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On the Role of Interfacial Reactions, Dissolution and Secondary Precipitation During the Laser Additive Manufacturing of Metal Matrix Composites: A Review

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Abstract

Since current trends in the transportation, energy or mechanical industries impose increasingly demanding service conditions for metallic parts, metal matrix composites (MMCs) are the object of a growing interest. Powder-based laser additive manufacturing, which allows making parts with complex shapes, appears particularly adapted for the production of MMCs. This paper reviews the current state-of-the-art in the production of MMCs by additive processes, with the aim of assessing the potentials and difficulties offered by these techniques. Two main processing routes are envisaged, i.e. (1) the processing of ex situ composites in which the reinforcing phase as a powder—often of ceramic particles—is directly mixed with the powder of the matrix alloy, and both powders are simultaneously processed by the laser. (2) Alternatively, the reinforcing phase can be produced in situ by a chemical reaction during the fabrication of the composite. For both processing routes, a careful control is needed to overcome challenges brought, e.g. by the behaviour of the reinforcement particles in the laser beam, by changes in laser absorptivity or by the dissolution of the reinforcing particles in the molten metal, in order to produce MMCs with enhanced usage properties.

Keywords: metal matrix composites, interfacial reactions, solidification, additive manufacturing, laser processing

1. Introduction

Current requirements for improved efficiency in the mechanical and energy industries impose ever more demanding service conditions for metallic parts, e.g. higher service temperatures,

corrosive environments and/or increased mechanical loads. At the same time, demands for metallic materials with enhanced specific properties are also increasing in view of the trends for lightweighting in portable applications. In this context, metal matrix composites (MMCs), combining the advantages of the metallic matrix with the beneficial contribution of a well-selected second phase, appear as materials of choice that can be designed and tailor-made in view of a specific application, in bulk or as coating [1].

The vast choice of potential second phases opens unlimited possibilities in terms of the usage properties that can be attained. Indeed, the reinforcements may take on different morphology (i.e. long fibres, short fibres or particles) and size (i.e. in the micro- or nano-size range) [1]. Various reinforcements may even be combined to make a hybrid composite [1, 2]. Among the most popular types of reinforcements, carbides such as tungsten (WC) [3–7], chromium (Cr_3C_2) [3, 8], silicon (SiC) [2, 9–12] or titanium carbides (TiC) [13–15] have often been used in view of their high hardness to enhance the wear resistance of the composites. Oxides [16, 17], nitrides [18] or borides [19, 20] also proved of interest as reinforcement, as did intermetallics [9, 15]. Alternatively, the second phase may also be selected in order to fulfil a specific function, such as, self-cleaning [21], self-healing [22, 23] or as solid lubricant in self-lubricating MMCs that are currently attracting a growing interest for applications where classical lubrication methods do not work [23–26].

A number of different methods can be used for the fabrication of MMCs. Melting metallurgical processes include infiltration of a preform by squeeze casting [1, 27], reaction infiltration or stir casting [1]. Powder metallurgy processes involve sintering, pressing or forging of a mixture of powders or of composite powders [1, 24], while severe plastic deformation processes such as friction stir processing rely solely on solid-state material flow [27, 28]. These conventional processes for the elaboration of MMCs share a common limitation. Indeed, it is very difficult to fabricate MMC components with complex shapes by these methods [2]. On the other hand, additive manufacturing and particularly powder-based additive techniques offer the possibility to fabricate any complex geometry directly from the powders [2, 29]. General features of additive manufacturing processes suitable for the fabrication of MMCs will be reviewed in more details in the second section of this chapter, while Sections 3 and 4 will focus on some specific examples of MMCs processed by additive manufacturing, along with their properties and envisioned applications.

2. Additive manufacturing techniques for the production of metal matrix composites

Following standard ASTM F2792-10, additive manufacturing is defined as “*the processing of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing technologies*”. This definition encompasses a large variety of manufacturing processes suitable for the fabrication of MMCs (**Table 1**). 3D printing that relies on a binding agent to consolidate a powder has been used successfully to produce polymer matrix composites with particulate reinforcements [29]. This technique can also be applied to the manufac-

turing of metallic materials, but due to the intrinsic nature of its consolidation process [29, 30], it does not allow for making as dense products as can be obtained from polymers. In this case, the advantage of additive manufacturing lies in the excellent dimensional accuracy of the part [30] and in the possibility to design and fabricate directional 3D preforms with optimised out-of-plane mechanical properties [31]. Fully dense parts can only be obtained by further infiltrating the porous preform [29, 30]. This process is thus very similar to the conventional processing of MMCs by infiltration or squeeze casting, and it will not be discussed in more details in this chapter.

Classification	Technology	Description	Raw materials	Comment
Sheet lamination	Laminate object manufacturing (LOM) Ultrasonic consolidation (UC)	Builds part by joining sheets or foils of materials	Laminates or foils	Composite laminates or sheets must be prepared prior to the fabrication of a 3D part.
Binder jetting	3D printing	Builds parts by depositing locally a binding agent	Powders	This process is suitable for the production of porous preforms. Further infiltration is needed to make fully dense composites.
Beam deposition	Direct metal deposition (DMD) Laser deposition Laser cladding	Fusing a material with a laser during simultaneous deposition on a substrate	Powders or wires	Suitable for the fabrication of MMCs including functionally graded materials (FGMs).
Powder-bed Fusion	Direct metal laser sintering (DMLS) Selective laser melting (SLM) Laser beam melting (LBM) Selective laser sintering (SLS)	Uses a laser to melt a powder bed at desired locations	Powders	Suitable for the fabrication of MMCs with a constant volume fraction of second phase.

Table 1. Classification of additive manufacturing processes for the production of metal matrix composites (MMCs) [12, 29, 32].

Laminated object manufacturing allows the fabrication of MMCs reinforced with either particulates or fibres (**Table 1**) [29]. However, this process requires the production of composite sheets prior to making the composite 3D part, as is also the case for ultrasonic consolidation in which metallic—or MMC—foils are joined together by ultrasonic welding (**Table 1**) [29]. Both these methods offer the possibility to control precisely the placement of the reinforcement

inside the final component, but they are not particularly well adapted to the fabrication of MMCs parts with complex geometries.

When it comes to making MMCs components with complicated shapes, powder-based additive manufacturing techniques demonstrate the greatest potential, in spite of being generally limited to particulate reinforcements (**Table 1**) [12, 29]. Powder-based additive manufacturing techniques can be classified into two broad categories, i.e. (1) beam deposition processes in which a high-energy beam, typically a laser, is used to fuse a powdered material as it is projected onto a substrate and (2) powder-bed fusion processes that use a focused energy beam to melt locally selected zones of a powder bed. The first category encompasses the processes known as direct metal deposition (DMD), laser deposition (LD), laser engineering net shaping (LENS) or laser cladding (LC)—the latter denomination can also be used to designate the laser surface treatment of pre-deposited powdered layer. Direct metal laser sintering (DMLS), laser beam melting (LBM) and selective laser melting (SLM) are examples of the second category [12, 29, 32].

From a practical viewpoint, powder-bed fusion processes require that the two constituents of the composite, i.e. the matrix and reinforcing powders, should be pre-mixed prior to their spreading in the powder bed [2]. In beam deposition processes, on the other hand, it is also possible to feed the two powders into the beam from two separate hoppers, without pre-mixing. This latter set-up is favourable in order to avoid any segregation of the constituents due to difference in the densities of the powders that could impair a precise compositional control of the composite material [15]. Moreover, it opens the possibility of gradually varying the ratio of the matrix and reinforcement powders during processing so as to make functionally graded materials (FGMs) [10, 11, 15, 18]. LC of pre-deposited pre-mixed powders may still be preferred in some occasions, e.g. for depositing a composite layer on a substrate characterised by a very high reflectivity [26]. Finally, it is worth noting that while the vast majority of the research on the production of MMCs by beam deposition processes has been focused on powder-feed techniques, few investigations have also been carried out into the fabrication of composites by a mixed wire- and powder-feed process [6, 33].

Practical differences set aside, all powder-based laser additive manufacturing processes are faced with similar issues and challenges during the fabrication of MMCs reinforced by ceramic particles. These challenges are related

1. to interactions between the ceramic particles and the laser beam: In a few instances, the reinforcing particles have been reported to melt or decompose when exposed to the action of the laser [25, 34]. Besides, absorptivity of the laser beam by ceramic particles may differ significantly from the absorptivity by metallic powders, thus affecting the transfer of energy from the laser to the built [2, 5, 14, 15, 35]. As a consequence, it may prove necessary to adjust continuously the processing parameters as a function of the volume fraction of ceramic particles during the fabrication of FGMs [15]. Alternatively, Przybyłowicz and Kusinski [5] suggested to coat WC or TiC particles with nickel to lower down their absorption coefficient to values comparable to the absorption coefficient of the metallic powders.

2. to interactions between the ceramic particles and the metallic melt pool: while a few examples of matrix-reinforcement pairs exist for which the dissolution of the reinforcing particles in the melt pool remains very limited [19], most often ceramic particles tend to dissolve at least partially in the melt pool [8, 11–13], as illustrated in **Figure 1** in the case of a stainless steel 316L-WC composite [36]. Consequently, new phases may form as a result of secondary precipitation inside the metallic matrix. Due to the ultra-fast thermal cycles typically imposed by laser additive manufacturing processes, these new phases generally exhibit ultra-fine structures often resulting in enhanced hardness and wear properties [2, 11, 35, 36]. Interfacial reactions, dissolution and secondary precipitation phenomena have even been used to synthesise the reinforcing phase of MMCs by in situ reactions. In this case, the energy of the laser is not only used to fuse the powdered materials but also to overcome the activation energy barrier for the reaction and form new chemical compounds [2, 29, 37–41].

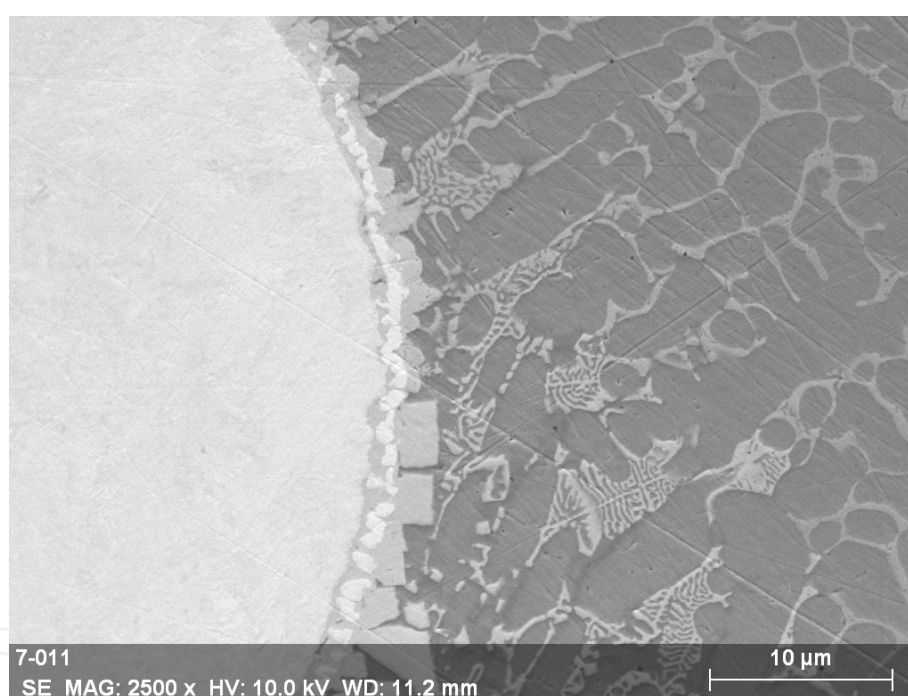


Figure 1. SEM micrograph of a stainless steel 316L composite coating with 16 vol% of tungsten carbides deposited by laser cladding [36].

Either way, in both the ex situ and the in situ processing of MMCs, a careful control of the reactions taking place during laser additive manufacturing is needed in order to produce MMCs with enhanced properties. The following sections of this chapter thus aim at reviewing systematically pairs of metallic matrix and reinforcing phase that have already been produced by additive manufacturing, challenges that were met during the production of these composites and the properties that could be attained. Section 3 focuses on the fabrication of ex situ MMCs, and Section 4 on the in situ synthesis of MMCs. A synoptic table summarising the

major characteristics of these MMCs is proposed in Section 5. Special care is also taken to identify current fundamental issues that should more particularly be the object of future work.

3. Ex situ MMCs produced by laser additive manufacturing

3.1. Aluminium matrix composites

3.1.1. Aluminium matrix composites reinforced with carbides

A major concern during the fabrication of aluminium (Al) matrix composites reinforced with carbide particles is to avoid the formation of aluminium carbide Al_4C_3 through interfacial reactions between the liquid Al and the particles [6, 13, 42]. Indeed, the presence of Al_4C_3 in the composite is potentially detrimental to both its mechanical and its corrosion resistance, as it is well known that Al_4C_3 is extremely brittle [13] and susceptible to hydrolysis in humid environment, thus giving rise to high corrosion rate [6]. A number of different strategies have been devised with various levels of success in order to solve this problem, including the careful selection of the carbide particles used as reinforcement [2, 13], the chemical modification of the matrix alloy [6, 12] or the optimisation of the processing conditions, e.g. to promote the formation of less deleterious aluminium carbides such as the mixed aluminium-silicon carbide Al_4SiC_4 [2, 19, 43, 44].

In their investigation into the fabrication by DMLS of AlSi10Mg matrix composites with 10 wt % of SiC particles, Manfredi et al. [12] relied on the earlier observation that the addition of a high amount (i.e. of at least 7 at% [42]) of silicon in the matrix alloy could suppress the reaction between the Al alloy and the SiC particles leading to the formation of Al_4C_3 during the fabrication of Al matrix composites by conventional processes such as melt infiltration. The experimental parameters for the DMLS process were set as follows: the scan speed was varied between 500 and 700 mm/s, the laser power between 180 and 195 W, the layer thickness was set at 30 μ m and the hatching distance at 0.17 mm. Although the hardness of the composite materials was significantly increased in comparison with AlSi10Mg processed in the same conditions, analysis of the AlSi10Mg/SiC composites by X-Ray Diffraction (XRD) showed that the SiC particles had almost fully disappeared while a significant amount of Al_4C_3 had been formed [12]. The behaviour of the DMLS AlSi10Mg/SiC composites was thus found to differ significantly from their conventional counterparts.

Also investigating the fabrication of AlSi10Mg/SiC composites by SLM, Chang et al. [2] used the same layer thickness of 30 μ m as used by Manfredi et al. [12], with a smaller hatch spacing of 0.05 mm, a lower laser power of 100 W and a lower scan speed of 100 mm/s. Dissolution of the SiC particles was also observed in their study, but this time, the reaction product was the mixed Al_4SiC_4 carbide, that has the advantages of being chemically inert in humid environment and of being less brittle than Al_4C_3 . By considering the energy density per unit volume for both studies, it is found that the set of experimental parameters used by Manfredi et al. [12] resulted in a much lower value of the energy density of 77 J/mm³ when compared to the set of processing parameters of Chang et al. [2] giving rise to an energy density of 666 J/mm³. As a consequence, the samples of Chang et al. [2] experienced a greater heat accumulation during fabrication and

a higher temperature when compared with the samples of Manfredi et al. [12]. The processing strategy of Chang et al. [2] thus proved successful in favouring the formation of Al_4SiC_4 that is expected to form at temperatures above 1350–1400°C, whereas the formation of the deleterious Al_4C_3 cannot be avoided at lower processing temperatures [2, 19], in spite of the high silicon content of the matrix alloy [12].

Ghosh et al. [43, 44], on the other hand, investigated the fabrication of Al-4.5Cu-3Mg/SiC composites by DMLS using a pulsed Nd:YAG laser while varying the SiC volume fraction and particles size. However, due to the strongly non-uniform nature of the temperature distribution created by the pulsed laser, their composites were subjected to high internal stresses that resulted in extensive cracking in all their specimens [44, 45].

In a similar way to silicon carbides, tungsten carbides (WC) present a strong tendency to dissolve in Al alloys during LD, leading to the formation of Al–W intermetallics and of the detrimental Al_4C_3 [6]. In order to avoid the formation of the latter phase, Li et al. [6] attempted to modify the chemical composition of their Al-11 wt% Si matrix alloy by adding pure elemental Ti powder together with the WC particles. The addition of Ti in the melt pool was found successful in inhibiting the formation of the deleterious Al_4C_3 by promoting the precipitation of titanium carbides (TiC) both as dispersed phase within the Al matrix and as a passivation layer at the interface between the WC particles and the Al matrix. Mixed Al–Ti (Al_3Ti or AlTi) and Al–W (Al_{12}W or Al_4W) intermetallic compounds were also detected by XRD.

On the other hand, titanium carbides (TiC) present a much lower reactivity with Al than SiC and WC [13]. Indeed, TiC possesses a low solubility in Al, and its dissolution rate is also slower than for SiC. Coatings with a matrix of Al-12 wt% Si and 40 wt% TiC as reinforcement were successfully produced by LC [13]. Very limited dissolution of the TiC particles into the Al matrix led to the formation of a small amount (about 3%) of finely dispersed Ti_3SiC_2 , whereas the formation of the deleterious Al_4C_3 was completely avoided. Both the hardness and the sliding wear resistance of the composite coating were significantly improved by the TiC addition.

In view of their excellent thermodynamic stability, TiC nanoparticles have also been used as reinforcement in AlSi10Mg matrix composites [46–49]. Due to their strong tendency to form clusters and agglomerates [22, 29], nanoparticles may reflect poorly on the flowability and/or the spreadability of the powders, and nanostructured or nanocomposite powders of micron-size are usually preferred for the additive manufacturing of nanocomposites. In various studies [46–49], careful mixing of TiC nanoparticles with an average size of 50 nm and of AlSi10Mg particles with an average size of 30 μm in a planetary ball mill resulted in the uniform distribution of the TiC nanoparticles around the surface of the AlSi10Mg particles, thus forming nanostructured particles suitable for further processing by SLM.

In a first set of studies [46, 47], the effect of the linear laser energy density on parts density, microstructure, hardness and wear behaviour was investigated by adjusting the scan speed at a constant laser power of 110 W. The second phases present in the composites were identified as TiC and Mg_2Si , the latter formed by natural aging of the AlSi10Mg matrix alloy. Moreover, the highest investigated linear laser energy density of 733 J/m was found to result in parts with

an optimum relative density of 98%, uniform distribution of the TiC nanoparticles throughout the composite and optimised hardness and wear resistance. Dai and Gu [48] reported on the optimisation of the surface finish of AlSi10Mg/TiC nanocomposites by varying the scan speed at a constant laser power of 150 W. In this case, medium values of the linear laser energy density gave the best result. Lower linear laser energy densities resulted in an excessive viscosity and poor spreading of the melt pool on the underlying solid surface [46, 47]. Higher linear laser energy density, on the other hand, led to excessive vaporisation of the melt [48]. Both situations resulted in a smaller melt pool and in a poorer surface finish. Finally, in an attempt to optimise the tensile properties of TiC/AlSi10Mg nanocomposites produced by SLM, Gu et al. [49] reported on an investigation of the influence of the processing parameters on the dispersion of the nanoparticles. Gu et al. [49] demonstrated the feasibility of tailoring the spatial distribution of the TiC nanoparticles in the composite by means of a careful control of the balance of the torque forces in the melt pool and of repulsive capillary forces arising between the nanoparticles under specific processing conditions.

3.1.2. Aluminium matrix composites reinforced with borides

In opposition to carbides and particularly to SiC or WC whose reactions with liquid Al may result in the formation of brittle and deleterious compounds, titanium diboride (TiB_2) is attracting a growing interest for use as reinforcement in Al matrix composites due to its very low reactivity with Al. Anandkumar et al. [19] thus investigated the LC of an Al-12 wt% Si alloy with 40 wt% TiB_2 . Using processing parameters similar to those reported for the LC of Al-12 wt% Si/TiC composites [13], the Al-12 wt% Si/ TiB_2 composites did not present any sign of dissolution of the TiB_2 particles, nor of interfacial reactions between the particles and the Al matrix [19]. Moreover, when compared with the matrix alloy, the wear resistance of the Al-12 wt% Si/ TiB_2 composite coating, as characterised by dry sliding wear tests using a counterbody of quenched and tempered AISI440C tool steel, was greatly increased by the addition of the TiB_2 particles. Being much harder than the counterbody (2550 HV vs 800 HV), protruding TiB_2 particles proved very efficient in supporting the contact stresses with the counterbody and protecting the Al-12 wt% Si matrix from continued intense plastic deformation.

3.1.3. Aluminium matrix composites reinforced with oxides

Little information is available in literature on the laser additive manufacturing of Al matrix composites with ex situ oxide particles. Manfredi et al. [12] investigated the fabrication of AlSi10Mg matrix composites with nanoparticles of the aluminium-magnesium spinel MgAl_2O_4 using DMLS, with limited success. In order to avoid processability issues caused by the tendency of nanoparticles for clustering [22, 29], a nanostructured powder was prepared by mixing the AlSi10Mg and the MgAl_2O_4 powders using a ball milling system for 48 hours prior to conducting the DMLS experiments. Even the best of the produced composite specimens still exhibited a non-negligible volume fraction of residual porosity ranging from 2.2 to 3.5%. The microstructure of the composites was also found to be much more inhomogeneous than for the AlSi10Mg alloy processed under the same conditions without spinel nanoparticles, thus suggesting that the spinel nanoparticles might affect the solidification process during

DMLS. And finally, the hardness of the AlSi10Mg/spinel nanoparticles composite was decreased by 11% in comparison with the AlSi10Mg DMLS samples without nanoparticles.

3.2. Ferrous matrix composites

3.2.1. Ferrous matrix composites reinforced with carbides

Silicon carbides have been extensively used as reinforcement in mild [10], medium-carbon [50] or stainless steels [11, 51–53]. A compositionally graded mild steel/SiC composite coating produced by LC was found to exhibit enhanced hardness, wear and corrosion resistance when compared to the bare mild steel substrate [10]. The improvement of the mechanical properties was ascribed not only to the addition of the SiC particles but also to the secondary precipitation of iron silicide Fe_2Si consequent to the partial dissolution of the SiC particles. Depending on the processing conditions, Fe_3Si or Fe_3Si_5 have also been observed [50, 51], and, when SiC particles were dispersed in stainless steel, chromium carbides such as Cr_3C_2 [11, 51, 53] or Cr_7C_3 [52] were also formed. This is a major issue for the laser processing of stainless steel/carbides composites, since an excessive precipitation of chromium carbides might deplete the chromium content of the stainless steel matrix hence compromising its corrosion resistance [3]. However, provided the precipitation of chromium carbides remains limited, Dutta Majumdar and Li [53] have demonstrated that stainless steel 316L/SiC composites could achieve a corrosion resistance that is equivalent or better when compared with conventional stainless steel 316L, in combination with improved hardness and wear resistance [11, 53].

Tungsten carbides (WC) have also been widely used as reinforcement in steels, and like SiC, they exhibit a strong tendency to dissolve in the ferrous matrix [3, 35, 51, 54], giving way to the secondary precipitation of finely dispersed mixed carbide phases as, e.g. M_6C , M_{23}C_6 or M_7C_3 where M stands for Fe, W or Cr (in stainless steel matrix composites). WC particles were found extremely efficient in increasing the hardness and wear resistance of steel matrix composites due to the combined hardening effect of the surviving particles, of the finely dispersed secondary precipitates and of the solid solution strengthening of W dissolved in the steel matrix [3, 35, 51]. Since it is known that the uniform distribution of very fine hard phases may be beneficial in view of improving the cavitation erosion resistance of stainless steel, Lo et al. [35] added deliberately small ($\sim 1\mu\text{m}$) WC particles in a stainless steel 316 composite coating, so as to favour the complete dissolution of the WC particles and the reprecipitation of finely dispersed carbides. However, as mentioned earlier, secondary precipitation of mixed carbides may prove detrimental to the corrosion resistance of stainless steel/WC composites if the depletion of chromium in the stainless steel matrix reach such an extent as to reduce the capacity of the material to withstand corrosion, as observed by Betts et al. [3] in the case of a stainless steel/WC coating.

Titanium carbides (TiC), on the contrary, are characterised by a great chemical stability in presence of ferrous melts. Cheng et al. [51], for example, did not observe any significant dissolution or reaction during the LC of a stainless steel/TiC composite coating. However, decreasing the size of the TiC particles could result in their partial dissolution [55]. Due to the difference in density between TiC and stainless steel, the TiC particles tend to float at the

surface of the stainless steel melt pool. As a consequence, special care must be taken when injecting the TiC particles in the melt, for fear that the TiC particles may distribute unevenly in the composite [51, 55]. When added to a Fe-36% Ni Invar36 alloy, on the other hand, TiC particles dissolved at least partially [56]. Enrichment of the Invar36 matrix with Ti resulted in the stabilisation of the body-centred cubic (BCC) α structure at the expense of the face-centred cubic (FCC) γ phase, significant increase of the coefficient of thermal expansion of the matrix alloy and the loss of its “invar” property whereas the wear resistance of the composite exhibited very little improvement.

Chromium carbides, finally, tend to dissolve at least partially in ferrous matrix, giving rise to the secondary precipitation of small amount of mixed M_7C_3 or $M_{23}C_6$ carbides [3, 51]. Cr_3C_2 particles did not appear as efficient as WC particles in view of enhancing the hardness and wear resistance of stainless steel matrix composites, but they also proved less deleterious to the corrosion resistance [3]. Although secondary precipitation in stainless steel/ Cr_3C_2 composite might still have caused some depletion of Cr in the stainless steel matrix, this phenomenon was less severe than in stainless steel/WC composites.

3.2.2. Ferrous matrix composites reinforced with oxides

Attempts to reinforce ferrous matrix composites with oxide particles have met little success so far. In their investigation into the deposition of a stainless steel AISI304/ Al_2O_3 composite coating by LC, Xu et al. [34] found that the Al_2O_3 particles were melted upon heating in the laser beam. Al atoms liberated by the dissociation of Al_2O_3 then dissolved in the stainless steel matrix, with positive effect on the hardness of the coating due to the combined effect of the solid solution strengthening of the austenitic stainless steel matrix by Al and of a partial transformation of the austenite into hard martensite. Betts et al. [3] also reported an extensive dissociation of Al_2O_3 particles during the direct LD of AISI316/ Al_2O_3 composite coating. Dissociation of Al_2O_3 was complete at higher laser power, whereas the lower laser power resulted only in a low survival rate of the Al_2O_3 . The hardness of the AISI316/ Al_2O_3 composite was actually decreased in comparison with the AISI316 base material. The LC of Cr_2O_3 in an austenitic stainless steel matrix [51] also proved unsatisfactory: the composite coating exhibited extensive cracking and a poor bonding with the stainless steel substrate.

3.2.3. Ferrous matrix composites reinforced with other types of particles

The LC of chromium borides CrB_2 in austenitic stainless steel UNS S31603 resulted in a significant increase of the composite layer hardness and of its cavitation erosion resistance, in comparison with the base material [51]. Improved properties were linked not only to the presence of surviving CrB_2 particles but also to the secondary precipitation of finely dispersed chromium borides (CrB and Cr_2B) and iron borides (Fe_2B) following the partial dissolution of the initial CrB_2 particles. Li et al. [57] added CeO_2 nanopowder in laser-cladded FeCrBSi/NbC composites: CeO_2 nanoparticles acted as heterogeneous nuclei, favouring higher solidification rates and enhancing the in situ synthesis of finely dispersed NbC (see also Section 4.2).

Hydroxyapatite (HA), in micro- or nano-size, has been used as addition in stainless steel matrix composites produced by SLM for biomedical applications [58, 59]. Stainless steel 316L presents good mechanical and chemical properties for use in load-bearing implants, but it does not promote bone adhesion or tissue regrowth on the implant. HA, on the other hand, lacks in ductility and toughness for load-bearing applications, but it is very efficient in favouring bone and tissue regrowth. By combining the properties of the two materials, load-bearing and bioactive implants have been fabricated. Since the density of HA is significantly lower than the density of SS 316L, the ceramic particles tend to float at the surface of the melt pool and to aggregate, resulting in insufficient wetting or “balling”, and in the increased formation of porosities and cracks in the SS316L/HA composites. Consequently, a careful optimisation of the SLM processing parameters was necessary in order to avoid these problems. Optimised SLM SS316L/nano-HA composites were found to exhibit a higher tensile strength than their bulk SS316L counterparts, in combination with a good ductility [59].

3.3. Nickel and nickel alloys matrix composites

Carbides, and particularly WC, are by far the most widely used ceramic reinforcements in Ni-based composites. WC actually presents a lower reactivity with Ni-based alloys than with ferrous alloys [54]. As a consequence, nickel is sometimes used to coat ceramic powder particles prior to their use as reinforcement, to slow down the dissolution of the ceramic particles in, e.g. ferrous matrix composites [3, 35, 60] and to lower the laser absorptivity of the ceramic to values similar to the laser absorptivity of metallic materials [5]. Due to the low reactivity of WC with Ni-based alloys, it is fairly easy to control the rate of dissolution of the WC particles in Ni-matrix composites by optimising the processing parameters (e.g. by decreasing the laser power) [5, 61]. Partial dissolution of WC in Ni alloys has been reported, leading to secondary precipitation of various types of tungsten carbides (secondary WC, W_2C ...) as well as of mixed carbides (M_7C_3 , $M_{23}C_6$...) [5, 60, 62]. Ni–W intermetallics (Ni_2W_4C , $Ni_{17}W_3$...) were also observed in NiCrBSi/WC composites processed by LC at high laser power and on a substrate pre-heated up to 400°C [63]. MMCs reinforced with WC have been successfully produced in a wide range of Ni-based alloys: pure Ni [60, 64], NiCrSiFe [65], NiCrBSi alloys [62, 63], Ni35 (containing Cr, Si, B and Fe) [61] or Ni60 (containing also Co) [66].

Addition of chromium carbide Cr_3C_2 in alloy Inconel 625 gave good results in terms of wear resistance, due to the partial dissolution of Cr_3C_2 in the metallic matrix and reprecipitation of fine Cr-rich M_7C_3 carbides [8]. Titanium carbides (TiC) were also deemed very promising for use as reinforcement in Inconel 625 [67] and Inconel 690 [68]. Minimal dissolution of TiC was observed in Inconel 690 [68], leading to the formation of fine dendritic $M_{23}C_6$.

Other reinforcements suitable for use in Ni-based matrix composites include titanium diboride (TiB_2) [26], and rare earth oxides like CeO_2 [17] or Y_2O_3 nanoparticles [69]. Both types of oxide nanoparticles were found very efficient in refining the microstructure and in improving the corrosion resistance of the composites. Hydroxyapatite also proved interesting for biomedical applications, e.g. as second phase in nitinol (i.e. NiTi intermetallic alloy) matrix composites [70].

3.4. Others

In view of their comparatively high cost, titanium matrix composites are somewhat less popular than Al-based or ferrous matrix composites. Again, carbides—particularly TiC [14, 15, 33, 71, 72], but also WC [73] or SiC [74]—have attracted a great interest as reinforcement in titanium matrix composites, with positive effect on their hardness and wear behaviour. TiB, TiB₂ [20, 75] and TiN [18] have also been used as alternative or in combination with TiC.

Copper (Cu) alloys are rather difficult to process by laser additive processes, due to their high reflectivity to laser light [26]. Nevertheless, the DLS of Cu matrix composites reinforced with Co/WC particles has been studied extensively, with the aim of combining the excellent thermal and electrical conductivity of the Cu matrix with the high strength and hardness of the Co/WC reinforcement [76, 77]. Rare earth oxides nanoparticles (CeO₂, La₂O₃) have been added in these Cu + Co/WC composites to favour microstructural refinement [78]. More recently, the direct addition of WC particles in Cu matrix composites processed by SLM has also been investigated [79].

Researches on Co-based matrix composites have been largely focused on the LC of composite reinforced with WC or other cermet particles, in view of applications necessitating a very high abrasion resistance as, e.g. in cutting tools [5, 80–82]. WC present a greater reactivity with Co alloys than with Ni alloys, and the partial dissolution of WC accompanied by secondary precipitation of finely dispersed complex carbides is commonly reported. A recent publication also reports on the LC of self-lubricating Co-based composite coatings with additions of TiC and CaF₂ [83].

4. Laser-induced in situ synthesis of MMCs

Reinforcement particles can also be synthesised in situ during the laser additive manufacturing of MMCs, either from a mixture of pure elemental powders [37, 84] or from ceramic particles that would decompose under the effect of laser irradiation and/or dissolve into the melt pool [2, 35, 38, 85]. The energy brought by the laser is used to fuse the metallic matrix powder and form new chemical compounds. Alternatively, the thermal energy brought by the laser may also trigger an exothermic chemical reaction that will not only produce new chemical compounds but also in itself generate enough thermal energy to propagate more chemical reactions [29, 86]. This process, known as self-propagating high-temperature synthesis, was originally used in combination with Selective Laser Sintering to produce Ni–Al intermetallics [39] and later extended to the synthesis of NiTi-matrix composites [40]. In this case, laser additive manufacturing can sometimes be pursued under a lower laser energy since the latent heat generated by the chemical reactions also contributes to increase the temperature of the melt pool [41, 86]. Besides, the in situ synthesis of MMCs has several other advantages: it allows for a better wetting and cohesion of ceramic particles with the metallic matrix, and for obtaining a fine and uniform distribution of the reinforcing phases [29].

The boundary between the ex situ fabrication and the in situ synthesis of MMCs is actually quite blurred. Indeed, in a few instances, the processing parameters for the fabrication of metal-

ceramic composites and the size of the ceramic particles have been deliberately adjusted in such a way as to favour the partial dissolution of the ceramic and obtain reaction products with a well-tailored, fine and uniform distribution, thus taking advantage of the combined strengthening effect of the initial ceramic particles and of the secondary precipitates [2]. As a line of demarcation, the present section focuses on reviewing systematically works that involve a *conscious and deliberate* usage of chemical reactions in view of tailoring the microstructure and properties of MMCs.

4.1. In situ synthesis of aluminium matrix composites

Chang et al. [2] provides an interesting example of a careful and deliberate control of chemical reactions during the SLM of AlSi10Mg/SiC composites, making profit from the strong tendency of SiC to dissolve in Al and its alloys. As outlined previously (Section 3.1.1), the SLM processing parameters were adjusted in such a way as to favour the formation of mixed Al_4SiC_4 carbides over the potentially deleterious Al_4C_3 . Moreover, the effect of the size of the SiC particles on the extent of secondary precipitation was investigated. It was found that the smallest average particle size of 5 μm gave way to the optimised distribution of refined Al_4SiC_4 precipitates and to the greatest improvement in hardness and wear behaviour.

Xu et al. [84] studied the in situ synthesis of Al-matrix composites reinforced with titanium diborides (TiB_2) from pure elemental Al, Ti and B powders. B powder was coated with Fe in order to avoid its burning during interaction with the laser. The resulting Al-matrix composites were reinforced with TiB_2 presenting a bimodal size distribution (i.e. with particles in size range 20–30 μm and smaller particles with a size < 500 nm). Besides, intermetallics Al_3Ti and Al_3Fe were also produced, and the wear resistance of the composites under low loads showed a marked improvement.

Dadbakhsh and Hao [87] attempted to produce Al matrix/oxides by SLM of Fe_2O_3 particles mixed with pure Al powder or various other Al alloys. This resulted in a very fine dispersion of Al_2O_3 and Al–Fe intermetallics with a size < 400 nm. Unfortunately, the mechanical behaviour of all the produced composites was dramatically compromised by an excessive volume fraction of porosities (i.e. at least 20 vol% or higher). Indeed, the oxygen introduced in the composite by the addition of Fe_2O_3 favoured the formation of an Al_2O_3 layer at the surface of the solidified material, thus preventing its proper wetting by the melt pool and a sufficient adhesion between successive layers which is a well-known issue in the SLM of Al alloys [88–90].

4.2. In situ synthesis of ferrous matrix composites

Ferrous matrix composites reinforced with various types of carbides have already been synthesised successfully using laser additive manufacturing techniques. Fe/TiC composites have been produced by LC, resulting in a significant increase in the hardness of the composite coating when compared to the substrate [37, 91]. Finely dispersed NbC were obtained from blended elemental powders during the LC of FeCrBSi matrix composites, with the addition of CeO_2 nanoparticles acting as heterogeneous nuclei enhancing the precipitation of NbC [57].

Song et al. [85] took advantage of the dissolution and reprecipitation of SiC micron-sized particles in pure Fe during SLM to produce Fe/SiC bulk nanocomposites. Similarly, Lo et al. [35] favoured the complete dissolution of WC particles and the reprecipitation of finely dispersed mixed carbides by selecting deliberately small ($\sim 1 \mu\text{m}$) starting WC particles, with the aim of improving the cavitation erosion resistance of AISI316/WC composites.

As alternative to Fe/carbides composites, laser-cladded ferrous matrix composites reinforced with titanium diboride (TiB_2), exhibiting excellent hardness and wear resistance, were successfully synthesised from Fe–B and Fe–Ti alloyed powders [92]. In a study by Tan et al. [38], FeO_2 powder was added in a blend of pure elemental Fe, Ni, Cr, Al and graphite powders, with the aim of promoting the formation of finely distributed Al_2O_3 and various mixed carbides. A slight grain coarsening was observed in some specimens and interpreted as a consequence of the latent heat of reaction released by the exothermic formation of Al_2O_3 .

4.3. In situ synthesis of MMCs in Ni- or Ti-based alloys

Ni-based composites reinforced with Cr_3C_2 [93], TiC and WC [86] carbides have been synthesised in situ from elemental powders. Lou et al. [93] investigated more particularly the influence of the Cr/C ratio on the resulting microstructure of NiCr/chromium carbides composites, with the aim of favouring the formation of Cr_3C_2 over mixed M_7C_3 and M_{23}C_6 carbides that are characterised by lower hardness and melting point in comparison with Cr_3C_2 . Man et al. [86] reported on the successful laser-induced self-propagating high-temperature synthesis of TiC and WC in a NiAl intermetallic alloy. The latent heat of reaction released by the strongly exothermic formation of TiC was found to play an important role in promoting the formation of WC and of finely dispersed Al_3Ni_2 and Al_3Ni intermetallics, with a positive effect on the hardness of the composite clad layers.

Comparatively, the in situ synthesis of Ti-matrix composites reinforced with carbides has attracted less attention. Mixed (TiB+TiC)/Ti composites were synthesised in situ during the LC of blended boron carbide (B_4C) with pure elemental Ti and Al powder, resulting in excellent wear resistance [94]. Mixed (TiN+TiB)/Ti composites were synthesised during the LC of hexagonal boron nitride (h-BN) with Ti powders on a Ti-3Al-2V substrate, with the aim of combining the high hardness and Young's modulus of TiB with the enhanced high-temperature plastic behaviour of TiN [95]. High laser power should be preferred in order to ensure the complete dissociation of h-BN and an optimised formation of TiN and TiB, resulting in marked improvement of the wear resistance of the composite coating. In situ synthesised TiB/Ti composites have been the most popular so far among in situ Ti-based composites [96–99]. Earlier works [96, 97] focused on the obtention of a fine and uniform distribution of TiB precipitates in Ti-6Al-4V matrix composites. Recently, TiB particles have attracted a renewed interest in order to improve the wear resistance of Ti–Nb–Zr–Ta matrix composites for use in orthopaedic femoral implants, with the added advantage that additive manufacturing allows for the custom-designed fabrication of the implants [98, 99].

5. Synoptic table of laser additive manufacturing of MMCs and concluding remarks

The major characteristics of the different MMCs reviewed in Sections 3 and 4 are summarised in **Table 2**. In the following concluding remarks, special care is also taken to identify current trends and important fundamental issues in the laser additive manufacturing of MMCs.

Composite	Resulting microstructure	Remarks
Al-matrix with carbides		
AlSi10Mg + SiC by selective laser melting (SLM) / direct metal laser sintering (DMLS)	Partial dissolution of SiC and precipitation of finely dispersed Al ₄ SiC ₄ [2] Dissolution of SiC and precipitation of Al ₄ C ₃ [12]	Improved hardness and wear resistance [2] Moderate improvement in hardness [12]
Al-4,5Cu-3Mg + SiC by DMLS with pulsed laser	Partial dissolution of SiC and precipitation of Al ₄ C ₃ [43, 44]	Extensive cracking due to high thermal gradients [43, 44]
Al-11 wt% Si + addition of Ti and WC by mixed wire/powder laser deposition	Ti added in the Al melt to promote the formation of TiC and inhibit the formation of Al ₄ C ₃ . Al-W and Al-Ti intermetallics are also observed [6]	–
Al-12 wt% Si + TiC by laser cladding	Very limited dissolution of TiC and formation of small amount of Ti ₃ SiC ₂ [13]	Significant improvement in hardness and wear resistance [13]
AlSi10Mg + nano-TiC by SLM	AlSi10Mg and nano-TiC are pre-mixed to form a nanostructured powder [46–49]	Enhanced hardness and wear resistance [47]
Al-matrix with borides		
Al-12 wt% Si + TiB ₂ by laser cladding	No sign of dissolution of TiB ₂ [19]	Enhanced wear resistance [19]
Al + TiB ₂ by in situ synthesis	Precipitation of finely dispersed TiB ₂ , Al ₃ Ti and Al ₃ Fe [84]	Enhanced wear resistance [84]
Al-matrix with oxides		
AlSi10Mg + nano-MgAl ₂ O ₄ spinel by DMLS	Significant volume fraction of residual porosity, nanoparticles affect the solidification process [12]	Decrease in hardness [12]
Al + Fe ₂ O ₃ by SLM	Excessive formation of Al ₂ O ₃ , high	–

Composite	Resulting microstructure	Remarks
	volume fraction of porosity [87]	
Fe-matrix with carbides		
Mild steel + SiC by laser cladding	Partial dissolution of SiC, formation of Fe ₂ Si [10]	Enhanced hardness, wear and corrosion resistance [10]
Stainless steel + SiC by laser cladding	Partial dissolution of SiC, precipitation of Fe ₂ Si, Fe ₃ Si, Fe ₃ Si ₅ , Cr ₃ C ₂ , Cr ₇ C ₃ [11, 51–53]	Enhanced hardness and wear resistance [11, 51–53]
Fe + nano-SiC by DMLS	Dissolution of micron-size SiC and reprecipitation to form finely dispersed nano-SiC [85]	–
Stainless steel + WC by laser cladding	Partial dissolution of WC, precipitation of M ₆ C, M ₂₃ C ₆ , M ₇ C ₃ [3, 35, 51, 54]	Enhanced hardness and wear resistance [3, 35, 51]
Stainless steel + TiC by laser cladding	Very little dissolution of TiC [51, 55]	–
Fe + TiC by in situ synthesis	Fine dispersion of TiC [37, 91]	Increase in hardness [37, 91]
Fe-36Ni “invar” + TiC by DMLS	Partial dissolution of TiC [56]	Loss of “invar” properties due to the enrichment of the FeNi matrix with Ti [56]
Stainless steel + Cr ₃ C ₂ by laser cladding	Partial dissolution of Cr ₃ C ₂ and precipitation of mixed M ₇ C ₃ and M ₂₃ C ₆ [3, 51]	Corrosion resistance is less compromised than with WC [3, 51]
Fe-matrix with oxides		
Stainless steel + Al ₂ O ₃ by laser cladding	Al ₂ O ₃ decomposes under laser irradiation [3, 34]	–
Stainless steel + Cr ₂ O ₃ by laser cladding	–	Extensive cracking [51]
Fe-Ni-Cr-Al + Al ₂ O ₃ by in situ synthesis	Finely dispersed Al ₂ O ₃ and mixed carbides [92]	–
Fe-matrix with other particles		
Stainless steel + CrB ₂ by laser cladding	Partial dissolution of CrB ₂ and precipitation of finely dispersed CrB, Cr ₂ B and Fe ₂ B [51]	Enhanced hardness and cavitation erosion resistance [51]
FeCrBSi + NbC and nano-CeO ₂	CeO ₂ favours a fine dispersion NbC	–

Composite	Resulting microstructure	Remarks
by laser cladding	by acting as heterogeneous nuclei during solidification [57]	
Fe + TiB ₂ by in situ synthesis	Finely dispersed TiB ₂ [92]	–
Stainless steel + hydroxyapatite by SLM	–	Bioactive implants [58, 59]
Ni-matrix with carbides		
Ni + WC by laser cladding	Partial dissolution of WC and precipitation of various carbides [5, 60, 62]	–
NiCrBSi + WC by laser cladding	Partial dissolution of WC and precipitation of Ni–W intermetallics [63]	–
NiAl + WC and TiC by in situ synthesis	Ni–Al intermetallics are also observed [86]	Enhanced hardness [86]
Inconel 625 + Cr ₃ C ₂ by laser cladding	Partial dissolution of Cr ₃ C ₂ and precipitation of finely dispersed Cr-rich M ₇ C ₃ [8]	Improved wear resistance [8]
NiCr + Cr ₃ C ₂ by in situ synthesis	–	Cr/C ratio is varied to control the reaction products [93]
Inconel 625 or Inconel 690 + TiC by laser cladding	Minimal dissolution of TiC and precipitation of fine dendritic M ₂₃ C ₆ [68]	–
Ni-matrix with other particles		
Ni + TiB ₂ by laser cladding	Dispersed TiB ₂ [26]	–
Ni + CeO ₂ or Y ₂ O ₃	CeO ₂ and Y ₂ O ₃ act as grain refiner [17, 69]	–
Nitinol + hydroxyapatite by SLS/SLM	–	Biomedical applications [70]
Ti-matrix composites		
Additions of TiC, WC, SiC, TiB, TiB ₂ or TiN	–	–
Ti + TiB and TiC by in situ synthesis	–	Excellent wear resistance [94]
Ti + TiB and TiN by in situ synthesis from h-BN	–	High laser power is recommended to ensure the full dissociation of h-BN [95]
Ti-6Al-4V + TiB by in situ synthesis	Fine dispersion of TiB [96, 97]	–

Composite	Resulting microstructure	Remarks
Ti-Nb-Zr-Ta + TiB	–	Enhanced wear resistance for use in femoral implant [98, 99]
Cu-matrix composites		
Cu + WC/Co by DMLS	–	Hardness and strength combined with good electrical and thermal conductivity [76–78]
Cu + WC by SLM	–	–
Co-matrix composites		
Co + WC	Partial dissolution of WC and precipitation of complex carbides [5, 80–82]	Applications in cutting tools [5, 80–82]
Co + TiC and CaF ₂ by laser cladding	–	Self-lubricating MMCs [83]

Table 2. Synoptic table of representative MMCs fabricated by laser additive manufacturing.

Data from **Table 2** highlight the importance of carefully selecting the reinforcing phase of the composites in view of not only the desired properties and application but also considering the compatibility of the reinforcement with the metallic matrix:

- Carbides constitute the most popular reinforcement in combination with a wide range of metallic materials. However, in some occasions, they may give rise to deleterious reaction products such as the brittle Al₄C₃ in Al matrix composites or chromium carbides that may compromise the corrosion resistance of stainless steels. A careful optimisation of the laser additive manufacturing processing parameters may be necessary in order to avoid the formation of these undesirable reaction products.
- Nitrides and borides are interesting alternative to carbides, in view of their generally good chemical stability and of their excellent mechanical properties.
- As a general rule, oxides appear much less promising for use as reinforcing phase in MMCs fabricated by laser additive manufacturing. Oxide particles may easily decompose during laser irradiation, and they present a strong tendency to dissolve in the melt pool and reprecipitate as a detrimental oxide skin that would compromise the good cohesion of successive additive-manufactured layers. A notable exception is the addition of rare earth oxide nanoparticles that act as very potent microstructural refiner, with beneficial effects on the mechanical and corrosion properties of the MMCs.
- Nanocomposites with enhanced properties have been successfully fabricated by laser additive manufacturing. However, specific procedures are necessary in order to avoid the processability issues related with the high tendency of nanoparticles to agglomerate and with their low flowability. For the production of ex situ MMCs, a nanostructured powder

should be prepared by carefully mixing the nanoparticles with the metallic powder used for the matrix. Laser-induced in situ synthesis of MMCs is a very interesting alternative, allowing for a refined and uniform distribution of nanoparticles.

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