

PM HIGH SPEED STEEL MATRIX COMPOSITES. STATE OF THE ART

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Abstract

Several studies have been carried out in relation with composite materials using high speed steel as a matrix, with the idea of obtaining an improvement in wear resistance and hardness, without losing toughness. The main objective of these composite materials is to cover the existing gap, in terms of properties between HSS and cemented carbides. This article takes the form of a general review of the matter, considering the different types of reinforcement materials and focusing on the different conformation solutions, which lead to an improvement in the properties of the base steels.

Keywords: *high speed steels, metal matrix composites, carbides, hard material*

INTRODUCTION

High Speed Steels (HSS) have traditionally been used in the cutting materials industry, and specifically for applications which require high speed cutting, due to their capacity to retain high levels of hardness at the temperatures reached in these operations [1], i.e. in the range of 500°C - 600°C. After the development of cemented carbides, a gap between them and HSS appeared (in terms of hardness). Cutting applications of HSS were then reduced, being preferentially used for tooling and other uses combining wear and strength. Nevertheless, this family of steels has maintained the name due to historical reason.

HSS compete in many of their applications with cemented carbides, though each one has advantages and disadvantages and there is a gap in properties between them which is covered by the development of intermediate materials. Regarding this, high-speed steels reinforced with ceramic particles have been one of the most studied families of materials since seventies. This first approach to the composite using ceramic particles seemed, the closest with the steel nature if we take into account that the most common non-metallic inclusions are ceramics [2]. The main objective of the development of this type of material is to improve the wear resistance of the base material while maintaining its good properties in terms of toughness, hot hardness and machinability. Also, there are economic and environmental aspects involved, since the raw materials for the manufacture of these materials are less expensive and environmentally friendly than those for cemented carbides. This concept of combining the most interesting properties of the base material with those of the reinforcing material, and the high volumetric fraction of addition, have led these materials to be classified as metal matrix composites, which is how they are known in the specialised literature [3]. It should be noted that this type of material can only be developed using powder metallurgy (PM) techniques.

Another way which could improve the surface hardness of HSS, and approach them to cemented carbides, is to use ceramic coatings, usually by PVD or CVD techniques [4, 5], or laser surface treatments [6]. We didn't consider these ways in this review paper.

Wear resistance is not an intrinsic property of a material but of a mechanical system, though certain material properties such as its hardness or toughness exert an influence on this. In the case of HSS, wear resistance is a function of the hardness of the matrix and of the size, shape and distribution of the carbides formed from C and the alloy elements during its manufacture process. By increasing the number of carbides, wear resistance and hardness increase. In wrought HSS the number of carbides is limited by the amount of C and alloy elements that are possible to introduce in the initial melt, but powder metallurgy (PM) permits to add the carbide particles to the metal by mixing powders in an appropriated way. The study of wear mechanisms in this new PM family of materials has produced several papers in recent times [7, 8]. As a result of these studies, a reduction in wear coefficient, k (m^2/N), of about 55% has been reported when 8 vol.% of NbC particles are added to a M3/2 HSS matrix through conventional PM techniques. When using HIP, the wear coefficient decreases, for the same percentage of addition, in 80% (plain M3/2 hippe has a reduction in the wear coefficient of 40%). The TRS values for these materials also increase, reaching 2399 MPa for hippe M3/2 + 8 vol.% NbC, in comparison with the 2200 MPa obtained for hippe base M3/2.

However, the manufacture of composite materials of metal matrix and ceramic reinforcement by PM is a complex process in which good results depend fundamentally on the existence of a certain reactivity between the matrix and the reinforcement, so that the latter is well integrated in the former. Ceramics are highly stable compounds, with strong covalent bonds, low toughness, a high Young modulus, and much lower thermal expansion coefficients than metals, this being a highly important characteristic when it comes to making metal/ceramic bonds because it determines the field of residual stresses in the resulting composite. Refractory metal carbides such as TiC, VC, WC, NbC and TaC are the hardest, and those that present the greatest Young modulus among the ceramic particles used for the reinforcement of metals. These carbides are the most compatible with matrixes like HSS as some of them (VC, WC) are primary carbides in this type of steel, and the others form solid solutions mainly with VC [10, 11] (always present in HSS). So a kind of reactivity exists between the HSS as the matrix, and the reinforcement carbides, that permits one to expect success in the production of these materials. Moreover, PM techniques allow the selection of the most suitable matrixes and reinforcements and their processing to the final material, and many authors have studied the manufacture methods and the properties of these kind of materials.

REINFORCEMENTS USED

Oxides and nitrides

Table 1 presents a general summary of the types of reinforcement most commonly used. These are: Al_2O_3 , TiC, WC and TiN, though studies have also been carried out with TiO_2 , ZrO_2 stabilized with the assistance of Y_2O_3 and carbides such as NbC, TaC, etc.

The first studies presented using Al_2O_3 as reinforcement, were carried out by Queeny et al. [12, 13]. In these, an increase in the wear resistance of high speed steels M2 and M3 was achieved by means of the addition of up to 10% of alumina particles with sizes of less than 10 μm , though there is a reduction in the flexural or bending strength. For larger quantities of addition, they found it necessary to use HIP after vacuum sintering, in order to remove the porosity [14]. The relative low bending strength of materials with

alumina reinforcement, may be due to the fact that there is no chemical interaction with the steel and that matrix-reinforcement bonds do not occur. The use of Cu_3P to improve sinterability does not improve the bending strength values [15].

The coating of alumina particles with TiN by means of Chemical Vapour Deposition (CVD) prior to sintering produces significant improvements in the mechanical properties of compound materials based on M3/2, by improving the cohesion between the matrix and the coating of reinforcement particles. This has been shown by authors such as Oliveira [16, 17, 18] and Jouanny-Tresy [9, 19, 20].

Oliveira and Bolton [21, 22] made additions of TiN particles (up to 10 vol.%) in M3/2 high speed steels with the assistance of Cu_3P as a liquid phase former. The result is compound materials which present TRS values of the same range as those obtained for the materials without reinforcement (1.2 - 1.4 GPa), and which possess microstructures free of porosity due to the good cohesion of the ceramic particles in the matrix by the precipitation of V and Ti rich carbides at the matrix-ceramic interface. However, there is a reduction of sinterability in comparison with the base material. These same authors attempted the addition of TiO_2 and TiC particles. In the case of the addition of TiO_2 , dense materials were not obtained due to the low wettability of these particles by the liquid phase. In addition to this, decarburisations and a worse sinterability were seen. However, in the case of the addition of TiC, the same positive results were achieved as with TiN but with an improvement of the sinterability, and to a greater extent by reducing the particle size.

Tab.1. Summary of works on HSS reinforced with hard particles.

Reinforcement	Authors	Comments
Al_2O_3	Queeney et. Al [12,13,14]	M2,M3 base, <10%. Vacuum.
$\text{Al}_2\text{O}_3/\text{TiN}$	Martins and Oliveira [16,17,18]	M3/2 base. Al_2O_3 coated by TiN.
$\text{Al}_2\text{O}_3/\text{TiN}$	Jouanny-Tresy [9,19,20]	M3/2 base. Al_2O_3 coated by TiN.
TiN	Oliveira [21,22]	M3/2 base. <10 vol.%. Cu_3P addit. Vacuum.
TiC	Kieffer [35]	M2 base. <10 wt.%.
	Bolton [26,27]	M3/2 base. Vacuum and heat treat. Cu_3P add.
	Oliveira [22]	M3/2 base. <10 vol.%
	Torralba [30]	M2,T15 base. + Co. Vacuum and gas sint.
	Martín [28]	M3/2 + MnS
	Liu [23]	M2 base. Mechanical alloying and MIM
VC	Kieffer [35]	M2 base. <10 wt.%.
	Bolton [24]	M3/2 base. 5%. Vacuum.
WC	Gutmanas [31]	T15 base. Different additions.
	Torralba [30]	M2,T15 base. + Co. Vacuum and gas sint.
	Berns [25]	WC/ W_2C , 4.6Mo-0.3Si, <30 vol.%, HIP
NbC	Kieffer [35]	M2 base. <10 wt.%.
	Talacchia [33,34]	N_2 atmosphere.
	Pischang [42]	T42 base. Mechanical alloying.
	Zapata [40,41]	M2 base. Cu_3P additions. $\text{N}_2\text{-H}_2$ atm.
	Bolton [44,45]	M3/2 base + TiC + MnS
	Gordo [7,8,47]	+ TaC + Cu_3P additions.

Carbides

Titanium, vanadium and tungsten carbides

Bolton carried out the addition of 5% by weight of carbide particles from several elements (SiC , Cr_3C_2 , Mo_2C , WC , HfC , VC , TiC , ZrC) to a matrix of M3/2 high speed steel [26] in an attempt to improve the wear resistance. The results obtained during vacuum sintering and liquid phase sintering (Cu-P) led this author to classify the carbides in three classes: the least stable carbides, SiC and Cr_3C_2 , which dissolve completely in the steel; the carbides WC and Mo_2C , formed by elements which are normally found in the composition of high speed steel and which react with the matrix to form new carbides of the type of the primary carbides M_6C ; and stable carbides of the type TiC or VC , which retain their original shape but promote the formation of MC carbides in the matrix or at the matrix/ceramic interface. The WC and Mo_2C carbides improve the sinterability of the base material, while the TiC and VC carbides worsen it. The TiC and VC carbides, due to their limited solubility, remain as a disperse phase in the matrix while presenting a good bond with it; this makes them the best candidates of the group studied for providing good wear resistance.

In a subsequent study [27], up to 25 vol.% of TiC particles were incorporated, and in addition to studying the mechanical properties in sintered state, a study was made of the effect of heat treatments on the structure and properties of the metals formed. It was confirmed that there was a reduction in the density, hardness and bending strength when the quantity of reinforcement was increased. A heat treatment was established which provided good values for hardness (850 HV) and bending strength (1100 MPa) by means of austenitization at 950°C - 1000°C and tempering at 450°C - 550°C. It was not possible to use higher austenitization temperatures due to possible fusion at the grain boundaries of the eutectic formed during the liquid phase sintering. Recent studies use additions of MnS to the composite ($\text{M3/2} + \text{TiC}$) in order to minimize the friction with a slight improvement of wear behaviour, but with sensible losses in mechanical properties [28]. Also studied was the effect of machining additives, like MoS_2 , on HSS without any reinforcement, with similar effects [29].

Torralba et al [30] used additions of TiC and WC with cobalt, notably improving the sinterability and bending strength of the high speed base steels (M2 and T15). In this work the possibility was studied of using $\text{N}_2\text{-H}_2$ and vacuum atmospheres. Gutmanas and Zak [31] used WC and VC as reinforcement of a T15 high speed steel, and analysed the properties of hardness, bending strength and wear resistance of the heat treated steels; they found that when the amount of WC was increased, this led to a reduction of the bending strength (about 10%) and an increase in the wear resistance ($\approx 2.4\%$), while the hardness remained constant. Berns and Franco study the reinforcement with $\text{WC/W}_2\text{C}$ up to 30% in volume, and using hot isostatic pressing as a forming method with very good and competitive results from the point of view of wear [25].

Studies with the addition of VC particles [32] to a matrix of M3/2 steel provide similar results to those obtained with the addition of TiC . There is a good bonding of the particles with the matrix, forming MC carbides as a result of the reaction with the liquid phase. Talacchia [33, 34] studied the behaviour of a T42 steel with addition of VC , sintered in a nitrogen rich atmosphere, quenched and tempered. The result was the transformation of the VC carbides into carbonitrides by reaction with the atmosphere. Bending strength values were seen to be low and inversely proportional to the hardness values.

Kieffer, who was one of the pioneers in the attempt to sinter mixtures of high alloy powders with monocarbides, compares the properties of M2 steel with different additions:

TiC, VC, NbC and TaC in a proportion of 10% by weight [35]. The TiC particles improve the hardness and resistance to softening during tempering, while the NbC and TaC carbides present less hardness and slightly greater bending strength (of the order of 1500 MPa).

Niobium carbide

Other attempts to add NbC particles to high speed steel matrices have been made by different authors [34, 36, 37, 38, 40, 41, 42]. In general, it is shown in all these cases that when the quantity of reinforcement is increased, the hardness increases slightly [36] or remains constant [41], the values of the bending strength diminish and the sinterability worsens for percentages of addition more than 10%. Some authors indicate [43] that the addition of NbC to the steel by simple mixing gives rise to materials with low sinterability and heterogeneously distributed carbides, for which it is necessary to use a ball mill or mechanical alloying [42] in order to deagglomerate the powder and promote the uniform distribution of carbides. Dilatometry studies carried out by some authors [41], seem to indicate that NbC presents a certain reaction with the steel matrix in the presence of a liquid phase caused by the addition of P or Cu_3P . This statement is based on the strong contraction which is experienced by the reinforced material compared with that experienced by the base material. In the case of sintering in a $\text{N}_2\text{-H}_2\text{-CH}_4$ gaseous atmosphere [35] a reduction is also seen in the optimum sintering temperature (reaching densities close to the theoretic density at lower temperatures) for the materials containing NbC, which has been attributed to the formation of carbonitrides as in the case of the addition of VC.

Other studies consider the behaviour in heat treatment of high speed steels with the addition of NbC particles [40, 44, 45] prepared by means of compaction and vacuum sintering. In the case of the presence of liquid phase [40], the austenitization temperatures were low (950°C; tempering temperature of 550°C) to prevent intergranular fusions. In the absence of liquid phase [44, 45], the heat treatment follows the normal cycle for conventional high speed steels (preheating to 850°C and 1050°C, austenitization temperature between 1100°C and 1200°C, gas quenching and double tempering at several temperatures within the interval 450°C - 600°C). In this last case, the addition of NbC to a M3/2 matrix resulted in higher hardness peaks than in the base material and than in the material with TiC addition, both in sintered state, and after the complete heat treatment, whose most appropriate austenitization and tempering values were 1150°C and 525°C respectively. According to the authors, the high hardness values reached after tempering the materials with addition of NbC, could be caused by the formation of mixed Nb and V carbides. In [46] it has been demonstrated (through a complete X-ray diffraction analysis) that the presence of NbC in the composition removes the vanadium from the primary MC carbides, giving rise to the formation of mixed carbides (V,Nb)C. NbC additions produced higher bending strength values than with other additions, and similar to those of the base material, probably due to the capacity of NbC to anchor the grain growth during the heat treatment. Furthermore, small quantities of Nb were found in the steel matrix after quenching and tempering when the samples were analysed by EDX, which implies a certain dissolution of the carbide. However, this was observed when the samples had been prepared not by simple mixing, but by mixing in a ball mill for 100 hours in acetone. In Fig.1. we can observe the microstructure of these composites.

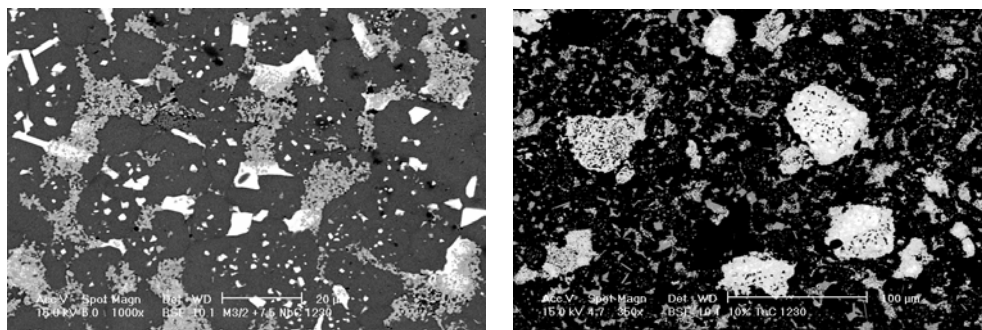


Fig.1. HSS M3/2 reinforced with 10 vol.% reinforcement, sintered at 1230°C. Left: NbC, right: TaC.

One of the most recent studies to appear [7, 47] simultaneously uses NbC and TaC, using pure mixed carbides as well as complex carbides of Ta and Nb obtained from a columbotantalite mineral. Though the latter are not as pure as the mixture of pure carbides, they sinter well in a vacuum and offer good wear behaviour.

In all the cases which have studied the fracture toughness (K_{Ic}) of compound materials with different additions of ceramic particles, no significant differences have been observed in comparison with the base material [15].

ADVANCED TECHNOLOGIES

In the last years, in the same way as conventional PM HSS as well the cemented carbides, papers related to HSS matrix composites include several references related to technologies that allows high densification (like HIP or hot extrusion) or high grain refinement and high reinforcement additions, like mechanical alloying. There are some interesting papers in this field. One of them is the previously mentioned study by Berns and Franco [25]. In [8] it is clearly shown how HIP can strongly improve, in the same material manufactured by conventional PM, the wear and mechanical features. This improvement is due to the refined microstructure than can be achieved with HIP technology (Fig.2.). Nowadays is relatively common to find different combined technologies, as in [48], where mechanical alloying is used in order to improve the interaction between the matrix (M2 HSS) and the reinforcement (TiC), and metal injection moulding is used as forming technique, with a consequence of high homogeneity of the microstructure. Gordo et al use mechanical alloying to introduce high-carbide contents in a HSS matrix (M3/2). Thanks to this technology, up to 50 wt.% of carbides (WC, TaC) can be introduced in the matrix, with good mechanical and wear behaviour [49] (Fig.3.). Currently, the only commercial materials using Fe matrix with a hard phase is Ferro-Titanit® (made by Edelstahl Witten-Krefeld, Germany). This material contain TiC up to 30 wt.%.

One new tendency in cemented carbides, is the development of new cermets with the substitution of Co and Ni as matrix. The use of Co in cemented carbides is based in the eutectic formed at a relatively low temperature, between Co and WC, that allows liquid phase sintering at temperatures below 1500°C. On the other hand, the use of Ni as matrix in cermets is due to the high wettability of this metal with the ceramic reinforcement, usually refractory metal carbides. Neither of these features exist in such extent between iron and WC, so alternative routes must be used in order to produce the composite material. This alternative route are new techniques that allow to introduce in a metallic matrix a high level (in percentage, equivalent to the reinforcement in cemented carbides) of hard particles of

different nature (carbides, nitrides, intermetallics,...). In this sense are the following works. Sadangi et al use plain iron as matrix with reinforcement of a complex carbide of Fe and Mo. The manufacturing way was hot pressing in H_2 , reaching good hot hardness values at temperatures up to 500°C . In this work, a conventional PM M2 HSS is used as reference, being the hot hardness values of the HSS about 40% lower than the composite reinforced with 68/74 vol.% carbides [50]. Finally, Parashivamurthy et al, use plain iron reinforced with TiC, made by combined cold and hot isostatic pressing (CHIP) and extrusion, obtaining good combined results of strength and wear for mould gears applications [51].

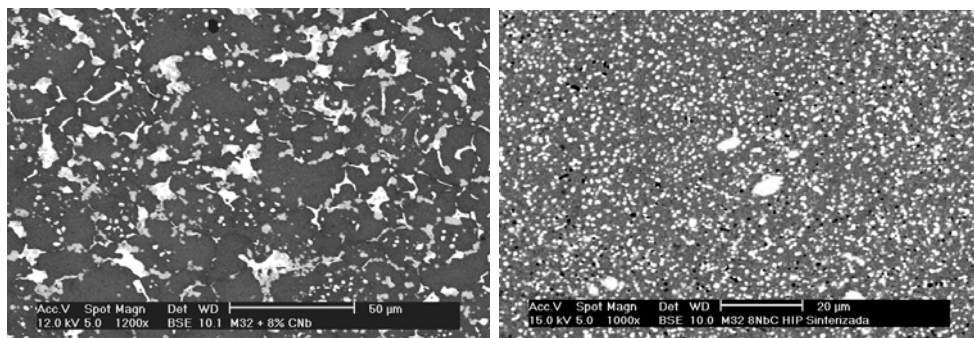


Fig.2. BSE images of M3/2 + 8 vol.% NbC, obtained by: (left) conventional pressing and sintering at 1285°C ; (right) HIP at $1150^\circ\text{C}/150\text{ MPa}$.

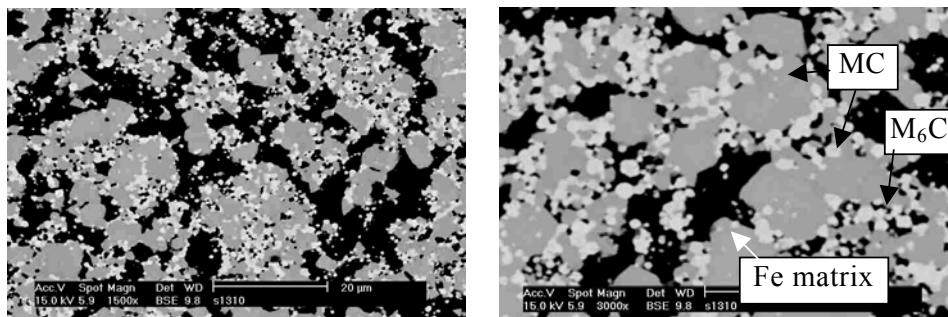


Fig.3. BSE images of M3/2 + 25 wt.% TaC + 25 wt.% WC sintered in vacuum at 1310°C .

CURRENT RESEARCH ACTIVITIES

There are several research teams at an international level actively working in this field. In the USA, the most important activity has been undertaken by the team headed by Professor Queeney, concentrating particularly on the reinforcement of high speed steels with Al_2O_3 . Probably the greatest contribution of this working group has been the in depth study of the mechanical properties of composite materials, as well as the optimization of the conformation processes which optimize the obtainment of these materials with improved properties. In Europe mention should be made of the consortium (University of Bradford, UK; INETI, Portugal; and the Pierre Marie Fourn Materials Centre of the Mining School of Paris, France) created for the purpose of a BRITE project, which having finalized in the year 1992 has permitted numerous research centers to follow these lines of work up to the

present. In this consortium special mention is made of the group in the University of Bradford which is probably that which has undertaken the greatest research effort. The main contribution of these groups is the use of sintering activators (as an alternative to the high density processes) which promote liquid phase sintering and a reduction of the sintering window, even in non-ideal sintering conditions (N_2-H_2 atmospheres). A large amount of work has been undertaken in other research centers (CEIT, Spain; Carlos III University of Madrid, Spain; IPEN and University of Santa Catarina, Brazil; etc.) basing their developments on work derived from the aforementioned consortium.

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