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Short Communication

Quasicrystal–polymer composites for selective laser sintering technology

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ABSTRACT

Selective laser sintering (SLS) process is a layered manufacturing technique used for building functional parts from 3D computer-aided design. Materials compatible with SLS usually consist of polymer-based composites reinforced by metal or ceramic particles. We have investigated a new composite powder compatible with the SLS technology and containing AlCuFeB quasicrystalline filler particles. The processed parts show reduced friction and improved wear resistance compared to other composites used in SLS technology. In addition, the functional parts contain almost no porosity and are leak-tight allowing their direct use in many fluidic applications.

1. Introduction

The selective laser sintering (SLS) process is a rapid prototyping technology used for building freeform parts based on 3D computer-aided design (CAD) data files converted in STL format (Stereolithography). The SLS process is an additive manufacturing technology which was developed by Deckard et al. and patented in 1988 [1]. The physical object is constructed layer by layer, as opposed to subtractive manufacturing technology. It uses a CO_2 laser beam which selectively fuses powdered materials by scanning cross sections generated from the STL file. First, a thin layer of heat-fusible powders is deposited via a roller mechanism onto the build chamber and is heated a few °C below its melting point. Then, cross section of the part is selectively drawn by the laser beam. The interaction of the laser beam with the powder raises the temperature up to its melting point, resulting in particle binding. This binding mechanism is sometime called liquid phase sintering [2–4]. The surrounding powders remain a loose compact and just serve as support during the construction. When the cross section is completed, the build platform is lowered by a distance corresponding to the layer thickness (usually 0.1 mm) and the roller spreads an additional layer on top of the previously scanned layer. This new layer is then sintered directly on top of the previous one and the process is repeated until the part is completed.

Additive manufacturing is used in many industrial activities worldwide, such as medical, aerospace or motor vehicles for example [2]. The SLS process is being used for prototyping, but also increasingly to produce small series of end-user parts. Indeed, large numbers of components, all packed into the powder bed, can be realized simultaneously in a highly productive way. The materials which are involved are metals, plastics or composites [3,4]. In the case of SLS, the most frequently used materials are polyamide-based composites, either filled or not with ceramic or metallic particles [3]. Aluminum particles are currently added in the polyamide matrix such as to obtain SLS parts with a metallic appearance, good finishing properties and high stiffness [5–7]. However, there is no material solution for tribological applications of parts fabricated by this process. Furthermore, those parts are not leak-tight, which forbids their use in many fluidic applications without post-impregnation of resin.

Here we show that such properties can be met by using quasicrystals as filler particles to produce polyamide-based composite parts processed by SLS as shown in Fig. 1.

Quasicrystals (QCs) are Complex Metallic Alloys (CMAs) possessing long range order without translation periodicity and presenting forbidden symmetries such as fivefold or ten-fold rotational axis [8]. Extensive studies of these CMAs have been carried out since their discovery in 1982 [8] to unravel their complex structure in relation to their physical properties. Unlike conventional Al alloys, quasicrystalline materials have useful surface properties, such as low friction coefficient, low adhesion and high wear resistance [9,10] but they are brittle at room temperature. One of the most studied quasicrystalline compound is the stable icosahedral (*i*-) $Al_{62.5}Cu_{25}Fe_{12.5}$ (at.%) phase discovered by Tsai et al. [11,12]. Several studies focussed on the influence of addition elements, such as boron, to circumvent its intrinsic brittleness [13]. It was shown that introduction of boron in the chemical composition induces extra crystalline phases embedded in the *i*-AlCuFe matrix. These extra phases result in higher fracture strength, increased hardness and lower friction coefficient for the *i*-$Al_{59}Cu_{25.5}Fe_{12.5}B_3$ phase compared to the canonical *i*-$Al_{62}Cu_{25.5}Fe_{12.5}$ phase [14–16]. Another possibility to circumvent their intrinsic brittleness and still benefit from their useful properties is to use them as coating materials [17] or as reinforcement particles in composite materials. Examples of such composites includes CMA precipitates in a matrix like maraging

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Fig. 1. Examples of freeform SLS composite parts with high dimensional accuracy consisting of a polymer matrix reinforced by quasicrystalline AlCuFeB particles. This SLS part has a volume fraction of porosity lower than 2% and is directly leak-tight without post-impregnation of resin. Courtesy of Ateliers CINI SA and MV2T.

steel [18–20], Al-based [19,20] or Mg-based alloys [21–24], or CMA particles to reinforce a metal matrix [25] or a polymer matrix [26]. The general conclusion from these studies is that CMAs have a large potential as effective reinforcement particles in a ductile matrix. Polymer matrix composites reinforced by QC AlCuFe powder have first been studied by Sheares and Bloom [26,27]. Authors mentioned that tribological properties and storage modulus of these materials are enhanced significantly compared to those of the polymer matrix [26–28].

In the following, we report on the manufacturing of nylon-based composites reinforced by *i*-AlCuFeB particles by SLS and recently patented [29]. We show that these composite parts have improved properties compared to other materials used today in SLS technology.

2. Materials and methods

The QC particles are produced by gas atomization and have a nominal composition of $Al_{59}Cu_{25.5}Fe_{12.5}B_3$ (at.%). It has been shown that introduction of boron induces extra crystalline phases embedded in the *i*-AlCuFe matrix. These extra phases result in higher fracture strength, increased hardness and lower friction coefficient for the *i*-AlCuFeB phase compared to the canonical *i*-AlCuFe phase [13–16]. The QC particles were sieved with a mesh size of 75 μm and blended with nylon particles (<75 μm) in a Turbula mixer (30 min) in the appropriate volume fraction (30 v.% of QC) optimized for the laser sintering process. QC and nylon powders were produced by Saint-Gobain Coating Solutions and 3D Systems (USA), respectively. Selective laser sintered parts were then constructed using a sPro™ 230 SLS® Center. Table 1 summarizes the main parameters used in producing parts by SLS. For comparison, non-reinforced nylon polyamide PA12 (PA) and nylon reinforced by Al particles (PA + Al) with particles size and volume fraction similar to those used for (PA + AlCuFeB) samples were also fabricated. Friction properties of disks sample (Ø 25 mm) made by SLS were investigated with a pin on disk tribometer. The sample surfaces were prepared by mechanical polishing using SiC paper in water lubricant (from 500 grit down to 4000 grit) and cleaned with methanol and dried with a hair dryer. Friction tests were carried out at room temperature in ambient atmosphere with a relative humidity of 50–60% and under non-lubricated conditions. The indenter was a 6 mm ball of 100Cr6 hard steel. The radius of the trace was 5 mm. The sliding velocity was 16 cm s^{-1} (300 RPM) and the normal load was 10 N. Abrasive wear tests were performed. Wear resistance of SLS disks were evaluated under water conditions using a standard polishing technique (SiC paper, 500 grit, normal load 10 N, 1 min). Wear is expressed by volume loss and was compared with hot pressed samples. Hardness was evaluated by Shore D Durometry. Standard ASTM D638 [30] traction tests were performed on rectangular-prism shaped samples built flat by SLS and laid parallel to the machine *x*-axis. In order to estimate the interfacial bonding affinity between the polymer and the filler particles, contact angle measurements were performed on pure crystalline aluminum and QC AlCuFeB bulk samples using a Digidrop Contact Meter. The liquid polymer droplets used for contact angle measurements is an epoxy resin. Sample surfaces were prepared using SiC paper in water lubricant (from 320 grit down to 4000 grit) and cleaned with methanol in an ultrasonic bath and dried with a hair dryer.

3. Results and discussion

Fig. 2a shows the variation of the friction coefficient for SLS samples, either unfilled polyamide (PA), (PA + Al) and (PA + AlCuFeB) composites. Composites containing AlCuFeB particles have a friction coefficient much lower than that of both SLS non-reinforced (PA) and reinforced (PA + Al) samples. These results are in agreement with those observed by Liu et al. [31] on PA/AlCuFe composites showing the beneficial influence of QC particles for the reduction of friction. In the case of (PA + Al) composite, all friction tests stop before the end of the test after about 65 m of sliding distance due to strong tangential forces induced by the transfer of aluminum from the sample to the indenter.

Scanning Electron Microscopy (SEM) investigations of the worn surface (Fig. 3) and indenter show that the wear track and the ball counterpart are covered by a transferred layer which is made up primarily of aluminum and oxygen (not shown here). When QC particles are used as fillers, no material transfer occurs. This can be explained by the high hardness of AlCuFeB particles which reinforce the polyamide matrix and decrease plastic deformations during the friction test or by the reduced adhesion force that is observed in vacuum against steel [32]. Indeed, hardness measurements indicate that AlCuFeB filler induces an average hardness value of about 79 ± 1 Shore D. The average hardness is about 74 ± 2 Shore D for the two others SLS samples. This difference in Shore D hardness is significant. Thus the high ductility of Al particles does not allow any significant increase of the hardness of the polyamide matrix.

Traction tests were performed on these three samples. It was found that SLS (PA + Al) and (PA + AlCuFeB) have similar elongation at break (2% ± 1) and similar tensile strength (35 ± 5 MPA). Mechanical properties also depend on the volume content of porosity. In the case of SLS (PA + Al), the apparent density reaches

Table 1
Experimental parameters used to construct SLS parts.

Laser conditions				Temperatures (°C)			Feed parameter
Power (W)	Beam diameter (mm)	Scan speed (mm/s)	Scan fill spacing (mm)	Bed	Feed	Piston	Layer thickness (mm)
48	0.42	12100	0.22	173	140	150	0.1

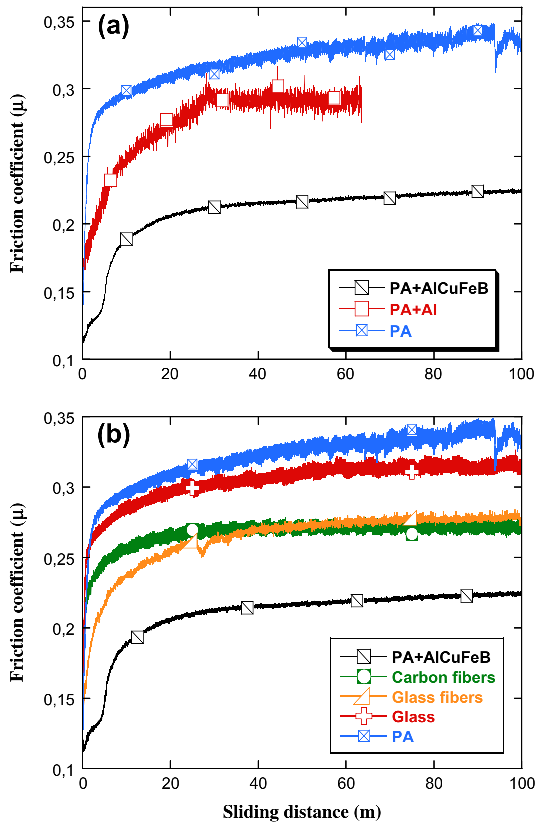

Fig. 2. (a) Variation of the friction coefficient for SLS samples with sliding distance. (b) Comparison of SLS composite reinforced by Qc particles with commercial SLS samples filled by glass particles, carbon fibers and glass fibers.

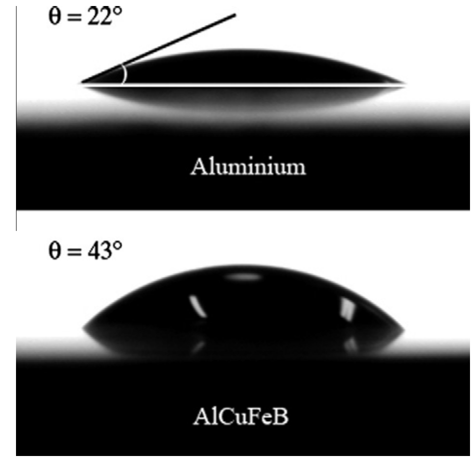

Fig. 4. Contact angles of polymer droplets deposited on surfaces of aluminum or quasicrystalline AlCuFeB bulk materials.

80% of the theoretical density. It exceeds 98% for the SLS (PA + AlCuFeB), which means a very low level of porosity in the samples. It is surprising that this difference in the porosity level does not correlate with improved traction properties. It is reasonable to speculate that bonding strength of QC particles with the polyamide matrix is lower than that of crystalline aluminum particles, thus counterbalancing the effect due to porosities.

To test this hypothesis, we have measured contact angles of liquid polymer droplets deposited on either aluminum or AlCuFeB bulk samples (Fig. 4). In both cases, contact angles are lower than 90° which indicates a good wettability of the metallic surfaces. However, contact angles measured on the aluminum surface are approximately two times smaller than those measured on the AlCuFeB surface. The work of adhesion W between the polymer droplet and the metallic substrate is related to the contact angle θ through the Young–Dupré equation $W = \gamma_l(1 + \cos\theta)$ where γ_l is the surface energy of the contact liquid.

Thus the lower contact angles measured on the Al surface suggests stronger interaction with the polymer matrix compared to the case of QC particles, an effect that could counterbalance the benefits due to the reduction of porosity level on the mechanical properties of the composite.

Additional leak tests under high air pressure (up to 7 bars) and water pressure (up to 7 bars) performed on SLS tube parts showed that only (PA + AlCuFeB) tubes are leak-tight. For all other commercial composite materials available for SLS like (PA + Al), (PA + glass filler), (PA + carbon fiber), an additional step of post-impregnation of the processed part with a resin is necessary in order to be leak-tight. This additional step drastically increases the production time by a factor of 2 approximately. Therefore the very low level of porosity in (PA + AlCuFeB) parts processed by SLS is one of the great advantages of this composite for many fluidic applications. An example of application is provided in Fig. 1. It shows an intake manifold of a car engine made by SLS with the (PA + AlCuFe) powder. The wall thickness is 2 mm. Because the manifold is directly leak-tight, it can be fabricated in a single operation. When using other SLS materials, such part must be manufactured in two halves by SLS station to allow for resin post-impregnation and then the two halves must be bonded together. Additional examples of applications already on the market are hoses, inserts, adaptors, connectors... used in automotive engineering. Other fields of development may concern prototyping for domestic appliances for example.

The quasi absence of porosity in quasicrystal–polymer SLS composites cannot be understood based on the wetting experiments, because QC particles have a poorer wettability with respect to the liquid polymer compared to Al particles. Actually, the

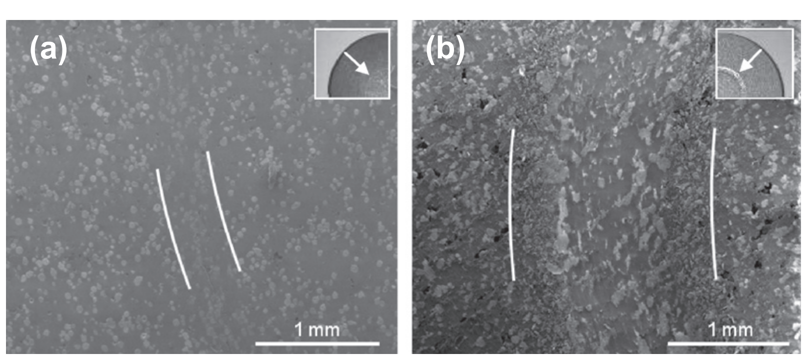

Fig. 3. Secondary electron SEM images showing the wear marks of SLS samples. (a) After 100 m of sliding distance for sample containing quasicrystalline particles. (b) After 60 m for sample containing aluminum particles, the wear track is covered by aluminum. Insets: photos of the wear marks. The curved lines are only guide for the eyes.

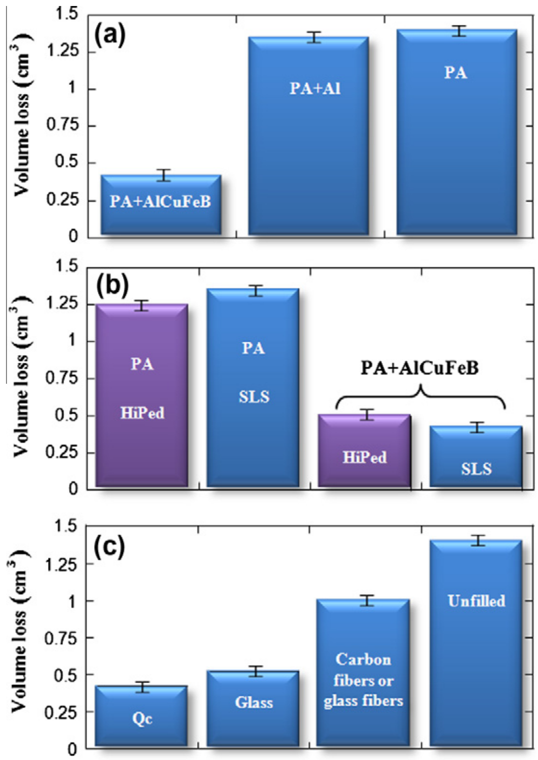

Fig. 5. (a) Volume loss for SLS samples. When aluminum particles are added to the PA matrix, no gain is observed compared to unfilled PA. Quasicrystalline particles (Qc) reduce the volume loss by about 70%. (b) Volume loss results of hot pressed samples (HiPed) compared to SLS samples. (c) Comparison of SLS composites reinforced by Qc particles with commercial SLS samples filled by glass particles, carbon fibers and glass fibers.

measured contact angles indicate good wetting in both cases. Thus another material property must be at the origin of the tightness of SLS parts. A possible origin could be related to the very low thermal conductivity of QC AlCuFeB particles which is one hundred times lower than that of crystalline aluminum. As a result, the energy supplied by the laser to fuse the polymer binder may be released less efficiently in the case of QC filler particles. This could increase the time laps during which the polymer is melted and can fill the pores leading to dense layer in SLS manufacturing. The use of AlCuFeB particles as fillers has also great advantages with respect to wear resistance of SLS machine parts.

Fig. 5a shows that (PA + AlCuFeB) samples present a reduction of the volume losses by about 70% compared to unfilled PA and (PA + Al) composites. For comparison, we have made both PA and (PA + AlCuFeB) composites by hot pressing method (180 °C, 5 min, 15 MPa) and found clearly different trends in wear losses (Fig. 5b) and friction tests (not shown here). These results demonstrate that the SLS process allows the direct fabrication of complex geometry parts made of composites reinforced by AlCuFeB particles that exhibit properties similar to those of samples manufactured by conventional polymer methods (hot pressing, extrusion, injection molding). Finally, we have compared the properties of this new (PA + AlCuFeB) composite with other commercialized composite powders for SLS process. Three SLS samples were made consisting of a polyamide matrix reinforced with different fillers (glass particles, carbon fibers and glass fibers). The volume fraction of the fillers in these commercial powders can vary and is determined such as to optimize the dimensional accuracy of the parts upon selective laser sintering. In all cases, our SLS composite samples have friction coefficient values (Fig. 2b) and volume losses (Fig. 5c) much higher than that of the composite samples filled with QC AlCuFeB particles.

4. Conclusions

A composite consisting of a nylon matrix reinforced by Al-based QC powders was adapted and commercialized for applications in selective laser sintering process. This new light-weight composite extends the materials choice compatible with the SLS process and offers improved functional properties. It shows promising applications in the rapid manufacturing of complex functional parts with high dimensional accuracy, high wear resistance and reduced friction coefficients. In addition, the low level of porosity allows the direct use of the parts for sealing applications, with no post-impregnation of resin, thus reducing drastically the manufacturing time.

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