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Metallographic changes in the sintering of grade T high speed steels in an industrial atmosphere and vacuum

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The metallographic changes taking place in three T grade steels, T42, T15 and T1 in the range of optimum sintering temperature to oversintering in vacuum and in an industrial atmosphere – base nitrogen – have been investigated using SEM and EDS techniques. M_6C and MC primary carbides have been observed for vacuum sintering and MX carbonitrides instead of MC carbides were found in the specimens sintered in the atmosphere. Small amounts of an eutectic carbide rich in Cr and Fe have been observed at the optimum sintering temperature. By oversintering in vacuum different type of eutectic carbides can be observed: MC, needle shape, M_6C, but only M_6C type eutectic carbide have been observed by oversintering the samples in the industrial atmosphere.

1. Introduction

Work carried out in the last twenty years on the sintering of high speed steels has allowed the development of appropriate routes for the fabrication of high speed steels, which are now well established [1–7]. Although it is well known that direct sintering takes place by a supersolidus sintering mechanism [8–10], the details of the different phases and carbides taking place in such process are not totally clarified. Several carbides (M_6C, M_2C, MC, $M_{23}C_6$ and M_3C) found at room temperature after sintering are supposed to take part in the sintering process. Recently two steels T42 [3, 11, 12] and M2 [13] sintered in vacuum have been studied in depth. In this work, which form part of an extended programme of the study of the influence of the atmosphere of sintering on the microstructure and the mechanical properties of several direct sintered high speed steels, the metallographic changes taking place during the sintering T grade steels in vacuum and in an industrial atmosphere, base nitrogen are analysed.

2. Experimental procedure

Annealed water atomized powders, with and without the addition of 0.2% of elemental carbon in the form of graphite, were cold compacted uniaxially at a pressure of 500 MPa. This resulted in green densities of 67–70% theoretical density. The compacts were sintered either in a flowing industrial atmosphere composed of 90% N_2–9% H_2–1% CH_4 or under vacuum better than 5×10^{-3} Pa. The samples were heated to the sintering temperature at a mean rate of $50\ K\ min^{-1}$ and soaked for 45 min. Specimens were then cooled at a rate of $250\ K\ min^{-1}$. The sintered samples were sectioned and prepared according to the standard metallographic techniques. Specimens in the as polished (with a 1 μm diamond) condition were observed in a 501B Philips scanning electron microscope fitted with an EDAX 9100 energy dispersive X-ray system, used to analyse the different carbides.

3. Results

3.1. T42 steel

Fig. 1 shows the typical SEM micrographs at the optimum sintering temperature for T42 + 0.2%C steel sintered in the gas atmosphere and in vacuum. The composition in weight percentage of the metallic elements of the different constituents marked in the micrographs are also included. The big round and grey MC carbides, rich in V, observed in the vacuum sintered specimens, are substituted by the small black and square MX carbonitrides, even richer in V than the MC carbides. In both micrographs the bright M_6C carbides, rich in W, present similar rectangular forms with nearly the same chemical composition. It is also observed that the Co is only present and in small amounts in the M_6C carbides. With increasing the sintering temperature there is a tendency to the formation of eutectic carbides, like those present in Fig. 2, in which also the composition in weight % of metallic elements of the different eutectic carbides is included. The following eutectic carbide types are observed:

(i) eutectic carbide, present at small amounts in all the samples at the optimum sintering temperature (type I);
(ii) eutectic carbide type MC, present only in vacuum sintered specimens (10 °C oversintering), with composition and contrast close to MC primary carbides;

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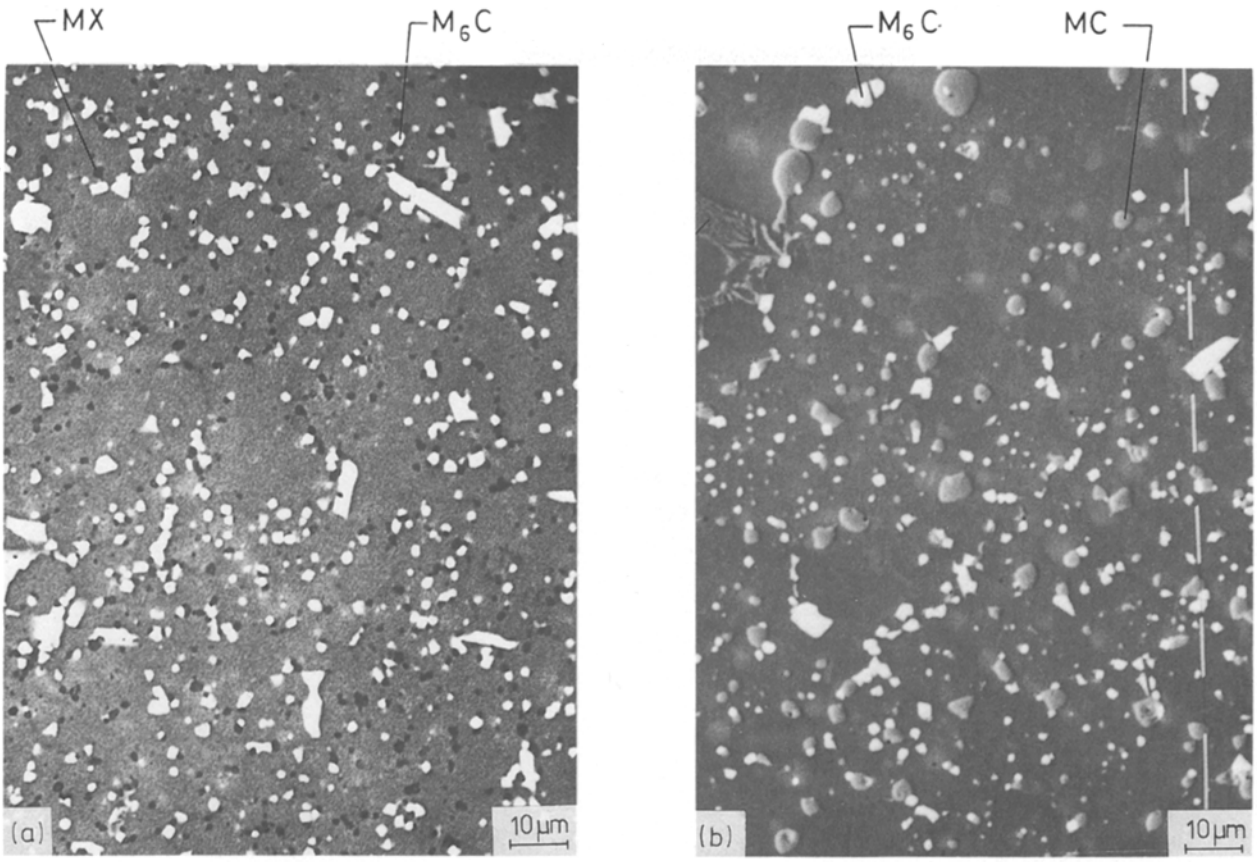

Figure 1 Microstructure of T42 + 0.2%C (1.45 C, 0.28 Si, 0.21 Mn, 0.48 Cr, 0.82 W, 3.22 Mo, 2.94 V, 9.44 Co) specimens sintered at the optimum temperature a) in the industrial atmosphere (1185 °C) and b) in vacuum (1215 °C).

Phase	Atmosphere	Mo	V	Cr weight percent	Fe	Co	W
M_6C	vacuum	16 + / − 2	3.8 + / − 0.0	3.2 + / − 0.2	27 + / − 1.4	4.3 + / − 0.1	46 + / − 3
M_6C	N_2 based	16.2 + / − 0.8	1.7 + / − 0.2	2.3 + / − 0.2	26.5 + / − 0.5	4.4 + / − 0.3	49 + / − 1.3
MC	vacuum	14 + / − 6	46 + / − 3	2.9 + / − 0.9	3 + / − 1	0.1 + / − 0.1	34 + / − 4
MX	N_2 based	5 + / − 2	72 + / − 6	5.7 + / − 0.8	7 + / − 1.9	1.0 + / − 0.5	9 + / − 2.6

(iii) eutectic carbide type M_6C similar in composition and contrast to M_6C carbide, with a clear dendritic shape; and
(iv) needle shape carbide, found only in vacuum sintered specimens at high oversinterings.

It is worth emphasizing that eutectic carbides type I and M_6C type present the similar composition when the specimens are sintered in vacuum or in industrial atmosphere and that MC and needle type eutectic carbides have been only observed in vacuum sintered specimens and never in those sintered in the industrial atmosphere. On the other hand in both materials eutectic carbides type I have been observed at the optimum sintering temperature, MC type eutectic carbides after only 10 °C oversintering in vacuum, M_6C type eutectic carbides after 10–30 °C oversintering in vacuum and 50–60 °C in the atmosphere sintering and needle shape type carbides after 40–50 °C oversintering in vacuum.

3.2. T15 steel

Fig. 3 shows two typical SEM micrographs of a T15 steel sintered at the optimum sintering temperature both in vacuum and in the industrial atmosphere. The chemical composition in metallic elements of the different constituents are also included in Fig. 3. It is clearly apparent that the M_6C carbides have nearly the same aspect and composition independently of the sintering media used, vacuum or industrial atmosphere (except in the minoritarium element, V, present in lower amounts in the specimens sintered in the industrial atmosphere). This is not the case with the MC carbides, which are transformed, changing from grey to small black carbonitrides, with a higher concentration in V, in the specimens sintered in the industrial atmosphere.

In this steel also eutectic carbides can be produced by sintering at temperatures higher than the optimum. Some examples of carbides present in eutectic form in oversintered T15 both in vacuum and in the industrial atmosphere are shown in Fig. 4. The chemical composition of the different eutectic carbides observed are also included in Fig. 4. In the case of type I eutectic carbides, which are observed after sintering in both vacuum and atmosphere at the optimum sintering temperature, a higher amount of Fe and lower concentration of W and V, in the atmosphere sintered speci-

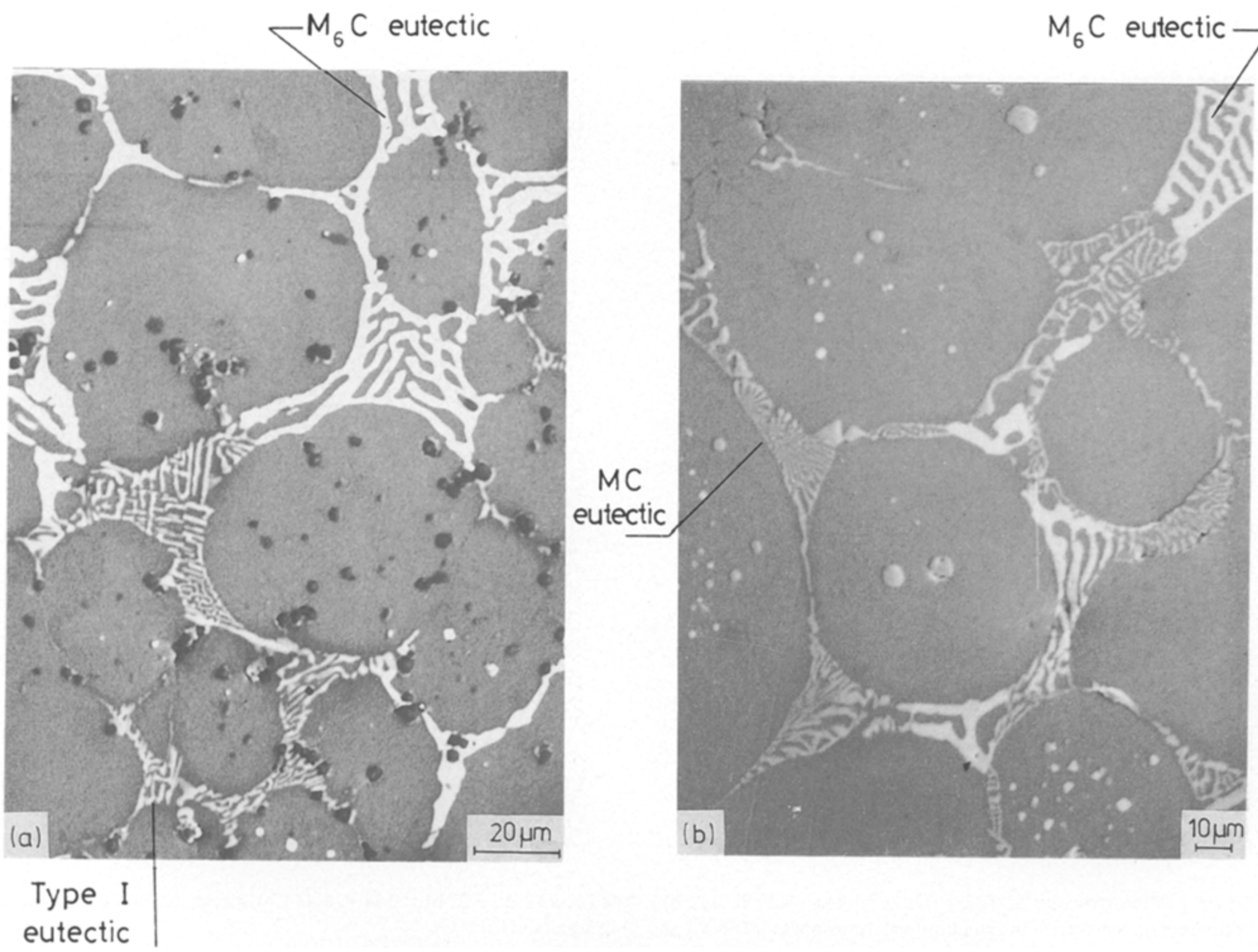

Figure 2 Microstructure of eutectic carbides in oversintered T42 + 0.2% C specimens. a) in the industrial atmosphere (ΔT = 40 °C) and b) in vacuum (ΔT = 30 °C).

Eutectic carbide	Mo	V	Cr	Fe	Co	W
				weight percent		
			Atmosphere: vacuum			
Type I	23.6 + / − 0.7	9.1 + / − 0.4	17 + / − 2.4	26 + / − 2.6	2.1 + / − 0.4	24 + / − 2.6
MC	14 + / − 3.0	35 + / − 2.6	5.5 + / − 0.8	17 + / − 3.4	1.8 + / − 0.5	28 + / − 2.3
M_6C	17 + / − 2	2.8 + / − 0.2	3.8 + / − 0.6	33 + / − 1.4	4.5 + / − 0.3	39 + / − 1
Needle	21.3 + / − 0.5	8.8 + / − 0.4	7.6 + / − 0.4	23 + / − 1.3	2.1 + / − 0.2	37 + / − 1.4
			Atmosphere N_2-based, methane 1 %			
Type I	25.2 + / − 0.8	7.0 + / − 0.4	19 + / − 2.4	22 + / − 2.6	1.0 + / − 0.4	25 + / − 2.6
M_6C	21 + / − 2.0	1.2 + / − 1.2	3 + / − 1.1	28 + / − 2.1	3.0 + / − 1.2	44 + / − 2.9

mens compared to the vacuum ones are observed. On the other hand, in the case of eutectic carbides type M_6C, which are also observed for both kind of sintering, but for oversinterings of 15–20 °C in vacuum and 50–55 °C in the atmosphere, the chemical compositions of the carbides are in both cases very similar. Also in this material a needle shape type eutectic carbide is observed only after vacuum oversinterings of 20–25 °C, an eutectic carbide type MC for oversinterings of 30–35 °C only in vacuum, and finally a new eutectic carbide, present only after vacuum sintering, called in the present work type II, rich in iron has been observed.

3.3. T1 steel

Fig. 5 shows two typical SEM micrographs corresponding to specimens sintered at the optimum sintering temperature both in vacuum and in the industrial atmosphere. The chemical composition in metallic elements corresponding to the different constituents present in the micrographs are also included in Fig. 5. One of the singular features of this material, when compared with rest of materials described above, is that no MC carbides were found in the material sintered in vacuum, and MX carbonitrides rich in V where present when the material was sintered in the atmosphere. On the other hand, the M_6C carbides are very similar in morphology, size and chemical composition for specimens sintered both in the atmosphere and in vacuum.

Sintering above the optimum sintering temperature results in the presence of carbides with eutectic morphology, like those shown in Fig. 6, where the chemical composition in metallic elements of the different eutectic carbides found are also summarized. Apart

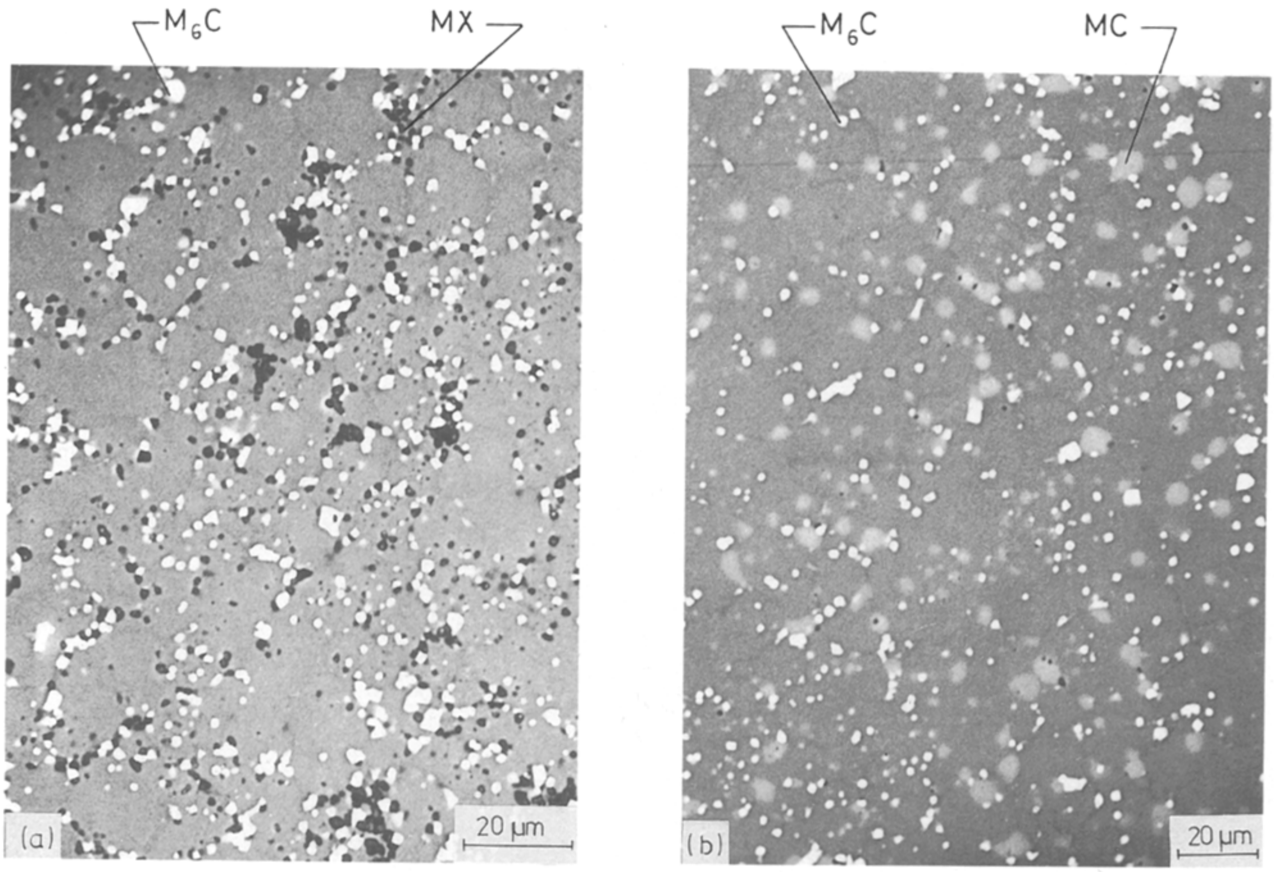

Figure 3 Microstructure of T15 (1.64 C, 0.25 Si, 0.24 Mn, 4.37 Cr, 12.4 W, 0.56 Mo, 4.7 V, 4.99 Co) specimens sintered at the optimum temperature a) in the industrial atmosphere (1225 °C) and b) in vacuum (1270 °C).

Phase	Atmosphere	Mo	V	Cr	Fe	Co	W
				weight percent			
M_6C	vacuum	6.8	3.4	3.0	26.8	1.4	58.7
M_6C	N_2 based	5.8	1.9	2.2	26.4	1.3	62.5
MC	vacuum	5.7	44.7	3.5	2.8	0.0	43.1
MX	N_2 based	1.3	72	4.4	6.2	0.1	6.2

from the M_6C eutectic carbides, which are very similar in specimens oversintered between 15–40 °C both in vacuum and the atmosphere an eutectic carbide rich in Fe and Cr is also observed in materials sintered by both methods for small oversinterings.

4. Discussion

Given the differences in chemical composition of the different steels analysed, it will be convenient for comparisons to transform the composition from weight % to atomic %. Referring first to the carbides, it is worth to emphasize that some precautions must be taken in the microanalysis of small particles, because in this case, the X-ray range can be bigger than the particle and some interference from the matrix can take place, giving a wrong particle analysis. In Table I it is clearly shown the influence of the particle size in chemical analysis obtained by EDX. It is clearly apparent that the bigger the particle size the lower the amount of Fe and Co coming from the matrix interference in the particle analysis.

4.1. M_6C primary carbides

In the case of M_6C carbides, the chemical composition could be analysed with good precision due to the fact that always some massive particle (> 4 µm) was present. Table II summarizes the chemical composition in atomic % of the M_6C primary carbides found in the different steels after sintering at the optimum temperature both in vacuum and in the industrial atmosphere. Although there are punctual differences due to the different chemical steels compositions, adding W + Mo and Fe + Co, results in practically constant values. Although the chemical composition of M_6C carbides are very similar for sintering in the atmosphere and vacuum, there is however a significant difference in the V concentration, being lower in the atmosphere sintered material. This is consequence of the higher concentration in this element found in the MX carbonitrides, as pointed out before. Also in Table I are the chemical composition of M_6C carbides analysed by other authors in T42 and T1 vacuum sintered steels, which result nearly identically to the values found in present work for vacuum

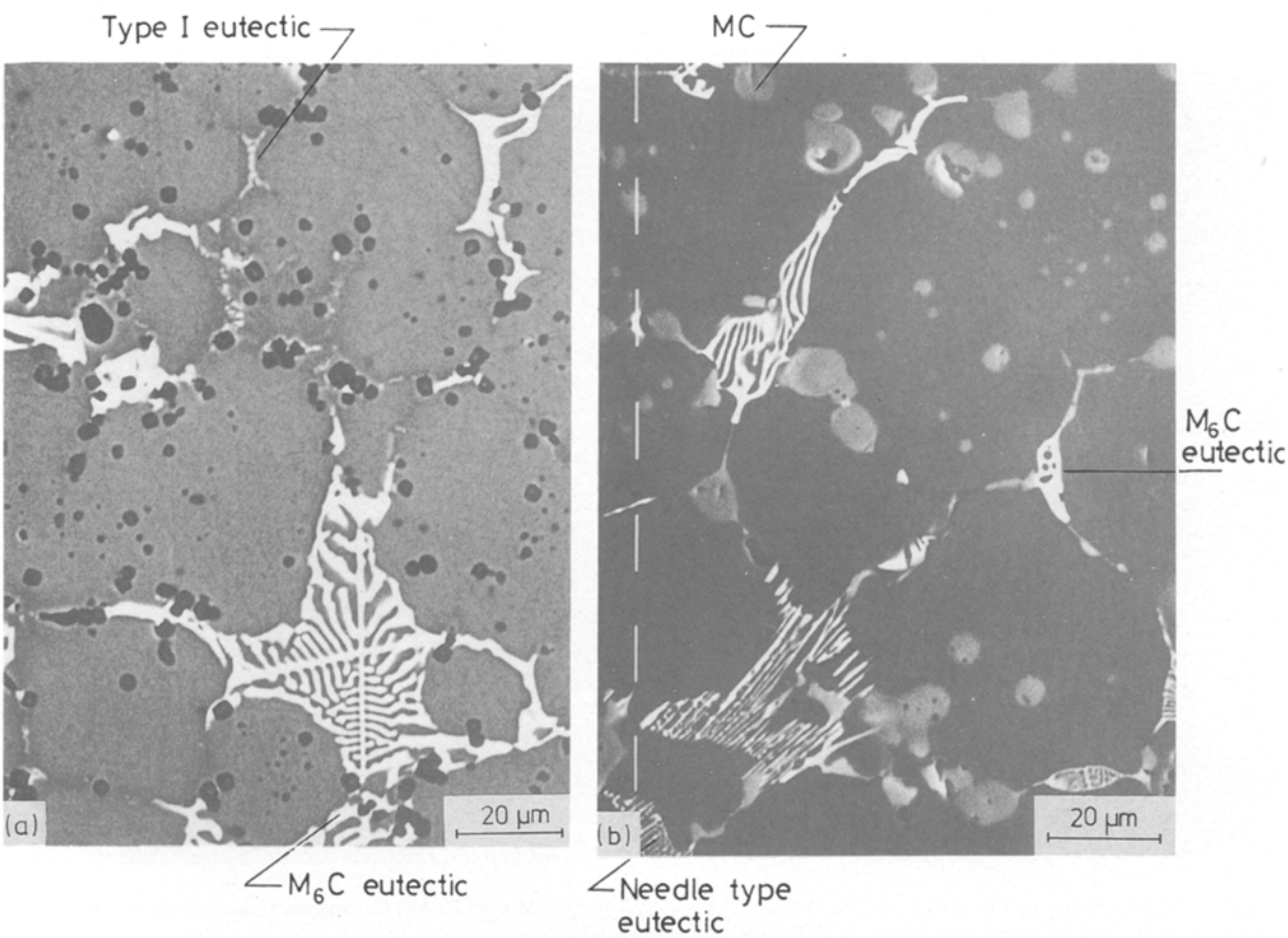

Figure 4 Microstructure of eutectic carbides in oversintered T15 specimens. a) in the industrial atmosphere ($\Delta T = 65\,°C$) and b) in vacuum ($\Delta T = 20\,°C$).

Eutectic carbide	Atmosphere	Mo	V	Cr weight percent	Fe	Co	W
Type I	vacuum	9.6	11.2	15.0	14.6	0.0	50.0
	N_2 based	9.4	5.9	18.4	36.1	1.0	29.3
MC	vacuum	3.8	41.6	3.2	7.6	0.1	43.6
M_6C	vacuum	7.9	3.3	4.6	28.5	0.7	55.0
	N_2 based	7.0	2.1	3.5	29.8	1.2	56.4
Needle type	vacuum	9.8	13.1	10.6	12.1	0.0	54.4

sintering. The mean stoichiometric composition of these carbides then results:

$$(Fe, Co)_3(W, Mo)_{2.5}(V, Cr)_{0.5}C$$

4.2. MC primary carbides, MX carbonitrides

Only in steels with a V composition equal or higher than 3 wt % the primary MC carbides were big enough (> 4 µm) to be analysed without the matrix interference; on the other hand, vacuum sintered T1 steel did not present MC carbides. The chemical composition of MC carbides for T42 and T15 vacuum sintered are shown in Table III, where it is observed that although the relative amounts of W and Mo are different, due to the different composition of the steels, however adding W + Mo results in a close value in both steels. This has been also observed in several M type steels [14]. It is also observed that the more important metallic element in this carbide is V and that the Co is not present in the carbide. Similar carbide compositions have been recently reported by Karagöz *et al.* [15].

When the steels are sintered in the industrial atmosphere, containing N_2, the incorporation of nitrogen

TABLE I M_6C carbides composition and size

Size/reference	Mo	V	Cr	Fe (atomic %)	Co	W
This work, gas, 1 µm	6	1	5	72	11	6
This work, gas, 2 µm	13	2	5	55	8	17
This work, vacuum, 4 µm	16	3	4	45	7	25
T42 [3]	13	5	6	46	5	23
T1 STEM [15]	21	5	5	51	–	19

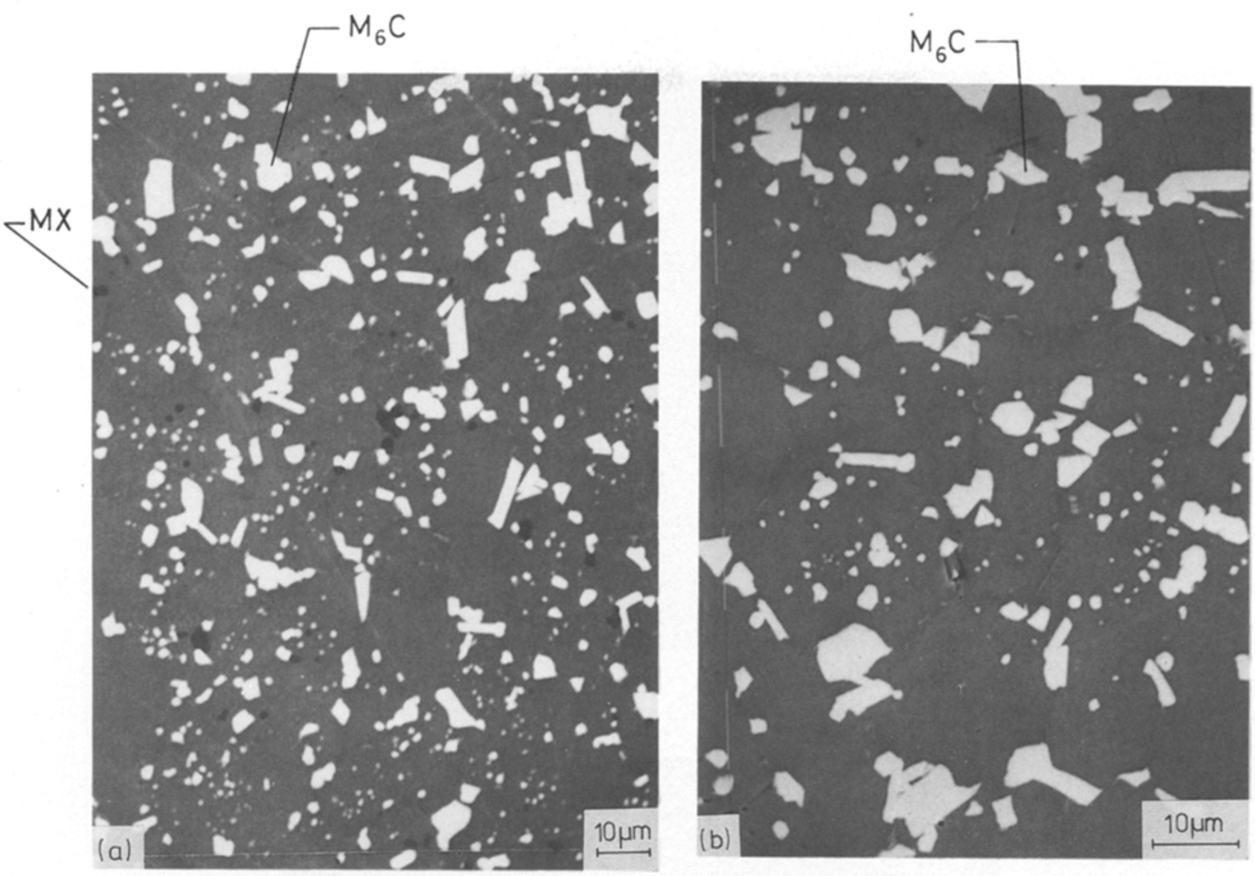

Figure 5 Microstructure of T1 (0.96 C, 0.16 Si, 0.39 Mn, 4.37 Cr, 17.59 W, 0.26 Mo, 1.09 V) specimens sintered at the optimum temperature a) in the industrial atmosphere (1330 °C) and b) in vacuum (1325 °C).

Phase	Atmosphere	Mo	V	Cr	Fe	W
			weight percent			
M_6C	vacuum	1.5	1.9	2.5	27.1	67
M_6C	N_2 based	2.4	1.6	2.3	25.5	68
MX	N_2 based	3.8	70.5	5.8	1.6	18.2

transform the MC carbides in carbonitrides, as reported by Palma *et al.* [7]. This is due to a higher stability of the nitride against the carbide. Table IV summarizes the chemical composition in metallic elements of the carbonitrides present at the different steels analyzed in the present work. Once again the composition is very similar for the different steels and if the results are compared with those of the MC carbide it is observed as an important increase in the amount of V in the MX carbonitrides. Very similar results have been obtained with several M type high speed steels [14].

4.3. Eutectic carbides

The eutectic carbides type MC and M_6C found in these materials present chemical compositions close to those observed in the primary carbides of the same type, but it is worth emphasizing that MC carbides have not been observed in steels sintered in the indus-

TABLE II M_6C carbides composition

Steel grade	Mo	V	Cr	Fe	Co	W	W + Mo	Fe + Co
					(atomic %)			
Atmosphere: vacuum								
T1	1.7	3.8	5.5	51.1	–	38.3	40	51
T15	6.9	6.5	5.6	47.2	2.3	31.4	38	49
T42	15.0	6.7	5.5	43.6	6.5	22.6	38	50
T6	3.8	5.1	6.4	39.1	8.0	37.6	41	47
Atmosphere: gas 1% methane								
T1	2.7	3.4	4.8	49.2	0.0	39.9	43	49
T15	6.2	3.8	4.4	48.5	2.3	34.9	41	51
T42	15.9	3.1	4.2	44.7	7.0	25.1	41	52
T6	3.0	4.0	5.4	40.6	9.0	38.0	41	50

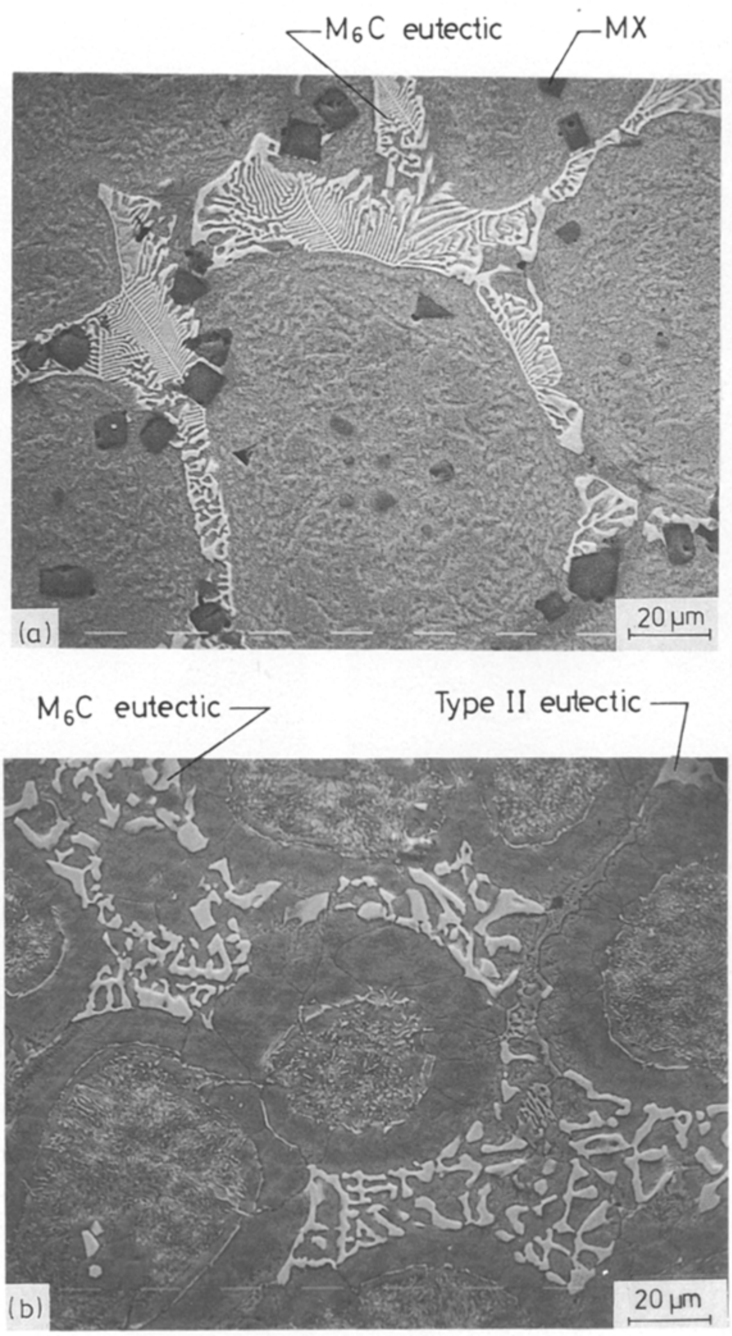

Figure 6 Microstructure of eutectic carbides in oversintered T1 specimens. a) in the industrial atmosphere ($\Delta T = 20\,°C$) and b) in vacuum ($\Delta T = 15\,°C$).

Eutectic carbide	Atmosphere	Mo	V	Cr	Fe	W
			weight percent			
Type II	vacuum	4.0	10.7	25.2	38.0	22.0
M_6C	vacuum	2.6	2.5	3.3	26.2	65.3
M_6C	N_2 based	12.0	3.4	4.3	28.9	51.4

TABLE III MC carbides composition

Steel grade	Mo	V	Cr	Fe	Co	W	W + Mo
			(atomic %)				
T15	4.6	68.0	5.3	3.9	0.0	18.2	23
T42	11.0	66.8	4.1	3.9	0.1	14.0	25

TABLE IV MX carbonitride composition

	atomic %		
Steel grade	V	W + Mo	Fe + Co
T1	83	8	2
T6	88	2	5
T15	83	6	7
T42	79	6	8

TABLE V Chemical analysis of $M_{23}C_6$

Steel	Particle	Mo	V	Cr	Fe (atomic %)	Co	W	W + Mo	Fe + Co
T15 (this work)	EI	9	19	25	23	0	24	31	23
T15 + N (this work)	EI	7	8	25	47	1	12	19	48
T15 + N $M_{23}C_6$ [21]		2	7	32	52	2	5	7	54
T15 + N C.G. [21]		2	11	27	55	0	5	7	55
T15 + N EI [21]		4	6	25	58	0	6	10	58
T42 (this work)	EI	18	13	24	34	3	9	27	37
T42 + N (this work)	EI	20	10	28	30	1	10	30	31
T42 $M_{23}C_6$ [22]		1	4	54	39	0	2	3	39
T42 C. eut [23]		14	8	18	49	5	6	20	54

trial atmosphere. This seems to be due to the fact that in the industrial atmosphere rich in nitrogen the MC carbides are transformed to MX carbonitrides and the possible transformation on cooling of the liquid to MX and austenite, which happens when MC carbide is formed, disappears or is shifted to much higher temperatures. This type of MC eutectic carbide was neither observed in T1, due to low V content of the steel. The presence of M_6C eutectic carbides both under vacuum and industrial atmosphere seems to define the limit of adecuated sintering. The addition of carbon or the introduction of nitrogen through the atmosphere does not affect strongly the temperature at which the first M_6C appears in each steel. But because the addition of carbon – in all cases – and the introduction of nitrogen – in some cases – decrease the optimum sintering temperature, the increase of concentration of both elements in the steel enlarge the sintering "gate".

The composition and morphology of the needle type eutectic carbide found in the T15 and T42 after important oversinterings in vacuum, is similar (adding W + Mo) to that found for steel M2 [16, 17] and M42 [18] and identified as M_2C. Several works [17, 19, 20] have shown that M_2C carbides are unstable and decompose during the cooling to M_6C and MC. In this work the cooling rate was very high and that could explain why this decomposition did not take place. To confirm this hypothesis, a T15 + 0.2%C sample was cooled slowly in the furnace (20 K h^{-1}) after an oversintering of 25 K. For this oversintering needle shape eutectic carbides were observed after the normal cooling of 250 K min^{-1}. In the metallographic analysis of the specimen after the slow cooling, this kind of needle shape eutectic carbides could not be found, but the coprecipitation of M_6C and MC carbides, indicating the possible transformation on cooling of M_2C to M_6C and MC as indicated by Fredricksson *et al.* [17]. A similar situation has been recently observed by Urrutibeaskoa *et al.* [14] in a M2 high speed steel. This needle type eutectic carbide was not observed in samples oversintered even by 50 K in the industrial atmosphere. It seems that the presence of nitrogen in the specimens sintered under the industrial atmosphere avoids the formation of this eutectic carbide, as has been observed by Steven [19] that by increasing the nitrogen content in M7 and M2 steels the formation of M_2C carbides is difficult.

The eutectic carbide called type I in the present work, found at the optimum sintering temperature and in some case 25 K below the optimum [18], has been also found by other authors in different high speed steels [15, 21, 22]. In Table V are compared the chemical composition of this type of eutectic carbide with other of the same kind found in the literature. This carbide type being rich in Cr and Fe could be of $M_{23}C_6$ type. In Table V are also included the chemical analysis of some $M_{23}C_6$ also reported in the literature, being the composition of this carbide similar to the type I found in the present work.

5. Conclusions

1. After cooling from the optimum sintering temperature in vacuum, primary carbides type M_6C were present in all the steels analysed and MC, although present in T42 and T15, was not found in T1 steel.
2. After sintering in the industrial atmosphere the same M_6C primary carbides are present, but the MC transform to a carbonitride MX of small size.
3. In all steels analysed, after sintering at the optimum temperature, either in the atmosphere or in vacuum, small amounts of an eutectic rich in Cr and Fe has been found.
4. Oversintering under vacuum at progressive higher temperatures produces eutectic carbides type: M_6C, needle shape and MC. These last two carbides are not present when the sintering takes place in the industrial atmosphere.
5. In all steels, sintered at the same medium, the chemical composition of the different type of carbides are the same if W + Mo and Fe + Co are added in atomic %.

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