

About composition, sintering parameters and heat treatments of sinterhardening steels

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The work is intended to focus the attention on different aspects of sinterhardening, starting from the main reason to use such a process to the final characterisation of produced samples. Sinterhardening allows the production of high apparent hardness parts; the process is rather attractive for components difficult to be quenched because of their dimensions. Admixed alloys, diffusion alloyed mixes, prealloyed ones or hybrid alloys can be used as starting powders, each having positive and negative aspects. Different mix compositions can be used to obtain a sinterhardened structure and, in function of the mix used, there are different sintering parameters and cooling speed to be performed. Properties can undergo sensible changes depending on the quantity of added carbon in the mix. Even though the need of secondary heat treatments may be avoided (and this is one of the main advantages of sinterhardening) it is clear that further treatments (nitriding or nitrocarburising) can only contribute to a sensible increase of surface properties, as it happens for some more traditional steels. This may extend the field of application of sintered parts to highly stressed parts.

Parole chiave: sinterizzazione, met. delle polveri, caratterizz. materiali

INTRODUCTION

Sinterhardening allows the production of powder metallurgy components having high apparent hardness and high strength, thus reducing the need for secondary heat treatments. Such a process is rather attractive for components difficult to be quenched because of their shape or dimensions and some important advantages can derive from its use. In fact parts are characterised by a lower distortion induced by a less drastic quenching, determining a better dimensional control; tempering is much easier (generally it occurs in air) and there is no need for eliminating oil from the structure before other finishing processes: the result is a concrete reduction of costs.

The main characteristics required to an alloy for sinterhardening can be resumed as follows:

- High hardenability
- High compressibility (in general 6.8 g/cm^3 or above for a compacting pressure of 600 MPa)
- Compatibility with sintering at conventional temperatures of 1120°C .

An alloy characterised by high hardenability has the possibility to transform to martensite avoiding the formation of secondary phases, even at slower cooling rates. Best sinterhardening materials should have a high hardenability so that the cooling rates needed to produce large proportions of martensite would be attainable [1].

The aim is to increase the hardenability by delaying the transformation:

Austenite \rightarrow Ferrite + Cementite.

The martensitic transformation does not imply a change in chemical composition but it determines a change into the crystal structure as austenite transform into martensite. The

structure of austenite is f.c.c. (face centred cubic) and at the end of transformation there is the change to a super saturated solid solution of carbon tied up in a body centred tetragonal structure by a combination of shearing actions. Generally it can be said that the degree of distortion increases with the increasing concentration of carbon [2]. Most sinterhardening materials contain a high quantity of carbon in order to increase the apparent hardness; therefore a tempering treatment is necessary after sintering in order to restore mechanical properties, and this is in function of the kind of property (i.e. strength or apparent hardness) to be optimised [3]. A variety of microstructures and properties can be obtained varying the post sintering cooling rate, and this happens mainly in function of the type of powder used (elements in the mix,...). By controlling the cooling rate, the microstructure can be changed in order to "create" the required proportion of martensite necessary to fulfill the properties expected.

POWDERS FOR SINTERHARDENING

Although carbon is required to increase the hardenability of steels, this element alone cannot enable the transformation of austenite to martensite in existing sintering furnaces [4]. The addition of alloying elements is therefore necessary to further increase the hardenability of the alloy, but care has to be taken in the study of the effect of the introduction of the element inside the mix. Different types of approaches may be used for the preparation of the alloyed steel powder mix for sinterhardening applications.

The alloying addition can be made to the base iron in the form of elemental powder, thus creating a simple "admixed" powder; this technique is the less expensive one and it gives the best results in terms of compressibility but, since the degree of alloying is related to the mutual diffusion of the alloying element and the iron, very often the structure results inhomogeneous [5]. High temperature sintering and extended time at high temperature are required to enhance the dif-

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Paper presented at the 7th European Conference EUROMAT 2001, Rimini 10-14 June 2001, organised by AIM

Memorie

9/2002

fusion rate [6]. Another important negative aspect to be considered is that this type of material is also subject to powder segregation and dusting during the handling and pressing phases.

Alternatively alloying elements may be diffusion alloyed to the base iron powder; the compressibility of iron base powder is then maintained but heterogeneous microstructures still remain, consisting of light alloyed particle cores with a continuous network of more highly alloyed interparticle bonds.

Alloying elements, apart from carbon, can be added to the melt before the process of atomisation. This latter process guarantee a high homogeneity of the structure but, at the same time, a decrease in compressibility.

Finally some elements (mainly copper or others) may be added to a previously alloyed mix during the preparation of the powder, creating the so called hybrid alloys.

The following table [1] makes a general qualitative classification of the effects of alloying elements into a ferrous prealloyed powder:

	Hardenability Factor	Effect on Compressibility	Affinity for oxygen
Higher	Manganese Chromium Molybdenum	Copper Nichel Chromium Manganese	Manganese Chromium Nichel
Lower	Copper Nichel	Molybdenum Copper	Molybdenum Copper

Table 1: Qualitative effect of alloying elements in prealloyed materials

Tabella 1: Ruolo degli elementi leganti in polveri prelegate

If applying the design criteria for wrought alloys to P/M products, high hardenability would be obtained through the massive introduction of manganese and chromium. However the reduction of Mn - Cr oxides may require higher sintering temperatures and lower dew points if compared to "normal" mixes.

As said before, the trasformation of austenite into martensite is a diffusionless reaction that takes place only during cooling. The reaction starts at a critical temperature defined as Ms; this temperature is strongly effected by the quantity of added carbon and by the concentration of other alloying element. The effect of the increasing alloying elements (especially manganese, molybdenum, chromium and nichel), as well as carbon, results in a concrete decrease of the critical temperature. The end temperature of martensitic transformation, Mf, cannot be clearly defined since a certain quantity of austenite is retained in the structure even at very low temperatures. Moreover this temperature strongly decreases when increasing the quantity of added carbon and alloying elements [3].

A possible way to examine the effect of alloying elements on the final microstructure of a steel, even for PM material, is using the characteristic isothermal transformation diagram.

Considering the presence of molybdenum in all powders for sinterhardening, listed in a following table, the following two figures 1a and 1b take in exam the influence of Mo on the I-T curves.

A shift towards the right in the nose of the molybdenum added material is visible in figure 2. This means that, in consequence of this shift, the time to reach the nose of the curve is bigger, hence martensite can be produced at slower cooling rates and finally the material has a higher hardenability. Similar results are obtained using different alloying elements as Ni, Cr, Cu and Mn.

Figure 1a: Isothermal transformation diagram of a steel of given composition without Mo additions

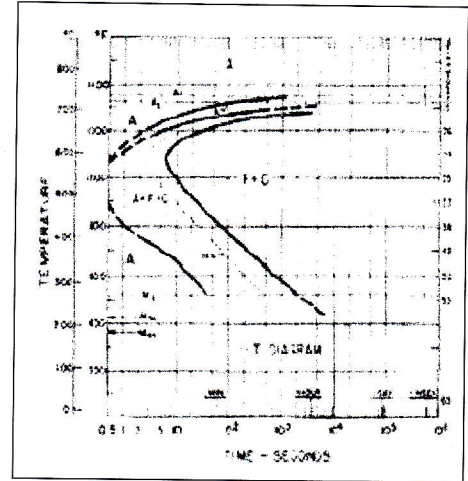


Figura 1a: Diagramma di trasformazione isoterma di un acciaio di data composizione senza aggiunta di Mo

Figure 1b: Isothermal transformation diagram of a steel of given composition with the addition of 0.24 wt. % Mo

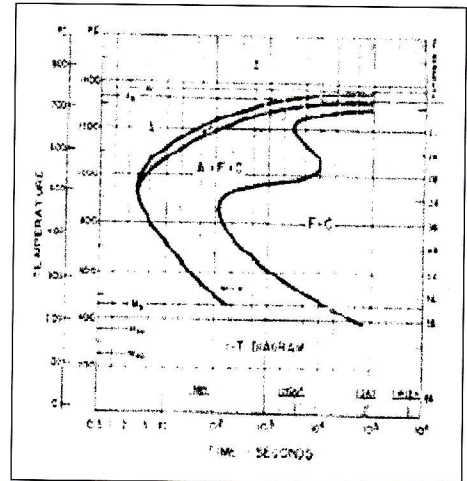


Figura 1b: Diagramma di trasformazione isoterma di un acciaio di data composizione con l'aggiunta dello 0.24% di Mo

In continuous cooling diagrams the transformation start and finish are translated to longer times and lower temperatures if compared to the I-T diagrams; however, since isothermal transformation and the CCT curves are related, the effect of alloying additions on the final microstructure found in I-T diagram will also be present in the continuous cooling diagrams. Table 2 indicates the composition of powders for sinterhardening currently available in commerce.

Quantities can vary from case to case, but they are generally located near 2 % wt. Carbon is added during the preparation of mixes, in quantities depending from mix to mix, but generally included into the range of 0.4 - 0.8 wt. %).

SINTERING AND POST SINTERING OPERATIONS

Dealing with sintering conditions, generally all powders are sintered in a nitrogen base atmosphere (90% N₂ - 10% H₂) at 1120 °C - 1140 °C; in case of sintering at higher temperatures (1250 °C), the atmosphere is 50% N₂ - 50% H₂.

However care has to be taken during the immediate post sintering operations, that is to say just after the hot area zone. In fact the control of cooling rate is of extreme importance in order to produce the required proportion of martensite which will lead to the desired mechanical properties [7].

For a given composition the CCT curves can be determined. The following figure shows the CCT diagram for one of the compositions related in the following table 2.

According to the diagram, when the material is sintered and then cooled under condition of 0.25°C/s the microstructure resulting will be a combination of bainite and martensite. When the cooling rate is higher than 1.2°C/s a fully martensitic structure can be obtained.

Table 2: Composition of some powder mixes for sinterhardening

Tabella 2: Composizioni di alcune miscele di polveri per sinterotempra

Powder type	%Wt. Element in alloy					
	Mo	Mn	Ni	Cr	Cu	C
Ancorsteel 737 SH	1.25	0.42	1.42		*	<0.01
Ancorsteel 150 HP	1.49	0.12			*	<0.01
Ancorsteel 85 HP	0.86	0.12			*	<0.01
KOBECO 46F2H	0.45-0.65	0.10-0.30	0.40-0.60		*	<0.02
KOBECO 46F2H	0.95-1.10	0.10-0.30	1.45-1.60		*	<0.02
Domfer	0.7	0.34	1.7		*	<0.01
QMP	1	0.45	0.90	0.45	*	<0.01
Distaloy DHI	1.47				2.00	<0.01
Astaoly CrM	0.5			3.00		<0.01
Distaloy AE	0.5		4.00		1.50	<0.01
Distaloy DCI	1.47		2.10			<0.01

* copper is added during the preparation of the mix, to create the so called "hybrid system".

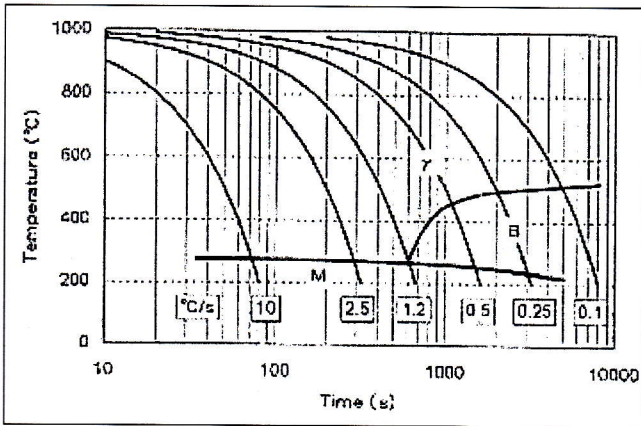


Figure 2: Continuous Cooling Transformation Diagram for an alloy for sinterhardening

Figura 2: Curve CCT per una lega per sinterotempra

THE INFLUENCE OF CARBON ON PROPERTIES

Different studies have been carried out to show the influence of increasing added quantities of carbon on properties of sinterhardening steels [1,6,7,8]. As related in [9] the general

trend of tensile strength, TRS and impact value vs. sintered carbon quantities can be summarised in the following plots (3a, 3b and 3c).

Tensile strength decreases above a certain carbon content; the reason for this has to be found in the appearing of increasing quantity of retained austenite when increasing the carbon content. Moreover elements like Ni, Mn, Cr and more particularly Mo shift the eutectoid transformation of steels to lower carbon concentrations as illustrated in figure 4.

The solubility of carbon in austenite is diminished and so it is believed that cementite grains nucleate and grow along the austenite grain boundaries because the post sintering cooling may not be fast enough to prevent such nucleation. This may affect the cohesion of the former austenite grain boundaries and locally reduce the strength of the material in consequence of the carbon depletion in the surrounding areas. [10]

POST SINTERING TREATMENTS

The use of a sinterhardened structure should avoid the need for post sintering treatments; however it has to be said that the execution of further treatments (nitriding or nitrocarburising) can only contribute to a sensible increase of surface properties, as it happens for some more traditional steels,

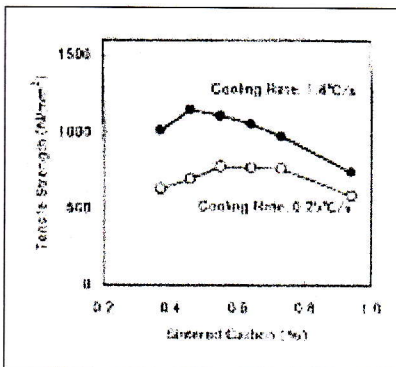


Figure 3a: Tensile strenght of a powder mix with different carbon content under accelerated and normal cooling

Figura 3a: Resistenza a trazione di una miscela di polvere con differenti quantitativi di C sottoposta a raffreddamento rapido e tradizionale

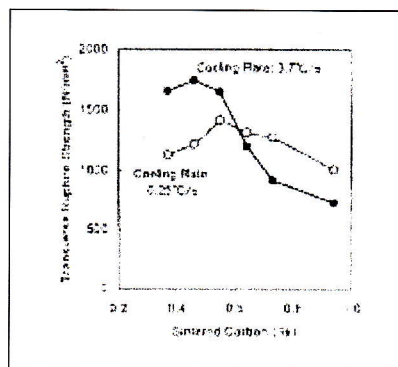


Figure 3b: TRS of a powder mix with different carbon content under accelerated and normal cooling

Figura 3b: Resistenza a flessione di una miscela di polvere con differenti quantitativi di C sottoposta a raffreddamento rapido e tradizionale

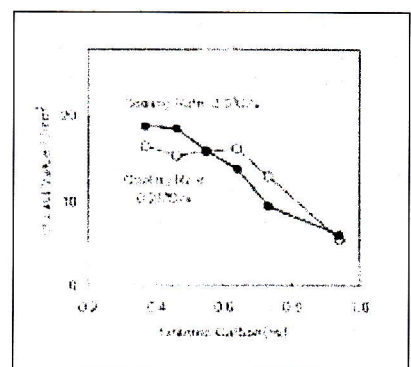


Figure 3c: Impact value of a powder mix with different carbon content under accelerated and normal cooling

Figura 3c: Resilienza di una miscela di polvere con differenti quantitativi di C sottoposta a raffreddamento rapido e tradizionale

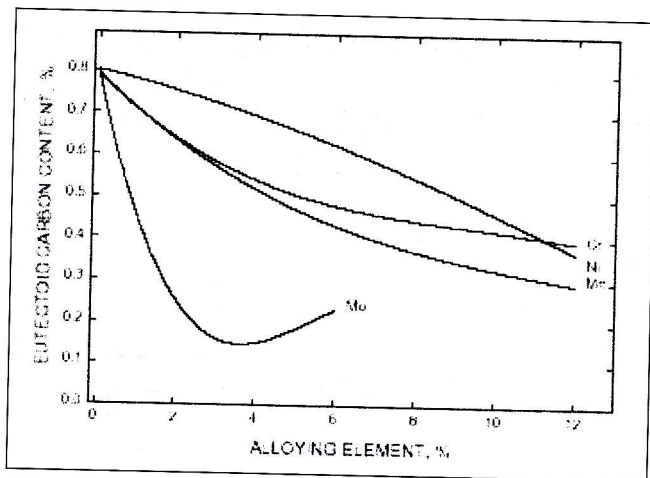


Figure 4: Effect of Cr, Ni, Mn and Mo concentration on the carbon content of the eutectoid point

Figura 4: Effetto della concentrazione di Cr, Ni, Mn e Mo sul contenuto di carbonio del punto eutettoidico

extending the field of application of sintered parts to highly stressed parts.

Two different sample compositions were studied and underwent different treatments. The composition of mixes studied is shown in the following table:

Samples	Chemical composition (wt.%)						
	C	Cu	Mo	Ni	Cr	V	Mn
SH	0,7	2	0,55	1,8	-	-	0,2
Distaloy DH	0,01	2	1,5	-	-	-	-

Table 3: Chemical composition of mixer for sinterhardening heat treated and examined

Tabella 3: Composizione chimica delle leghe da sinterotempra trattate termicamente ed esaminate

The different processes were:

- a plasma nitrocarburisation at 580 °C for 18 h in an atmosphere made of 76% nitrogen, 19% hydrogen and 5 % methane, quenching in nitrogen
- a gas nitridation at 750°C using an atmosphere of 50% endogas and 50% NH₃, quenching in oil [11]
- nitridation with fuse salt bath type Tenifer TF1, at 570 °C for 2 h.

The results in terms of hardness and microhardness are shown in the following figures.

It is clear the influence of composition, and especially of the quantity of carbon. The decrease in hardness after the pro-

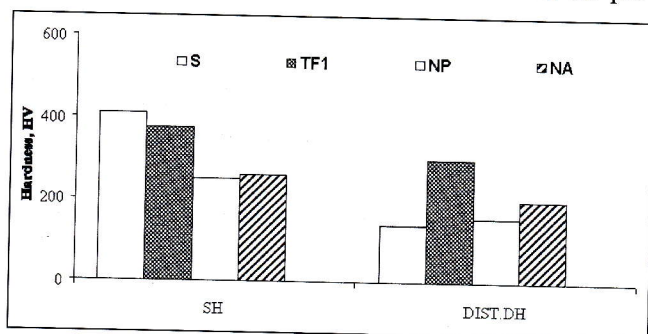


Figure 5: Hardness behaviour in function of the thermal treatment. S: only sintered, NP: plasma nitrocarburisation, NA: gas nitridation, TF1: nitridation with fuse salt bath

Figura 5: Durezza HV in funzione del trattamento termico. S: Campione sinterizzato, NP: nitrocarburazione in plasma, NA: nitridazione in gas, TF1: nitridazione in bagni di sali fusi

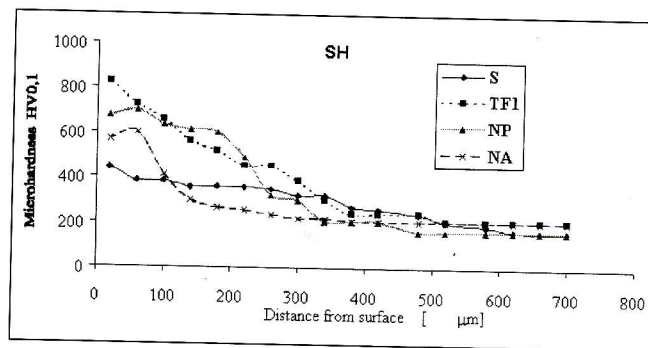


Figure 6: Microhardness profiles measured on SH steel as sintered and after treatments

Figura 6: Profili di microdurezza misurati sui campioni di acciaio SH dopo sinterizzazione e dopo trattamento termico

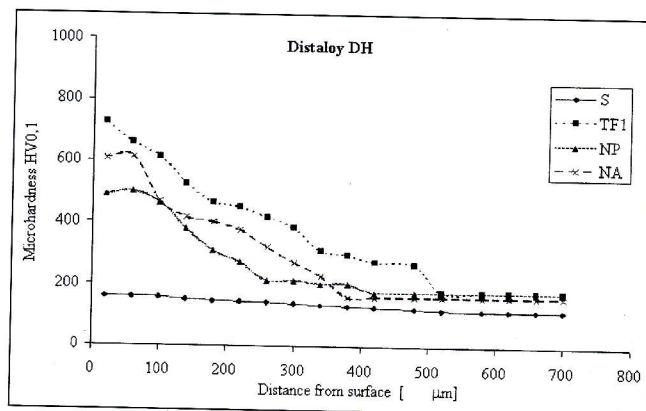


Figure 7: Microhardness profiles measured on Distaloy DH steel as sintered and after treatments

Figura 7: Profili di microdurezza misurati sui campioni di Distaloy DH dopo sinterizzazione e dopo trattamento termico

cesses of nitridation for the SH steel is probably due to an annealing effect of the material previously sinterhardened. As a matter of fact hardness, differently from microhardness, influences the inner layers of the material and not only the surface areas. The microstructural characteristics obviously strongly depend on the process done on the material. The following figures 8 and 9 show the microstructures of the surface areas deriving from treatments NP and NA. During plasma nitriding a thin composite layer forms; the diffusion of nitrogen and, in part, of carbon causes the precipitation of phases γ' ed ϵ , as well as of retained austenite, in particular when nickel and copper are present. A layer of white precipitates is visible on sample SH treated in plasma; the X ray analysis has confirmed that this layer is made of cementite. The SH alloy contains carbon at 0.7%; it is clear that the diffusion during the heat treatment has favoured the carbide precipitation. In samples undergoing gas nitrocarburising, at higher temperatures, the layer morphology strongly depend on the composition. The layer is very thin and in the diffusion area some nitride phases are seen to be present.

CONCLUSIONS

Using proper sinterhardening powders, the production of parts having high apparent hardness and high mechanical properties can be obtained often without the need of post sintering treatments. Proper selection of added elements has to be carried out, especially of carbon, in order to optimise the required properties.

Even if heat treatments do not have to be performed for the

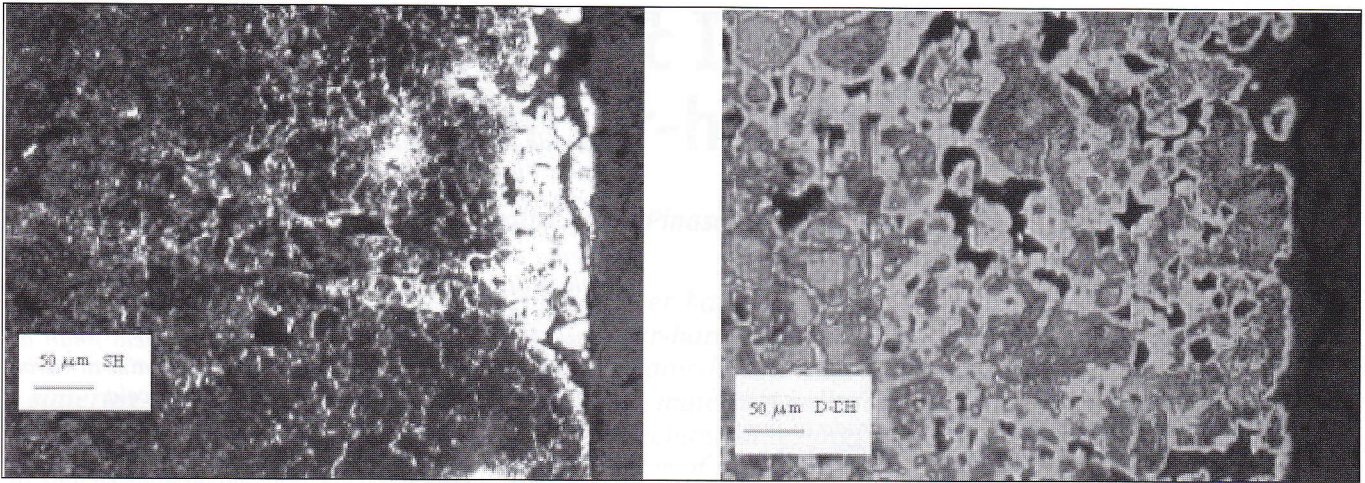


Figure 8: Microstructural characteristics of surface and diffusion areas on samples SH and DH after heat treatment NP.

Figura 8: Microstrutture delle aree superficiali e di diffusione dei campioni SH e DH dopo il trattamento termico NP

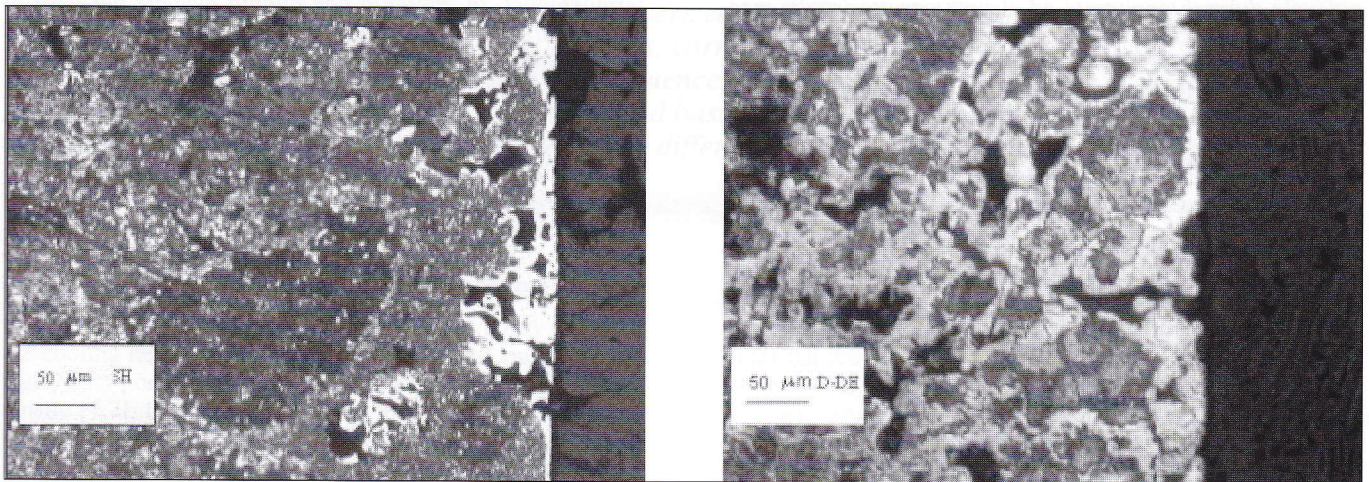


Figure 9: Microstructural characteristics of surface and diffusion areas on samples SH and DH after heat treatment NA

Figura 9: Microstrutture delle aree superficiali e di diffusione dei campioni SH e DH dopo il trattamento termico NA

final use, their eventual execution may be useful to tailor the microstructure and hence the mechanical properties of the sinterhardened components. Studies are currently carried out on different powders for sinterhardening thermally treated in order to further increase some properties such as wear resistance.

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**ACCIAI DA SINTEROTEMpra:
COMPOSIZIONI, PARAMETRI DI SINTERIZZAZIONE
E TRATTAMENTI TERMICI**

Il ciclo di sinterizzazione rappresenta il trattamento termico primario a cui devono essere sottoposti tutti i prodotti ottenuti mediante la Metallurgia delle Polveri. A valle di questo processo si possono effettuare trattamenti termici secondari, condotti in modo simile a quelli applicati ai pezzi ottenuti per via fusoria ed aventi composizione simile. Tuttavia i moderni forni di sinterizzazione possono essere equipaggiati con un dispositivo di raffreddamento rapido collocato immediatamente dopo la zona calda, che è in grado di imprimere una velocità di raffreddamento ($4 \div 6 \text{ }^\circ\text{C/s}$) ai pezzi appena sinterizzati, nell'intervallo di temperatura tra 900 e 600 $^\circ\text{C}$.

Tale processo (generalmente denominato "sinterotempra") consente la produzione di componenti che presentano una notevole durezza apparente ed elevate caratteristiche meccaniche; può venire così eliminata la necessità di trattamenti termici secondari. Questo tipo di processo risulta di interessante applicazione per quei pezzi che siano difficilmente trattabili a causa dalla loro forma e/o dimensione; sono inoltre possibili ulteriori vantaggi interessanti. I pezzi sono infatti caratterizzati da una distorsione minore rispetto al tradizionale trattamento di tempra in quanto la tempra stessa risulta effettuata in condizioni meno drastiche: il vantaggio immediato è un miglior controllo dimensionale. Si possono usare differenti procedure per la produzione dei

pezzi partendo dalle polveri: si può infatti partire dalla semplice miscelazione degli elementi, da elementi legati per diffusione, da elementi interamente prelegati e dalle cosiddette strutture "ibride"; ciascuno dei processi presenta aspetti positivi e negativi.

Sono disponibili numerose composizioni differenti per l'ottenimento di prodotti sinterotemprati ed a seconda della miscela utilizzata vi sono diversi parametri di processo da applicare, quali ad esempio temperatura di sinterizzazione e velocità di raffreddamento. Inoltre le proprietà finali dei pezzi sono strettamente dipendenti dalla quantità di carbonio aggiunto in fase di preparazione della miscela.

Il riferimento ad un materiale da sinterotempra di per sé non dovrebbe preludere all'esecuzione di ulteriori trattamenti termici; infatti tali leghe vengono prodotte ed utilizzate allo scopo specifico di ottenere i componenti sinterizzati già con caratteristiche adeguate per la loro messa in opera. Tuttavia è evidente che l'esecuzione di ulteriori trattamenti termochimici, in analogia con quanto avviene nel caso di alcune classi di acciai tradizionali, può portare ad ulteriori miglioramenti delle proprietà soprattutto superficiali. Inoltre, in altri casi, può essere interessante valutare i vantaggi ottenibili dalla sinterizzazione di composizioni da sinterotempra ma senza un adeguato contenuto di grafite, eseguendo in una fase successiva i trattamenti di cementazione o carbonitrurazione: la formazione di strati superficiali con elevate caratteristiche di durezza sarà in questo caso accompagnata dalla presenza di una struttura a cuore meno dura ma più tenace.