Influence of steel composition and sintering parameters on glow-discharge nitriding of sintered steels

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The present study evaluates the influence of steel composition, compacting and sintering parameters on the nitridability of sintered steel samples using factorial experimental design. Fe-C-Cr-Mo (Cr: 3 wt. %; Mo: 0.5 wt.%) steel powders with different carbon content (0.2, 0.35, 0.5 wt. %) were compacted at 700 MPa at 298 K (cold) or 423 K (warm) temperature; the samples were sintered at low (1393 K; t = 30 min) or high (1523 K; t = 60 min) temperature. Glow discharge nitriding treatment has been performed on sintered steel samples at 773 K for 8 and 24 hours using a 80 vol. % N_2 and 20 vol. % H_2 treatment atmosphere. The nitriding treatment produces a hardened surface layer, consisting in an outer compound layer, in which iron and chromium nitrides are presents and an inner diffusion layer, characterised by the presence of nitride precipitates dispersed in a nitrogen rich metal matrix. The hardened layer thickness increases as nitriding treatment time increases and ranges from ~ 200 (t = 8 h) to ~ 300 (t = 24 h) μm. The factorial experimental analysis bas shown that the case depth of the nitrided layer is significantly influenced by the sintering parameters: thicker hardened layers are obtained sintering the samples at 1393 K for 30 min.

Parole chiave: trattamenti termici, sinterizzazione, acciaio

INTRODUCTION

In the last decades powder metallurgy has obtained an increasing interest in many industrial fields and it has become competitive with traditional working technologies, like milling, forging or die casting of wrought materials. Sintered steel components of complex shape can be easily obtained with good dimensional precision, surface finish and mechanical properties (1). For many applications high wear and fatigue resistance is required and it can be achieved by proper surface treatments. Glow-discharge nitriding process is particularly suitable for surface hardening of sintered steel components, since the characteristics of the hardened layer appear not to be markedly affected by the inherent porosity of the material itself and a sealing procedure is not usually required (2-4). The addition of alloy elements, like chromium, molybdenum or aluminium, to increase the nitridability of the steels can complicate the sintering process, owing to the high oxygen affinity of these elements, so that reducing gas atmospheres or vacuum and high sintering temperatures are required (5, 6). The aim of the present study was to evaluate the influence of steel composition, compacting and sintering parameters on the nitridability of sintered steel samples; these parameters have been investigated using factorial experimental design.

EXPERIMENTAL PROCEDURE

Prismatic samples (5x10x22 mm) were obtained as Höganäs ACrM Fe-C-Cr-Mo (Cr: 3 wt. %; Mo: 0.5 wl.%) steel powders with different carbon content (0.2, 0.35, 0.5 wt. %). The samples were compacted at 700 MPa at 298 K (cold) or 423 K (warm) temperature; the samples were sintered at low (1393 K; t = 30 min) or high (1523 K; t = 60 min) temperature.

Glow discharge nitriding treatments were performed in a plasma equipment, similar to industrial ones, previously described (4, 7). Treatments were carried out at 773 K for 8 and 24 hours, at a pressure of 10 mbar, using a 80 vol. % N_2 and 20 vol. % H_2 treatment atmosphere.

The microstructure of the treated samples was examined by metallographic techniques using light and scanning electron (SEM) microscopy. Surface and bulk porosity was evaluated using light metallographic techniques and image analysis. X-ray diffraction analysis (Cu Kα radiation, λ = 1.5406 Å) was performed to identify the phases present in the modified surface layers. Microhardness measurements (Knoop indenter, 25 gf) were carried out on the modified layer and on the matrix.

The influence of steel composition and compacting and sintering parameters on the main characteristics of the as sinte-

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Factors		Levels –	Levels +
A	Carbon content	0.2	0.5
B	Compacting temperature	cold (T = 298 K)	warm (T = 423 K)
C	Sintering type	low (T = 1393 K; t = 30 min)	high (T = 1523 K; t 60 min)

Table 1 - Factors and levels of the experiment *Tabella 1 - Fattori e livelli della sperimentazione*

Memoria presentata al 18° Convegno Nazionale Trattamenti Termici - 2nd European Congress Heat and Surface Treatments, Rimini 12-14 June 2001

Material type	Factor A	Factor B	Factor C
CL1	–	–	–
CL3	+	–	–
WR1	–	+	–
WL3	+	+	–
WH1	–	+	+
WH3	+	+	+
CH1	–	–	+
CH3	+	–	+

Table 2 - Relationship between material type and factor levels

Tabella 2 - Relazione tra tipo di materiale e livelli dei fattori

red and nitrided samples was analysed by factorial experimental design. The trial was configured as a full factorial experiment with three factors and two levels, according to Table 1; the relationship between the material type and factor levels is shown in Table 2. Main and interaction effects were evaluated and t-test and analysis of variance (ANOVA) were performed for assessing their significance (8, 9).

RESULTS AND DISCUSSION

Porosity analysis of the as sintered materials

The as-sintered samples show pores with a near-spherical shape, in accordance with a suitable sintering process; at the surface zone of the samples the porosity is still interconnected. The porosity of the as sintered materials has been evaluated in the bulk and at the surface of the samples; the results are reported in Table 3. The porosity values are in the range ~ 2 - 5 vol. % for the bulk and ~ 7 – 12 vol. % at the surface. In order to evaluate the significance of the experimental factors for bulk and surface porosity, first, second and third order effects were evaluated and the 95 % confidence interval was estimated. The normal probability plot of the effect for bulk porosity and the response of the porosity to variations in the level of main and interaction effects are shown in Fig. I. The only significant factor affecting bulk porosity is sintering type: lower porosity values are achieved sintering the samples at 1523 K for 60 min. On the contrary, neither factors nor interactions appear to have significant influence on surface porosity.

Morphology and microstructure of the nitrided materials

The nitriding treatment produces a modified surface layer, consisting of an outer compound layer and an inner diffusion layer.

Fig.2 shows the diffraction spectrum of a sample nitrided for 24 hours. As shown by diffraction layer of all the treated samples consists essentially of iron nitrides, γ'-Fe_4N (f.c.c.) and ε-$Fe_{2\text{-}3}N$ (hex); small amounts of chromium nitride, CrN (f.c.c.), and iron oxide, Fe_3O_4 (magnetite; cubic) were also detected. The Fe_4N content of the compound layer increases, as the nitriding time increases. SEM analysis of the cross-section of the samples shows that the compound layer thickness is ~ 8 µm for a 8 h nitriding and ~ 12 µm for a 24 h nitriding. No significant influence of steel composition, compacting and sintering parameters on the composition

Material Type	C (wt %)	Compacting temperature	Sintering type	Surface porosity (vol. %)	Bulk porosity (vol. %)
CL1	0.2	cold	low	12.2±1.4	4.2±1.3
CL2	0.35	cold	low	8.9±1.0	4.0±0.7
CL3	0.5	cold	low	12.1±1.7	4.9±1.4
WL1	0.2	warm	low	9.0±0.7	3.2±0.9
WL2	0.35	warm	low	11.1 ± 1.7	3.4 ± 0.5
WL3	0.5	warm	low	9.4 ± 0.6	3.4 ± 0.7
WH1	0.2	warm	high	9.4 ± 0.8	2.8 ± 0.2
WH2	0.35	warm	high	9.4 ± 1.1	2.4 ± 0.3
WH3	0.5	warm	high	7.2 ± 0.1	2.1 ± 0.1
CH1	0.2	cold	high	7.6 ± 0.7	3.0 ± 1.3
CH2	0.35	cold	high	11.9 ± 1.3	2.4 ± 0.5
CH3	0.5	cold	high	9.7 ± 1.3	2.6 ± 0.5

Table 3 – Surface and bulk porosity values of the as sintered materials

Tabella 3 – Valori della porosità a cuore dei materiali sinterizzati

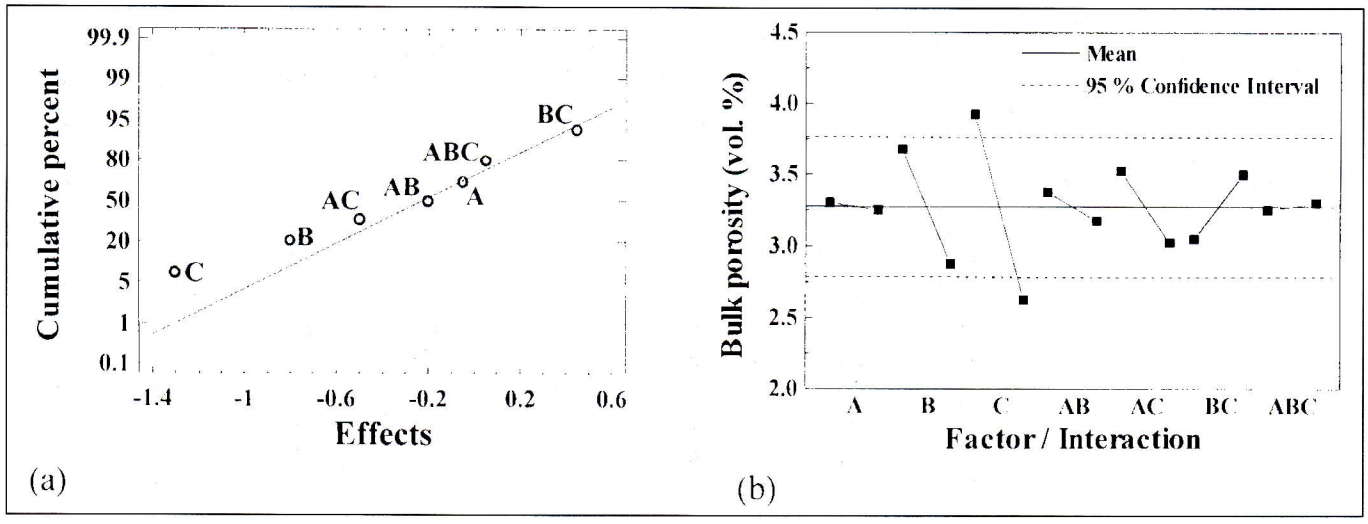

Fig. 1 – Normal probability plot of the effects estimated for bulk porosity (a) and response of bulk porosity to variations in the level of main and interaction effects (b)

Fig. 1 - Grafico della probabilità normale degli effetti stimati per la porosità a cuore (a) e risposta della porosità a cuore alle variazioni del livello degli effetti principali e delle interazioni (b)

and thickness of the compound layer has been observed. The diffusion layer of all the treated samples consists of iron and chromium nitrides precipitates dispersed in a nitrogen rich metal matrix. In Fig. 3 the typical microstructure of samples nitrided for 8 (a) and 24 (b) h is shown. As time increases, the diffusion layer thickness increases, in accordance with diffusion laws and it ranges from ~ 200 (8 h) to ~ 300 (24 h) mm. Thicker diffusion layers are observed on samples sintered at 1393 K for 30 min, as a consequence of their higher porosity, which promotes nitrogen diffusion.

Microhardness measurements of the nitrided materials

Microhardness measurements were performend on the modified layer and on the matrix of the treated samples. Typical microhardness profiles of samples nitrided for 8 and 24 h are shown in fig. 4; In Table 4 the maximum hardness values

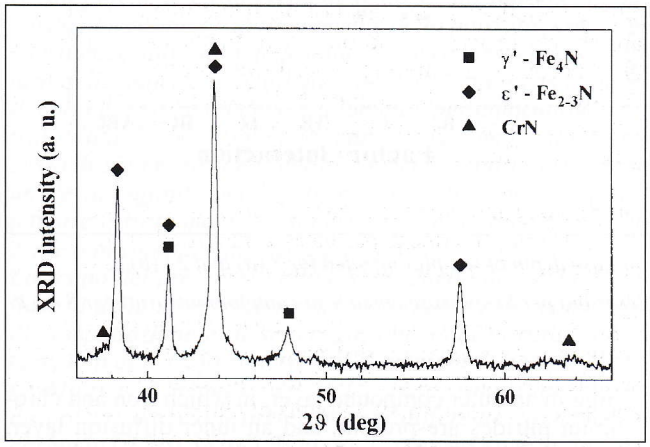

Fig. 2 – X-ray diffraction spectrum of a sample (WL3: 0.5 wt % C,warm compacted and sintered at 1393 K) nitrided at 773 K for 24 h.

Fig. 2 – Diffrattogramma di un campione (WL3: 0.5 peso di C, compattato a caldo e sinterizzato a 1393 K) nitrurato a 773 K per 24 ore

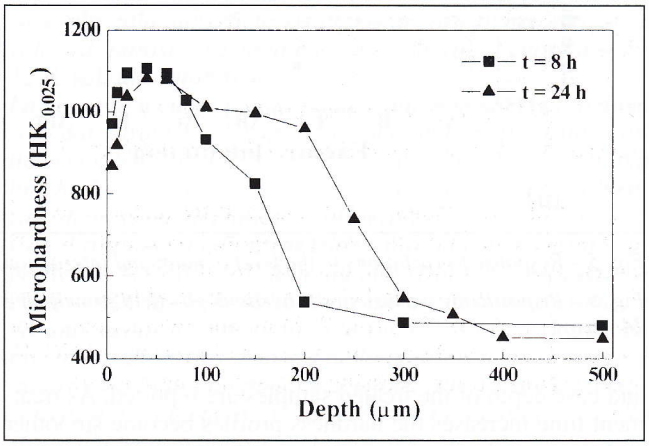

Fig. 4 – Microhardness profiles of samples (WL3: 0.5 wt % C, warm compacted and sintered at 1393 K) nitrided at 773 K for 8 and 24 h.

Fig. 4 - Profili di microdurezza di campioni (WL3: 0.5 % peso di C, compattati a caldo e sinterizzati a 1393 K) nitrurati a 773 K per 8 e 24 ore.

Fig. 3 – Micrographs of a modified layer of samples (WL3: 0.5 wt % C,warm compacted and sintered at 1393 K) nitrided at 773 K for 8 (a) and 24 (b) h.

Fig. 3 – Micrografie dello strato modificato di campioni (WL3: 0.5 % peso di C, compattato a caldo e sinterizzato a 1393 K) nitrurato a 773 K per 8 (a) e 24 (b) ore

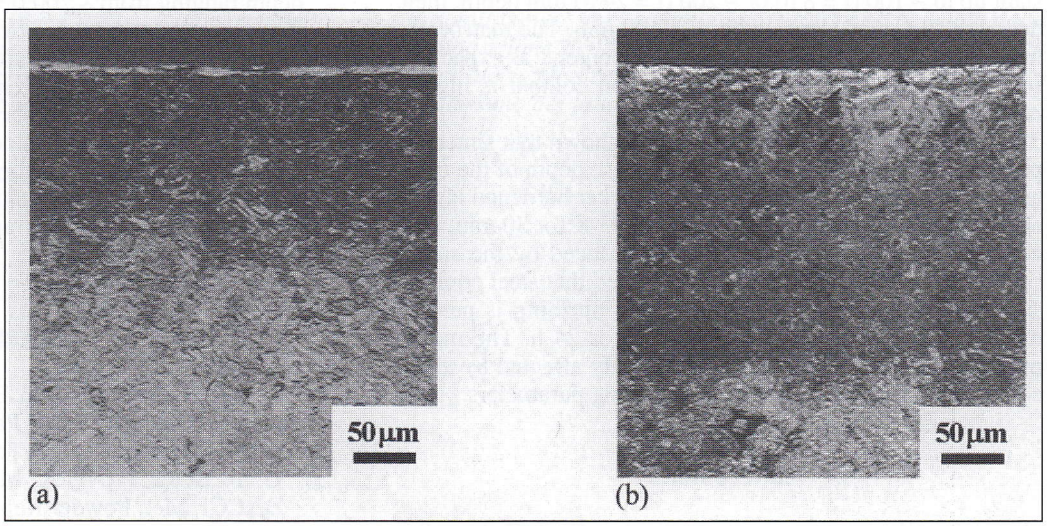

Table 4 – Maximum hardness value (Hkmax) and case depth (d_c) of samples nitrided at 773 K for 8 and 24 h

Tabella 4 – Valori massimi di durezza (Hkmax) e spessore efficace (d_c) di campioni nitrurati a 773 per 8 e 24 ore.

Material type	C (wt %)	Compacting temperature	Sintering type	t = 8h Hkmax ($HK_{0.025}$)	t = 8h d_c (μm)	t = 24 h Hkmax ($HK_{0.025}$)	t = 24 h d_c (μm)
CL1	0.2	cold	low	1095	195	1110	290
CL2	0.35	cold	low	1055	200	1045	305
CL3	0.5	cold	low	1095	195	1050	300
WL1	0.2	warm	low	1055	185	1040	300
WL2	0.35	warm	low	1100	185	1025	295
WL3	0.5	warm	low	1110	200	1085	300
WH1	0.2	warm	high	1075	170	975	285
WH2	0.35	warm	high	1065	180	1035	280
WH3	0.5	warm	high	1100	190	1055	300
CH1	0.2	cold	high	995	170	1085	285
CH2	0.35	cold	high	1060	185	1035	295
CH3	0.5	cold	high	1035	185	1025	290

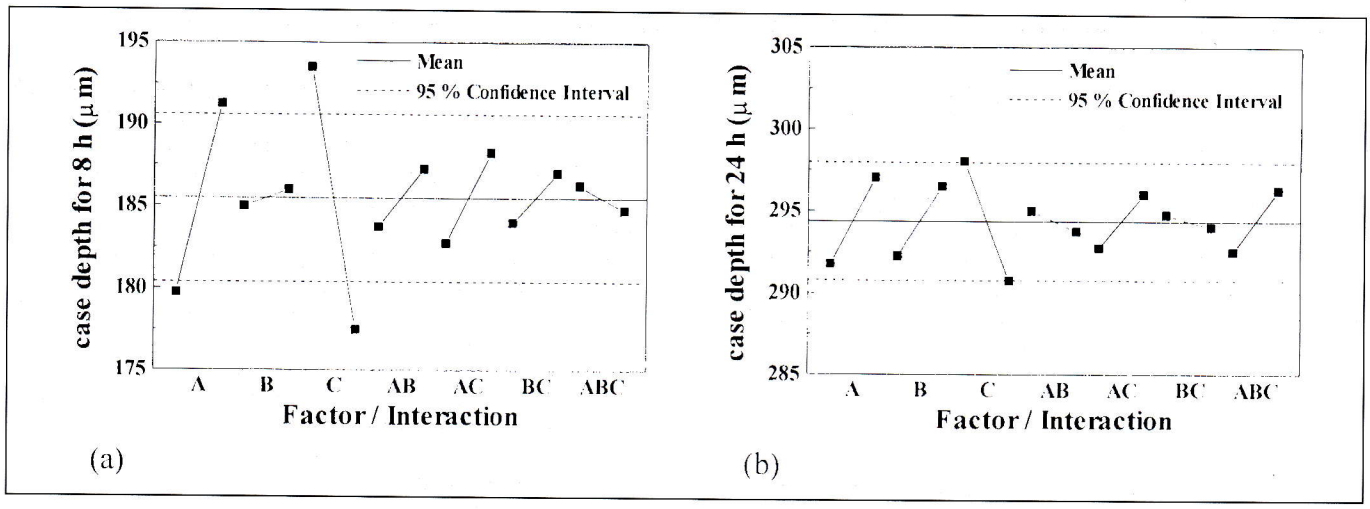

Fig. 5 – Response to variations in the level of main and interaction effects for case depth of samples nitrided for 8 (a) and 24 (b) h.

Fig. 5 – Risposta alle variazioni del livello degli effetti principali e delle interazioni per lo spessore efficace di campioni nitrurati per 8 (a) e 24 (b) ore

and case depth of the treated samples are reported. As treatment time increases the hardness profiles become smoother and the case depth of the hardened layer increases, also in accordance with the morphological observations. In all the treated samples the maximum hardness values of the modified layer are present not near the surface but at a depth ranging from ~ 20 to ~ 80 mm, as a consequence of surface decarburization phenomena, usually observed on nitrided steels (10). The hardness values remain essentonally constant up to ~ 100 (t = 8 h) or ~ 200 (t = 24 h) mm depth, then decrease to matrix values within ~ 100 mm. The matrix values are influenced by the alloy carbon content, as expected, so that hardness increases as the carbon content is higher ranging from ~ 400 to ~ 450 $HK_{0.025}$.

The factorial experimental analysis has shown that sintering parameters significantly influence the case depth of the treated samples, as it is shown in Fig. 5: thicker hardened layers are obtained sintering the samples at 1393 K for 30 min, as a consequence of the higher porosity produced by the sintering process. Moreover, it should be noted that steel composition bas a significant effect when the nitriding is performed for a 8 h treatment time, but not for 24 h. The maximum hardness values are not significantly affected by alloy composition and compacting and sintering parameters.

CONCLUSIONS

Sintered steel samples wwere obtained as Fe-C-Cr-Mo (Cr: 3 wt. %; Mo: 0.5 wt.%) steel powders with different carbon content(0.2, 0.35, 0.5 wt. %), compacted at 700 MPa at 298 K (cold) or 423 K (warm) and sintered at low (1393 K; t = 30 min) or high (1523 K; t = 60 min) temperature.

On the basis of the experimental results results the following main conclusion can be drawn:

- The as sintered materials show pores with a near-spherical shape; at the surface zone of the samples the pores are still interconnected. The porosity values are in the range ~ 2 ~ 5 vol. % for the bulk ~ 7 - 12 vol. % at the surface. Factorial experimental analysis has shown that bulk porosity is significantly influenced by the sintering parameters: lower porosity is achieved when sintering is performed at 1523 K for 60 min. On the contrary, neither steel composition nor compacting and sintering parameters affect the surface porosity.
- Glow-discharge nitriding treatments, performed at 773 K for 8 and 24 h, produce a hardened surface layer, consisting in an outer compound layer, in which iron and chromium nitrides are present, and an inner diffusion layer, consisting of nitrides precipitates dispersed in a nitrogen rich metal matrix. No significant influence of steel composition, compacting and sintering parameters on the composition and thickness of the compound layer has been observed.
- In all the treated samples the hardened surface layers show high hardness values (up to ~ 1100 $HK_{0.025}$)and a case depth ranging from ~ 200 (t = 8 h) to ~ 300 (t = 24 h) mm. Sintering parameters significantly influence the case depth of the treated samples: thicker hardened layers are obtained when samples are sintered at 1393 K for 30 min, as a consequence of their higher porosity which promotes nitrogen diffusion. Steel composition has a significant effect only when nitriding is performed for a 8 h treatment time.
- The maximum hardness values are not significantly affected by alloy composition and compacting and sintering parameters.

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NITRURAZIONE IONICA DI ACCIAI SINTERIZZATI: INFLUENZA DELLA COMPOSIZIONE DEL MATERIALE E DEI PARAMETRI DI SINTERIZZAZIONE

Il trattamento di nitrurazione in scarica ionica risulta essere particolarmente adatto per la nitrurazione di acciai sinterizzati perché le caratteristiche dello strato superficiale indurito non risentono marcatamente della porosità propria di questi materiali e quindi di solito non è richiesta una sigillatura della superficie. L'alligazione dell'acciaio con elementi, quali cromo, molibdeno o alluminio, per aumentare la nitrurabilità del materiale può rendere più complicato il processo di sinterizzazione: questi elementi, infatti, possiedono un'elevata affinità per l'ossigeno, cosicché è necessario effettuare il trattamento di sinterizzazione in atmosfera riducente o in vuoto a temperature elevate.

Lo scopo del presente studio è stato quello di valutare l'influenza della composizione del materiale e delle condizioni di compattazione e di sinterizzazione sulla nitrurabilità di campioni di acciaio sinterizzato. Campioni di acciaio Fe-C-Cr-Mo (Cr: 3 % peso; Mo: 0.5 % peso) sono stati ottenuti da polveri d'acciaio prelegate con differente contenuto di carbonio (0.2, 0.35, 0.5 % peso). Le polveri sono state compattate a 700 MPa ad una temperatura di 298 K (freddo) o 423 K (caldo) e i campioni sono stati sinterizzati a bassa (1393 K; t = 30 min) o alta (1523 K; t = 60 min) temperatura. I trattamenti di nitrurazione sono stati effettuati a 773 K per 8 e 24 h utilizzando 80 % vol. N_2 e 20 % vol. H_2 come atmosfera di trattamento. I campioni trattati sono stati analizzati mediante microscopia ottica ed elettronica a scansione e diffrazione di raggi X (sorgente: Cu Kα). L'influenza della composizione dell'acciaio e dei parametri di compattazione e sinterizzazione sulle caratteristiche principali del materiale tal quale e nitrurato è stata valutata mediante analisi fattoriale, sulla base una sperimentazione fattoriale completa a tre fattori (composizione del materiale, modalità di compattazione e di sinterizzazione) e due livelli. Sono stati valutati gli effetti principali e le interazioni e la loro significatività è stata stimata mediante t-test e analisi della varianza (ANOVA).

I campioni tal quali presentano pori di forma pressoché sferica, che alla superficie risultano ancora interconnessi. I valori di porosità variano da ~ 2 - 5 % vol. a cuore a ~ 7 - 12 % vol. alla superficie.

La porosità a cuore risulta influenzata in modo significativo solo dai parametri di sinterizzazione: minore porosità si ottiene con temperature di sinterizzazione più alte e tempi più lunghi. La porosità in superficie, invece, non risulta influenzata da nessuno dei fattori considerati.

Con il trattamento di nitrurazione si produce uno strato superficiale indurito, costituito da uno strato di composizione più esterno, in cui sono presenti nitruri di ferro e cromo, e da uno strato di diffusione, più interno, caratterizzato da precipitati di nitruri dispersi nella matrice ricca di azoto. I fattori esaminati non appaiono influenzare in modo significativo né il contenuto di fasi presenti né lo spessore dello strato di composizione.

Lo strato modificato presenta valori di durezza elevati (fino a ~ 1100 HK) e uno spessore efficace che va da ~ 200 (t = 8 h) a ~ 300 (t = 24 h) μm. I parametri di sinterizzazione influenzano in modo significativo lo spessore efficace: spessori induriti maggiori si ottengono quando la sinterizzazione è effettuata a bassa temperatura e per tempi brevi, in conseguenza della maggiore porosità prodotta; un ulteriore effetto significativo, per i campioni nitrurati per 8 h, è dato dalla composizione del materiale. Il valore massimo di durezza misurato negli strati induriti non risulta invece influenzato da nessuno dei fattori considerati.