higher Cr content. Instead, the absence of copper in the Ni-Mo steel effectively reduces the amount of retained austenite formed in the case of overcarburizing.

A solution annealing heat treatment effectively dissolves all the grain boundary carbides of the overcarburized Cr steel, but the resulting microhardness profile is too low. Tempering at 300°C destabilizes retained austenite in the Ni-Mo overcarburized steel, and in this case the microhardness profile is quite good.

Impact tests were carried out to investigate the embrittlement provided by low pressure carburizing. Impact toughness of the surface densified steels is quite similar (10-12 J). Contrarily, the warm compacted Cr steel has a higher toughness than the Ni-Mo one, because of the more ductile core microstructure.

This work confirms that low pressure carburizing can be used to improve the surface mechanical properties of sintered steels, provided that they do not contain too much residual open porosity.

Acknowledgements

REFERENCES

[1] Grafen, W., Bless, F.: Heat Treat. Met, vol. 3, 2003, p. 68
[2] Grafen, W., Edenhofer, B.: Ipsen on Top, vol. 2, 1999, p. 9
[3] Altena, H., Schrank, F.: Gear Technology, 2004, no. 2, p. 27
[4] Parrish, G.: Carburizing. Materials Park OH : ASM, 1999
[5] Danninger, H., Gierl, C., Kremel, S., Leitner, G., Jaenicke-Rössler, K., Yu, Y.: Powder Metallurgy Progress, vol. 2, 2002, no. 3, p. 125
[6] http://www.industrialheating.com
[7] Kremel, S., Danninger, H., Altena, H., Yu, Y.: Powder Metallurgy Progress, vol. 4, 2004, no. 3, p. 119
[8] Bengtsson, S., Forden, L.: Adv. Powder Metall. Particulate Mater., vol. 6, 2001, p. 84
[9] Bengtsson, S., Marcu, T.: Adv. Powder Metall. Particulate Mater., vol. 6, 2008, p. 152

[10] Santuliana, E., Menapace, C., Meli, G., Molinari, A., Microstructure, microhardness and impact toughness of low pressure carburized PM steels, submitted to Surface Engineering

[11] Santuliana, E., Molinari, A. In: Proc. EuroPM 2009 Congress and Exhibition. Vol. 1. Copenhagen, Denmark, October 2009, EPMA, p. 169

[12] Reed-Hill: Physical Metallurgy Principle, 2nd, 1973, Boston, PWSKent publishing