

A New Approach to Lean Alloy PM Steels

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ABSTRACT

Lean alloy PM steels are generally defined as materials containing less expensive alloying elements such as not only Ni and Mo but also Cu. Furthermore, low-cost elements such as Cr, Mn and Si may be introduced in either the melt prior to atomization or as admixed elements in the form of ferro and/or master alloys. In the latter case, high temperature sintering is generally required to promote the diffusion of the elements in the steel matrix.

This paper describes a new approach combining the use of low alloy steel powders with admixed ferroalloys, where carbon is introduced in the steel matrix by the use of a pre-alloyed carbon master alloy powder. Static and dynamic properties achieved with this new processing route are significantly improved compared to the use of free graphite as a carbon source.

INTRODUCTION

Powder metallurgy offers a unique way to achieve multiphase microstructures by mixing either diverse steel powders and/or admixing elements that will not completely diffuse during sintering. Steel mixes containing free nickel are a good example of this type of material. Nickel can also be diffusion bonded to the steel particles by a thermal treatment or by a chemical process known as binder treatment to prevent its segregation and dusting. However, since Ni is an expensive element and also because of its negative effect on human health, the PM industry is developing alternative Ni-free materials.

The use of steel powders mixed with ferroalloys (FeMn, FeCr and/or FeMo) and graphite, combined with high temperature sintering has been used for quite a long time and many parts are currently produced using this technology. These materials have been described in various patents¹⁻²⁻³⁻⁴. Elements like manganese, chromium, silicon or others can also be introduced via a master alloying route⁵⁻⁶⁻⁷⁻⁸⁻⁹⁻¹⁰⁻¹¹⁻¹². By selecting the right concentration of elements, it is possible to produce a liquid phase that when heated to the sintering temperature, promotes diffusion of the alloying elements. However, even in the master or ferroalloy forms, elements like manganese or chromium have a high tendency to oxidize. Therefore, furnace atmospheres with low dew points are required to prevent oxidation of these elements. Hryha and al.¹³ reported that oxidation of manganese gradually decreases as manganese is introduced; going from pure Mn powder to FeMn and to prealloyed Mn with an improvement in sintered properties. However as

the sintering temperature or the time at temperature increases, the difference between the various addition routes is decreased. Similar observations were made by Salak and al.¹⁴ with electrolytic manganese compared to medium and high carbon ferromanganese. Castro and al.¹⁵ reported that master alloys generating liquid during sintering dissolve a significant amount of iron, which prevents the oxidation of alloying elements and facilitates their diffusion in the iron matrix.

Also, some studies have been initiated to modify the way the carbon is introduced in the mixes. Danninger and al. and Gierl and al.¹⁶⁻¹⁷ described two methods: one where a master alloy containing up to 5% graphite is pre-diffused in steel powders by a subsequent annealing treatment and a second method using water atomization of a high carbon melt, 3.7-5.4 %C. For both production routes, a special annealing treatment, probably carbide spheroidization, is required to soften the powders and make them compressible when admixed with other steel powders. However, the sintered properties of these materials are similar to those of the reference material produced with free graphite.

This paper describes a new approach combining the use of low alloy steel powders admixed ferroalloys and a carbon master alloy that is produced from water atomization of a high carbon melt containing 1% Si. This material is then made malleable by a heat treatment, which precipitates graphite nodules in a ferritic matrix and improves its compressibility.

EXPERIMENTAL PROCEDURE

ATOMET 4001 and ATOMET 4401 were used as base steel powders for this study. The carbon master alloy (M.A. 1) was produced by water atomization of a Fe-2%C-1%Si melt. This powder was subsequently made malleable by a heat treatment, which is described more precisely in a previous paper¹⁸. The chemical and physical properties of these powders are given in Table 1.

Table 1. Chemical and physical properties of ATOMET 4001, ATOMET 4401 and carbon master alloy.

Powder grade	Mo, %	Mn, %	Si, %	C, %	O, %	+100 mesh, %	-100/+325 mesh, %	-325 mesh, %	Apparent density, g/cm ³	Flow, s/50g
ATOMET 4001	0.50	0.14	-	0.004	0.09	12	66	22	2.95	25
ATOMET 4401	0.85	0.16	-	0.008	0.08	12	66	22	2.95	25
M.A. 1	-	-	1.05	1.98	0.10	12	64	24	2.85	27

Mixes were prepared with ferromanganese and ferrochromium to reach nominal values of 0.9% Mn and 0.6% Cr. The carbon concentration was varied from 0.30 to 0.65% by changing the proportion of carbon master alloy in the mix. The concentration of molybdenum was kept constant at around 0.5% by modifying the proportion of ATOMET 4001 and ATOMET 4401 in the mixes, when using the carbon master alloy. Tests were also carried out to evaluate the effect of particle size of the carbon master alloy on sintered properties. The master alloy was screened on a 200 mesh sieve and the undersize was used to prepare the mixes. The results were compared to those reached with a reference material produced with graphite. All the mixes contained 0.75% wax as lubricant.

Transverse rupture strength (TRS) and dog bone specimens from each mix were pressed to 6.90 g/cm³ and sintered at either 1160 or 1190°C for 35 minutes in a 90%N₂/10%H₂ atmosphere. The post-sintering cooling rate in the range of 650 to 315°C was about 1°C/s for both sintering temperatures. All the specimens were tempered at 200°C for 60 minutes.

Dimensional change, apparent hardness, transverse rupture strength, tensile strength, yield strength and elongation were determined for each test condition. The plane bending fatigue strength was evaluated for one sintering temperature at a load ratio of R=0.1. The fatigue limit at 50% survival value was determined by the staircase method with a runout limit of 2.5 million cycles. The values are reported in terms of maximum stress. Finally, a microstructural characterization was performed by optical microscopy.

RESULTS

Results of the characterization are given in Table 2. The average concentrations of Mn, Cr and Mo were respectively 0.87, 0.60 and 0.49%. The Si concentration varied from 0.1% in the materials produced with free graphite up to 0.4% as the concentration of master alloy increased in the experimental materials.

Table 2. Sintered properties of Fe-0.9Mn-0.6Cr-0.5Mo-xC materials produced with M.A.-1 or free graphite as carbon sources and sintered at 1160 or 1190°C.

Carbon source		Carbon master alloy (M.A. 1)								Graphite	
		-200 mesh				-70 mesh					
Compacting pressure, MPa at 6.90 g/cm ³		539	563	590	617	530	560	586	607	480	492
C, %		0.31	0.47	0.55	0.64	0.38	0.47	0.57	0.67	0.40	0.57
Mn, %		0.87	0.88	0.87	0.85	0.86	0.87	0.88	0.89	0.87	0.91
Cr, %		0.59	0.57	0.56	0.55	0.62	0.61	0.62	0.63	0.62	0.63
Mo, %		0.45	0.45	0.43	0.44	0.45	0.54	0.52	0.54	0.53	0.49
Si, %		0.26	0.31	0.37	0.40	0.25	0.32	0.36	0.40	0.10	0.09
Sintered density, g/cm ³	1160°C	6.88	6.88	6.89	6.901	-	-	-	-	-	-
	1190°C	6.89	6.88	6.90	6.91	6.86	6.88	6.88	6.88	6.83	6.83
Dimensional change, % vs die size	1160°C	0.12	0.13	0.12	0.11	-	-	-	-	-	-
	1190°C	0.10	0.09	0.07	0.07	0.2	0.14	0.12	0.11	0.28	0.32
Transverse rupture strength, MPa	1160°C	1100	1233	1392	1488	-	-	-	-	-	-
	1190°C	1191	1337	1501	1609	1189	1289	1336	1432	1076	1124
Apparent hardness, HRB (HRC)	1160°C	80	84	90	97	-	-	-	-	-	-
	1190°C	80	87	89	(23)	80	87	93	(24)	78	85
Tensile strength, MPa	1160°C	630	708	802	853	-	-	-	-	-	-
	1190°C	655	732	847	913	648	698	750	796	604	626
Yield strength, MPa	1160°C	479	532	599	683	-	-	-	-	-	-
	1190°C	501	546	664	721	478	521	555	652	467	492
Elongation, %	1160°C	2.4	1.8	1.3	0.7	-	-	-	-	-	-
	1190°C	2.1	1.7	1.0	0.7	1.9	1.3	1	0.6	1.6	1.2
Bending fatigue strength, MPa	1190°C	-	-	-	-	-	350	378	392	-	328

Figure 1 shows the variation of compacting pressure with carbon concentration in the materials. Because of its lower compressibility compared to steel powders, the compacting pressure required to press the mix containing the carbon master alloy to 6.90 g/cm³ increases as its concentration increases in the mixes. On the other hand, it is almost unaffected for the mixes produced with free graphite. This is a linear relationship relative to the amount of master alloy; with an increase of about 24 MPa for each 0.1% C or about 5% increment of the master alloy added in the mix. Using a finer carbon master alloy slightly increases the compacting pressure. At about 0.5% C, the difference between the mixes containing free graphite and 25% master alloy is around 90 MPa at a green density of 6.9 g/cm³.

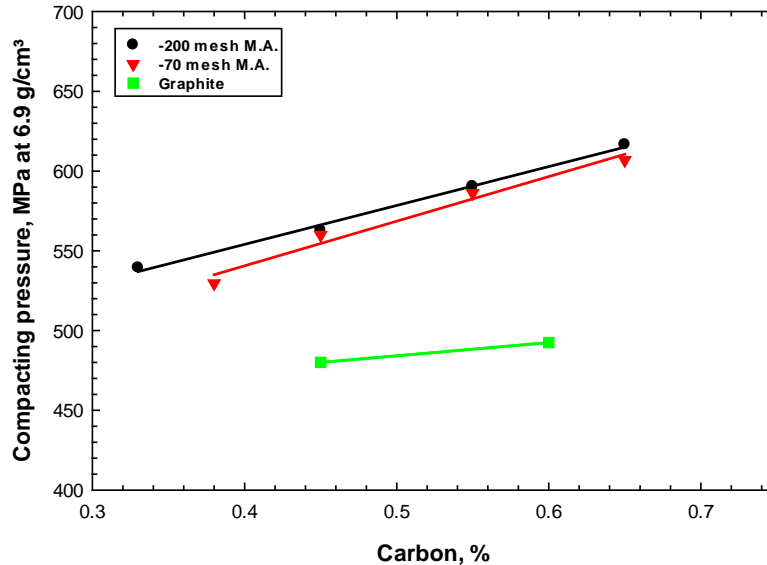


Figure 1. Variation of compacting pressure with carbon concentration in material containing either carbon master alloy or free graphite as carbon sources; green density of 6.9 g/cm³.

Figure 2 illustrates the variation of dimensional change from die size and the sintered density relative to carbon concentration in materials produced with carbon master alloy and free graphite for sintering temperatures of 1160 and 1190°C. It is interesting to note that the materials produced with free graphite exhibit significantly larger growth values than those containing the master alloy. The dimensional change values are almost 20 points larger in the case of the materials produced with free graphite. It is also worth noting that for materials containing master alloys, the dimensional change slightly decreases as the carbon concentration is raised, about -0.02% for each 0.1% C increment. Also, larger shrinkage, -0.04% on average, is observed when the sintering temperature increases from 1160 to 1190°C. Finally, larger shrinkage, -0.06% on average, is also observed when the finer master alloy is used. As a result, the sintered density is lower for the materials produced with free graphite while it slightly increases with an increase of the carbon concentration and sintering temperature and with the finest master alloy particle size for the materials containing the carbon master.

Figure 3 illustrates the variation of apparent hardness with carbon concentration of materials produced with carbon master alloy and with free graphite for sintering temperatures of 1160 and 1190°C. Higher apparent hardness values, +8 HRB on average, are observed for the materials produced with the master alloy as compared to those produced with free graphite and the difference increases as the carbon concentration increases i.e. as the proportion of master alloy in the mixes increases. One possible explanation for these results is the increase of the silicon concentration as the amount of master alloy increases but also to the larger proportion of ATOMET 4401 in the mix to maintain the Mo concentration at around 0.5%. For the materials with carbon master alloys, apparent hardness increases from about 80 HRB at 0.3-0.4% C to 18-25 HRC at 0.60-0.65% C. It is worth noting that for these materials, neither the sintering temperature nor the particle size of the master alloy seem to significantly affect apparent hardness.

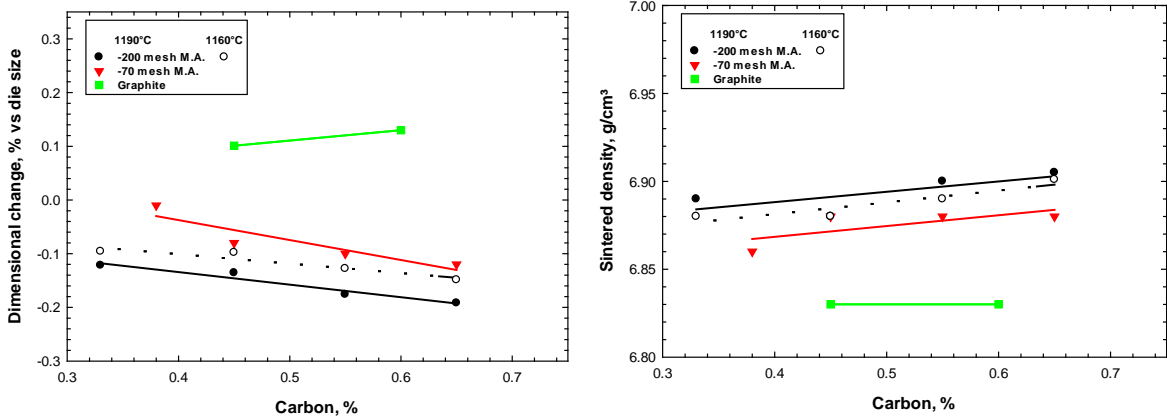


Figure 2. Effect of carbon concentration and sintering temperature on dimensional change and sintered density of Fe-xC-0.9Mn-0.6Cr-0.5Mo materials produced with both sizes of master alloy or free graphite as carbon sources; green density of 6.9 g/cm³.

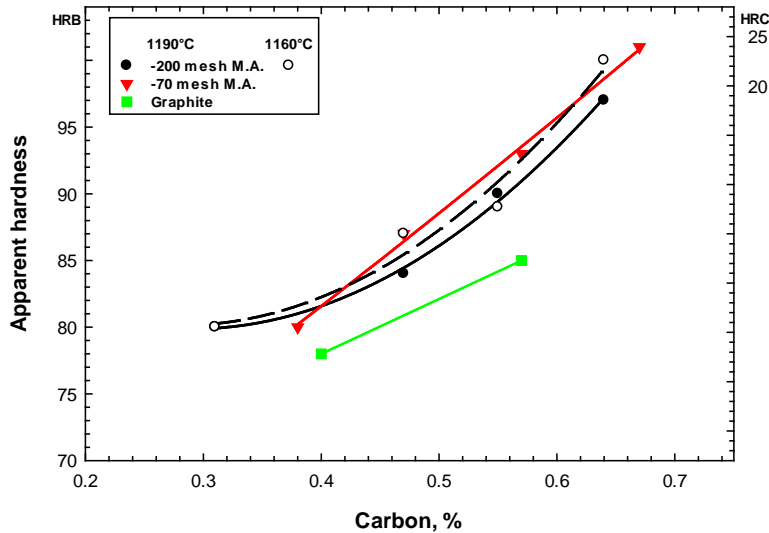


Figure 3. Effect carbon concentration and sintering temperature on apparent hardness of Fe-xC-0.9Mn-0.6Cr-0.5Mo materials produced with both sizes of master alloy or free graphite as carbon sources; green density of 6.9 g/cm³.

Figure 4 illustrates the effect of carbon concentration, sintering temperature and particle size of the master alloy on tensile properties and transverse rupture strength of materials produced with either carbon master alloy or free graphite as carbon source. Tensile strength increases linearly with carbon concentration for the various materials. However, significantly lower values are observed with the materials produced with free graphite, more than 20% within 0.45-0.60% C. Also, the effect of raising carbon concentration from 0.40 to 0.57% is almost negligible for these materials while it has a significant effect for the materials produced with the carbon master alloy. Indeed, because of the different slopes of the regressions, tensile strength values at the lowest carbon concentrations, 0.3-0.4%, are similar, around 650 MPa and the difference significantly increases with carbon concentration. The interesting observations are that at about 0.65% C, the highest tensile strength value is reached for the material with the finer carbon master alloy sintered at 1190°C, 915 MPa, followed by the same material sintered at 1160°C, 855 MPa, and the material made with the un-screened carbon master alloy sintered at 1190°C, 795 MPa.

For the yield strength, the relation with carbon concentration is almost linear except at the lowest carbon concentrations. As for tensile strength, the materials made with free graphite show the lowest yield strength, about 480 MPa vs about 570 MPa for the materials made with the carbon master alloys, i.e almost 20% lower for similar carbon concentrations. Also, as the carbon concentration is raised, the

difference between the various materials increases with higher yield strength values reached at 1190°C and 0.65% C for the material with the finest carbon master alloys, 720 MPa, followed by the same material sintered at 1160°C, 685 MPa and finally by the material with the unscreened master alloy sintered at 1190°C, 650 MPa.

Elongation values decrease with carbon concentration from 2.5% at 0.3%C to less than 1% at 0.65%C with no significant difference between the various materials.

Transverse rupture strength increases linearly with carbon concentration for the various materials. Again, for carbon concentrations in the range 0.45 to 0.60%, values reached with materials made with free graphite are about 20% lower than those with the carbon master alloy and the highest values reached at 1190°C for the materials with the finest carbon master alloy.

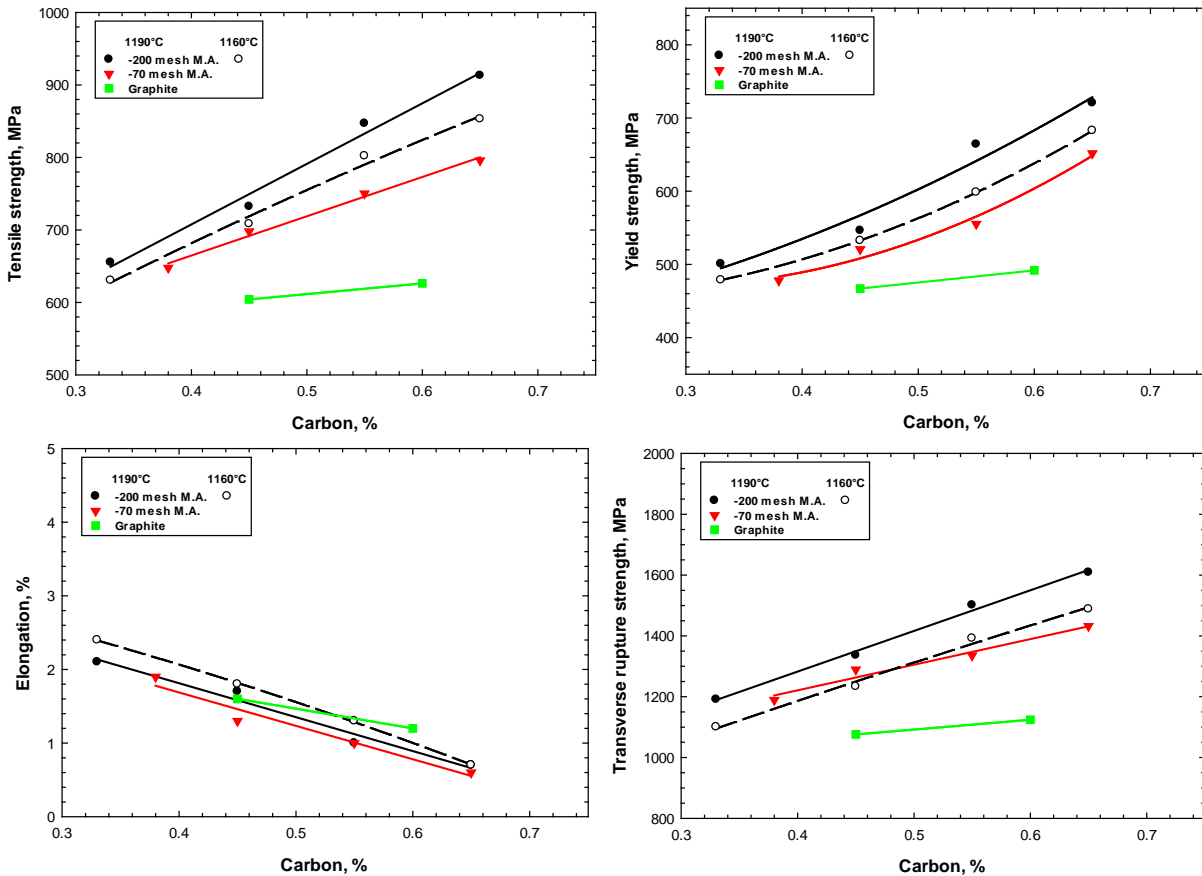


Figure 4. Effect of carbon concentration and sintering temperature on tensile properties and transverse rupture strength of Fe-xC-0.9Mn-0.6Cr-0.5Mo materials produced with both sizes of master alloy or free graphite as carbon sources; green density of 6.9 g/cm³.

Figure 5 shows the microstructures of Fe-0.55C-0.9Mn-0.6Cr-0.5Mo materials produced with the -200 mesh carbon master alloy sintered at either 1160 or 1190°C. These show multiphase microstructures with a lesser degree of diffusion at 1160 than at 1190°C. At higher magnification, the main constituents are a mixture of bainite, pearlite and martensite, the latter in a larger proportion at 1190°C, in line with a better diffusion of the ferroalloys. The main constituents of the prior carbon master alloy particles are mainly pearlite and bainite, as opposed to martensite and bainite for the low alloy steel particles. It is worth noting that at both sintering temperatures, some ferroalloy particles did not completely diffuse in the steel matrix.

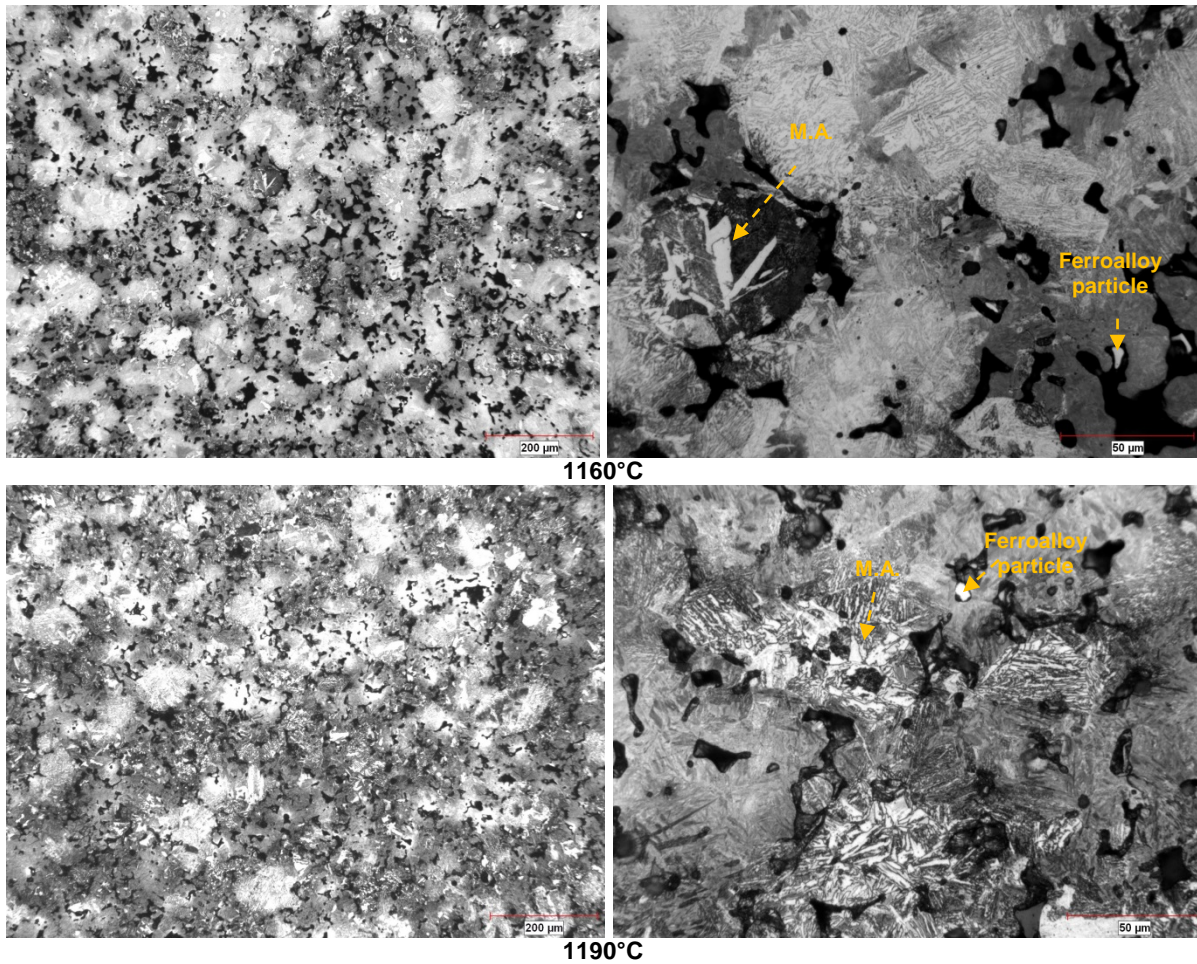


Figure 5. Microstructures of Fe-0.55C-0.9Mn-0.6Cr-0.5Mo materials containing -200 mesh carbon master alloy sintered at either 1160 or 1190°C; (Nital etching; 100 and 500X).

Figure 6 shows the microstructures of Fe-0.65C-0.9Mn-0.6Cr-0.5Mo materials produced with the -70 and -200 mesh carbon master alloy and with graphite sintered at 1190°C. For the materials containing carbon master alloys, the microstructures are composed mainly of martensite and bainite with pearlite located in the prior carbon master alloy particles. Decreasing the particle size of the master alloy reduces the dimension of the pearlitic areas. For the material produced with graphite as carbon source, the microstructure is mainly composed of bainite with martensitic areas located around the ferroalloy particles. It is also worth noting that the size of undissolved ferroalloy particles seems larger in this material compared to those produced with the carbon master alloy. This lack of diffusion which leads to a larger proportion of bainite in the microstructure is probably the main factor explaining the lower strength observed with these materials versus those produced with the carbon master alloy. It is also important to note that the presence of silicon in the master alloy could have also contributed to increase the strength of the materials.

Figure 7 illustrates the effect of carbon concentration on bending fatigue strength of Fe-xC-0.9Mn-0.6Cr-0.5Mo produced from both the 70 mesh carbon master alloy and free graphite, sintered at 1190°C. Bending fatigue strength increases almost linearly with carbon concentration from 350 MPa at 0.47% C to 392 MPa at 0.67% C. The material produced with graphite shows a bending fatigue strength value of 328 MPa at 0.57% C. For a similar carbon concentration, the material produced with the carbon master alloy shows a value of 378 MPa, 15% higher than the value reached with the material made with graphite. This

difference can be related to the different microstructures where a significantly larger proportion of martensite is present in the materials made with the carbon master alloys.

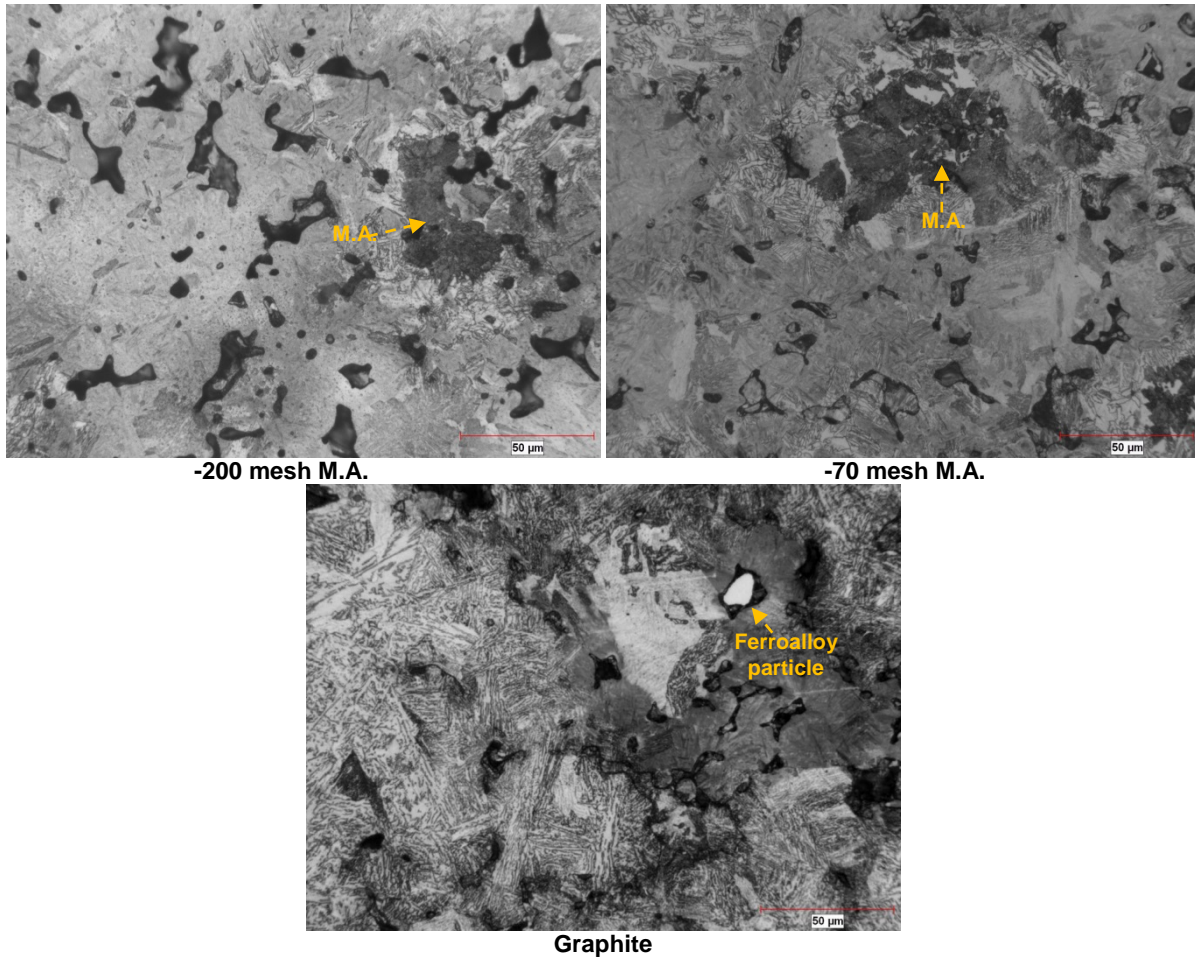


Figure 6. Microstructures of Fe-0.65C-0.9Mn-0.6Cr-0.5Mo materials produced with either carbon master alloy or graphite as carbon source sintered at 1190°C. (Nital etching; 500X).

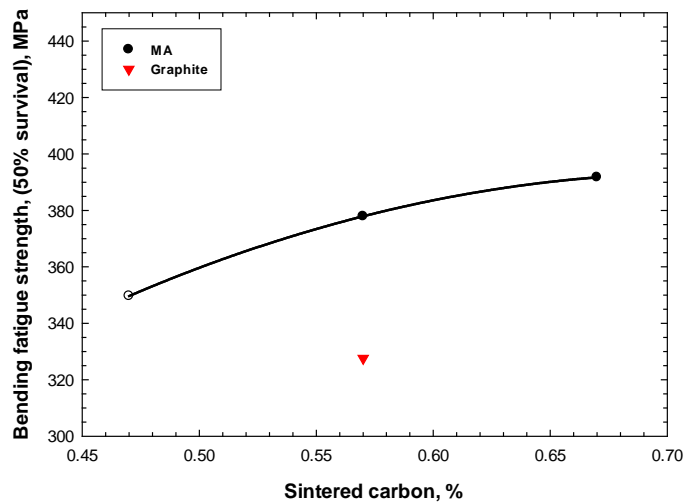


Figure 7. Effect of carbon concentration on bending fatigue strength of Fe-xC-0.9Mn-0.6Cr-0.5Mo materials produced with both sizes of master alloy or free graphite as carbon sources; green density of 6.9 g/cm³ and sintering temperature of 1190°C.

CONCLUSIONS

A novel approach to produce lean alloy PM steels was evaluated. This new production route involves the use of low alloy steel powders with admixed ferromanganese and ferrochromium and a carbon master alloy as carbon source, the latter being produced from a 2% carbon water atomized melt containing 1% Si. Within the carbon concentration range of the Fe-xC-0.9Mn-0.6Cr-0.5Mo materials and sintering temperatures used in this study, the following conclusions can be drawn:

1. The compressibility of the mixes containing the carbon master alloy is lower than that of the mixes produced with free graphite and it decreases as its proportion in the mixes increases.
2. The materials produced with the carbon master alloy shrank during sintering while those made with graphite as carbon source swelled. As a result, higher sintered densities were reached with the former materials.
3. For similar carbon concentrations, tensile properties of the materials made with the carbon master alloy were 20% higher than those made with free graphite. Also, the sintered properties improved by increasing the sintering temperature and by decreasing the size of the carbon master alloy particles.
4. For the various materials, apparent hardness increases with carbon concentration. The highest values are reached with materials containing the carbon master alloys. Also, for these materials, neither the particle size of the carbon master alloys nor the sintering temperature had any significant effect.
5. For a similar carbon concentration, the bending fatigue strength of the material made with the carbon master alloy was 15% higher than that of the material produced with graphite.
6. There was indication that the ferroalloys had a better diffusion in materials produced with the carbon master alloy.

FUTURE WORK

A detailed characterization of the effect of the C, Mn and Cr concentrations as well as the density, sintering temperature and post-sintering cooling rate is currently underway together with a study of the diffusion of the alloying elements.

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