

Manganese diffusion coating of cast irons

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Abstract

Previous work on the diffusion coating on steels and cast iron has been followed by systematic experiments on five types of cast irons with flake or nodular graphite.

Considerable diffusion depths were obtained at treatment temperatures somewhat lower than those previously used for steels. The treatment resulted in a very hard surface diffusion; primarily composed of manganese-replaced cementite.

Riassunto

Diffusione superficiale di manganese su ghise grafitiche.

In considerazione di precedenti esperienze sui trattamenti di diffusione superficiale del manganese su acciai e ghise, sono stati effettuati nuovi esperimenti sistematici di manganizzazione su cinque tipi di ghise a grafite lamellare o sferoidale. Sono stati ottenuti spessori dello strato di diffusione del manganese dello stesso ordine di grandezza di quelli che si ottengono sugli acciai, ma a temperature inferiori. Il trattamento origina uno strato superficiale molto duro, costituito essenzialmente da una cementite sostituita con manganese.

Introduction

Manganese diffusion coating (manganizing) has been extensively studied in recent years as a means of giving steels the typical tribological properties of manganese alloyed steels.

The automotive industry is now increasingly turning to cast iron (especially with nodular graphite) as a substitute for steel parts. It was therefore decided to investigate the effect of manganizing on some nodular and flake graphite cast iron extensively used by Italian automakers.

A preliminary study (1) of a small set of these materials showed that the treatment did not have the same effect as it does, where a manganese-rich on austenitic-like surface layer is produced. By contrast, in the graphitic cast iron a very hard layer was formed.

The composition of the diffusion mixture, the temperature (1000°C) and the treatment time (25 h) were the same as those adopted for the steels. X-ray diffraction analysis and the microprobe results showed that this layer primarily consisted of $(\text{Fe, Mn})_3\text{C}$. In the present paper, we report a comprehensive study of the effect of manganizing on several types of cast iron with either flake or nodular graphite.

The only difference by comparison with steels was that the temperature was lowered to 900°C to rule out any microfusions, likely to cause the local formation of replaced cementite in the presence of large amounts of both manganese and carbon. This lower temperature was feasible, as previous manganizing at 1000°C had resulted in a very high diffusion depth and a slightly lower temperature would in any event have caused considerable diffusion depths.

Table 1. Chemical composition of the cast iron

Type	C%	Si%	Mn%	Ni%	Cr%	Cu%	Sn%	S%	Pb%	P%	Ti%	Al%
190	3.30	2.09	0.54	0.10	0.13	0.29	0.017	0.14	tr	0.04	0.007	0.006
210	3.30	2.03	1.10	0.09	0.30	0.35	0.013	0.15	tr	0.04	0.009	0.005
60	3.60	2.25	0.21	0.04	0.03	0.30	0.006	0.012	tr	0.03	0.011	0.012
45	as 60; submitted to ferritization thermal treatment											
65	3.65	2.32	0.22	0.04	0.03	0.62	0.007	0.010	tr	—	—	—

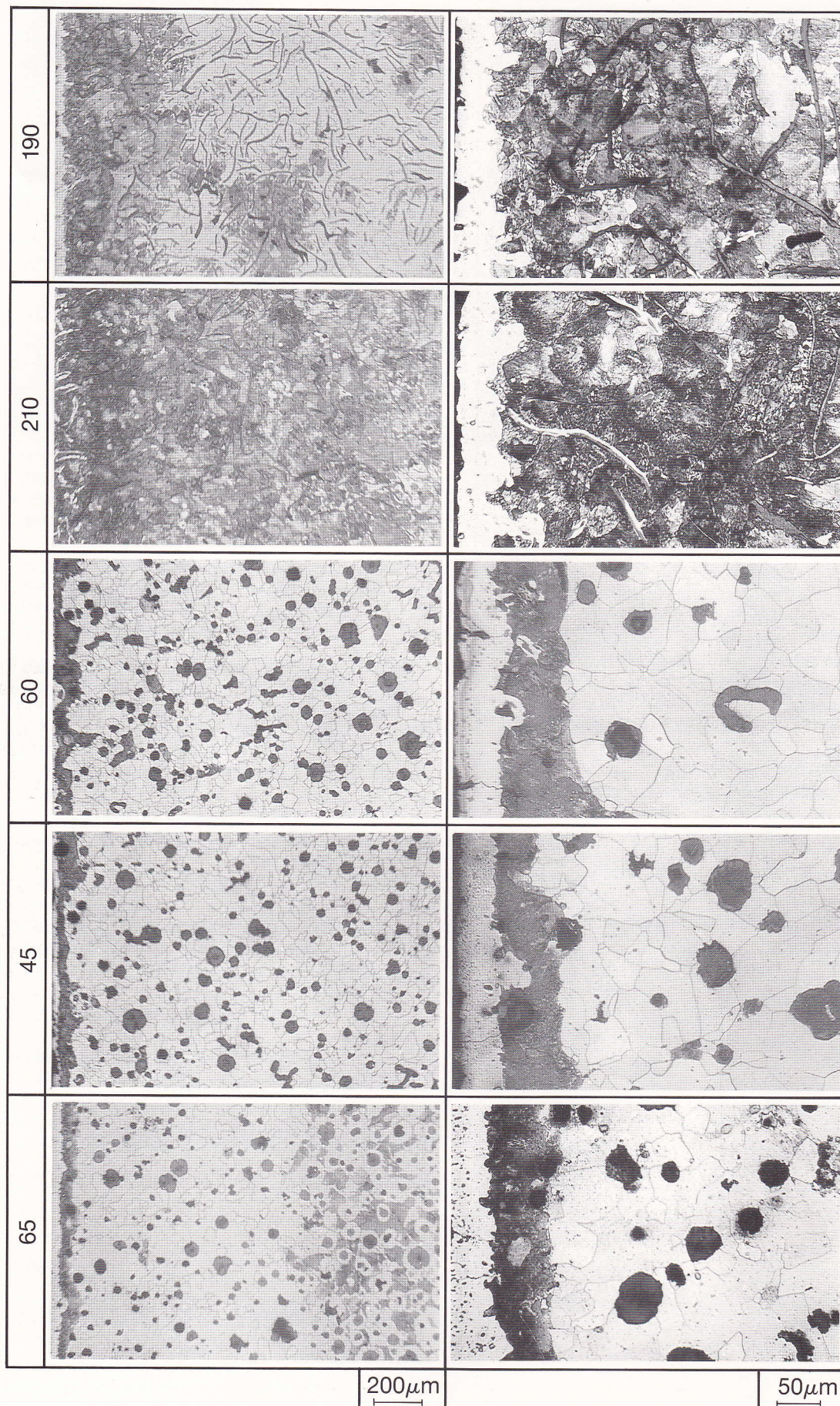


Fig. 1 - Cross-sections (at various magnifications) of surface layers of five manganized cast iron samples (Nital etched).

Experimental

Five types of graphitic cast iron from Teksid SpA (composition in Table I) were manganized: two pearlitic with flake graphite (types 190 and 210), two pearlitic with nodular graphite (types 60 and 65) and one ferritic with nodular graphite (type 45) obtained from type 60 by ferritization.

Manganizing was performed with a double-box system (2) on 15 mm diameter and 5 mm thickness specimens from 50 mm diameter round casting.

A diffusion powder mixture consisting of: 10 to 12% Fe, 55 to 57% Mn, 32 to 34% kaolin and 0.3% NH_4I , was used.

The samples were heated for 25 h at 900° C, cooled in the same furnace and then removed from the boxes after reaching room temperature.

Metallographic observation, Vickers microhardness tests (HV 0.05) and microprobe analysis to determine the distribution of manganese, carbon and silicon inside the diffusion layer (using electron microprobe analysis) were carried out on cross-sections of the specimens.

X-ray diffraction analysis was performed on the surface of manganized samples to detect the surface layer constitution. Cu K α radiation, was used, since its low

penetration, gives spectra with lines reflecting only the planes present in the outermost layer.

Results and discussion

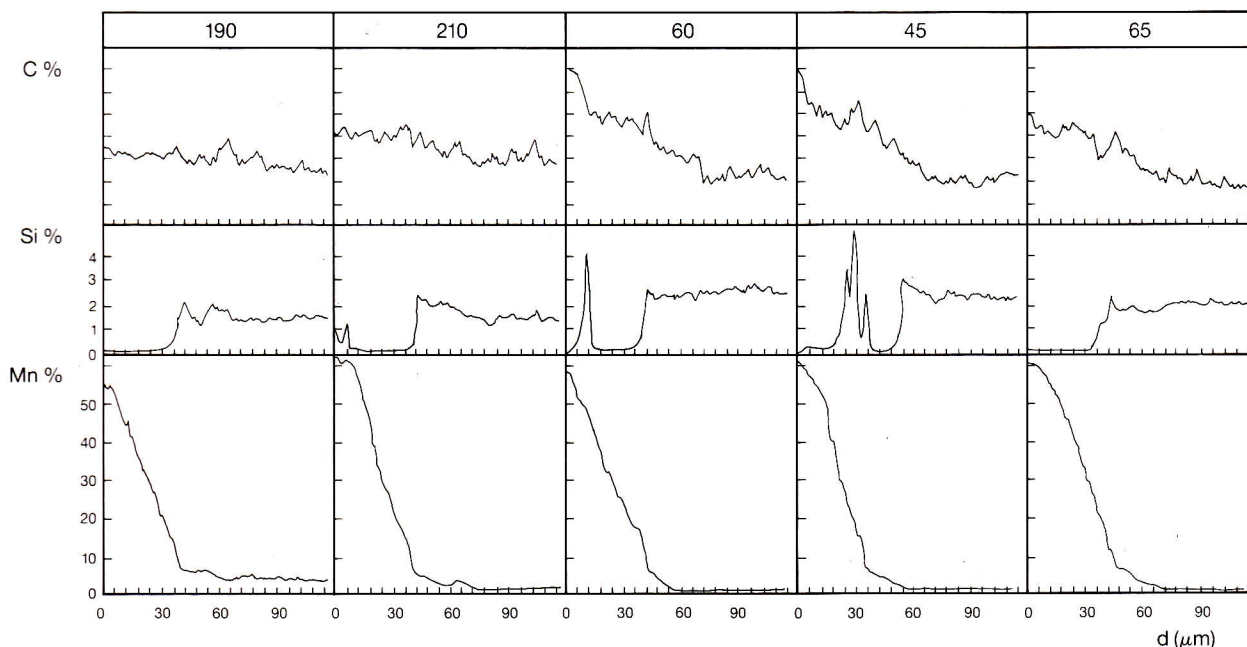
Metallography

Fig. 1 shows micrographs (at different magnifications) of cross-sections of the five cast irons after manganizing. Metallographic examination shows an external, continuous, weakly etched layer, followed by a grey layer, consisting mostly of fine pearlite and graphite; this is deeper on the flake graphite cast iron. Below the external layers, types 190 and 210 show the graphitic-pearlitic structure of the untreated materials.

Type 60 appears to have been ferritized, giving the ferritic-graphitic observed in type 45. Type 65 has been incompletely ferritized and a deep ferritic-graphitic layer is present, ahead of the pearlitic graphitic matrix.

This predominantly ferrite structure is probably formed, as in the case of manganized steels (3), during the slow cooling process in the furnace, because carbon migrates towards the manganese-rich zone as a result of his affinity to manganese.

Fig. 2 - Carbon (semiquantitative), silicon and manganese (quantitative) concentration profiles, measured on manganized cast iron samples by electron microprobe; d is the distance from the surface.



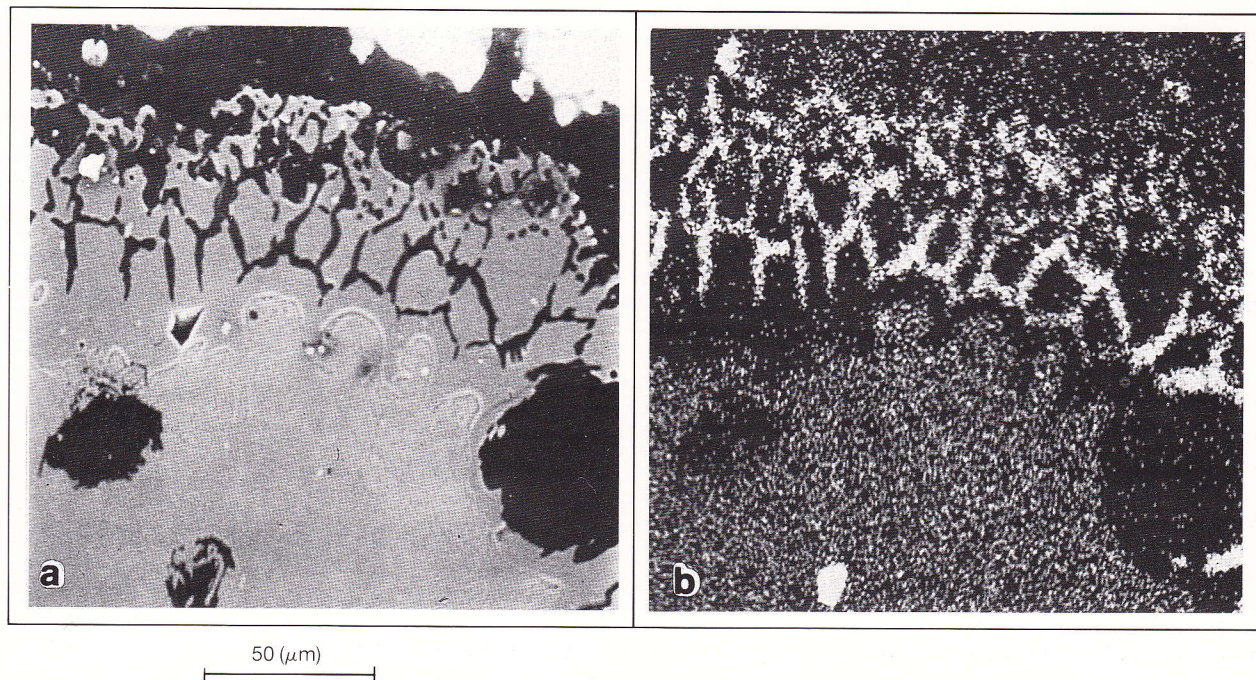


Fig. 3 - Positive electronic image (a) and silicon distribution (b) inside the diffusion layer of type 65 manganized cast iron sample, obtained by electron microprobe.,

Electron microprobe analysis

The manganese, carbon and silicon distribution inside the diffusion depth of the samples illustrated in Fig. 1 was measured by means of electron microprobe analysis (Fig. 2). Manganese and carbon concentration profiles are similar to those detected on manganized steels. Diffusion layer is also similar in thickness at a higher temperature (1000° C), showing that manganese diffuses more easily in cast iron than in steels, as expected.

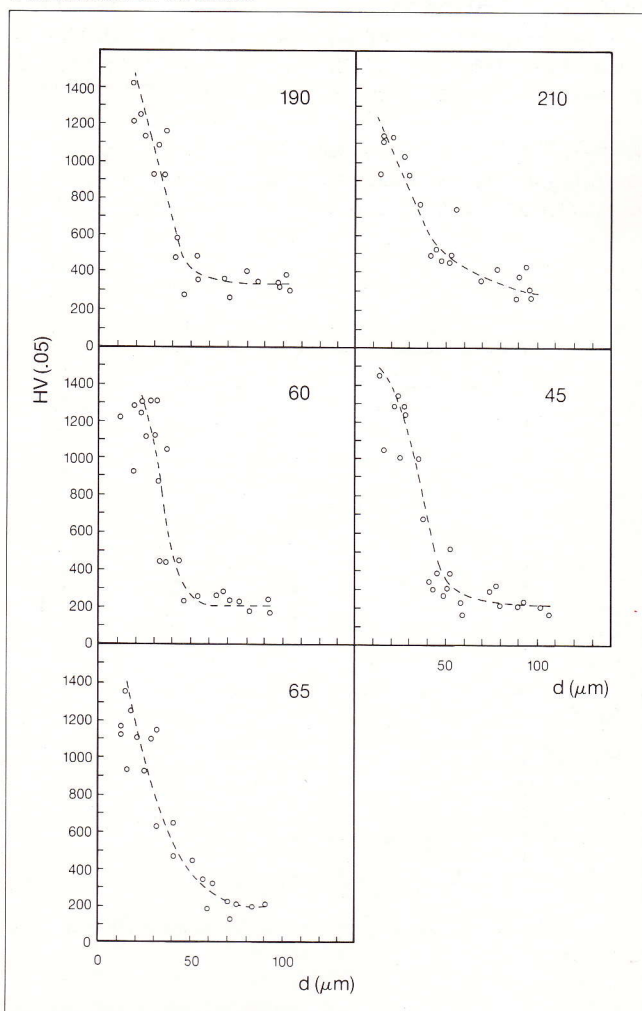
The average alloyed carbon concentration appears to decrease only slightly, proceeding into the diffusion and in the inner layer for both types of flake graphite cast iron (Fig. 2), whereas in the nodular graphite irons there is a pronounced increase of carbon concentration from the core, which is not involved in the manganese diffusion process, to the external layer.

Silicon distribution inside the diffusion layer is peculiar (Fig. 2). In the matrix, silicon appears regularly distributed, whereas within the diffusion layer it is more concentrated at the grain boundary; hence its concentration is very low in the contiguous areas (Fig. 3).

Microhardness

Very high Vickers microhardness values were measured on the external layers of the diffusion depth. The hardness decreases regularly towards the core, where it reached the same values as in the untreated materials (Fig. 4), below the manganese diffusion layer; this trend is similar to that of the manganese concentration profiles in Fig. 2.

Fig. 4 - Vickers (0.05) microhardness profiles of five manganized cast iron samples; d is the distance from the surface.



X-ray Analysis

A cementite like structure was detected by X-ray diffraction on the external layer of all manganized samples.

Given both the high microhardness values ($\Psi 1300$ HV) and the high manganese concentration, this structure is probably due to $(\text{Fe, Mn})_3\text{C}$. It is well known that when manganese atoms replace iron atoms in the orthorhombic cementite lattice, the unit cell volume decreases (4).

This phenomenon can be interpreted as an increase of the strength of the metal-non metal bonds, which acquire an augmented degree of covalent nature as iron is replaced by metal with fewer 3d electrons (5). Consequently, the unit cell shrinks, even if manganese atoms are larger than iron atoms.

The surface microhardness values are thus in good agreement with high manganese contents. Both manganese concentration and microhardness decrease toward the core.

Discussion

Various specific features of the constitution of the surface layers make the treatment of cast iron different from that of low and medium carbon steels (6). First of all, in the top layer, X-ray diffraction analysis indicates the presence of only $(\text{Fe, Mn})_3\text{C}$ in both pearlitic cast iron with nodular or flake graphite and in ferritic nodular cast iron.

Second, no graphite nodules or flakes can be seen in the entire top layer.

Third, in all cases the top layer is followed by a heavily carburized zone and then by an extensively decarburized portion.

Different explanations can be offered for these features. Results from a 0.7% C sintered steel, where the same top cementitic layer is encountered (7), point to a rationalization based on extensive carbon migration from the bulk to the surface, growth of the outermost layer leaving behind all the graphite carbon and a stabilizing action of manganese on substituted cementite at the external surface.

On the other hand it must be noted that the electron microprobe data point to higher than 50% wt manganese in the outermost layer.

Maximum manganese solubility in cementite however is much lower; it has therefore to be concluded that substituted cementite is accompanied by a very fine

manganese carbide precipitation. In the inner layers, even acicular martensite is present. This can be formed by small amounts of manganese (8).

Conclusions

Manganese-diffusion depths measured on five types of cast iron manganized at 900°C are closely similar to those obtained on steels manganized at 1000°C .

On cast irons, a very hard surface layer is formed with substituted cementite, carbides and small amounts of martensite; no austenitic-like manganese-rich structures of the type seen on manganized steels are detected.

In the external layer, the formation of substituted cementite is caused by the occurrence of high carbon and manganese local.

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