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Optimization of MWCNT – Metal Matrix Composites feedstocks

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Abstract

Micro powder injection moulding-µPIM is a powder injection moulding-PIM variant for microparts/devices. This study is about the optimization and respective production of nanocomposites feedstocks suitable to µPIM process. The optimization of MWCNT content in metal matrix composites-MMC feedstock were performed using torque rheometry until achieve homogeneous feedstocks with suitable flowability to µPIM process (60:40 vol.%). During debinding step, it is likely loss of MWCNT, forcing a new stage where physical connection between powders and MWCNTs should be established. Mechanical milling seems the suitable technique to be adopted to overcome this major problem. In preliminary route, the binder M1 (with or without SA addition) is mixed with copper or 316L steel powder. Therefore, two different routes were selected: route 1 – the addition of different MWCNT contents is done during the preparation of feedstock; route 2 – a mechanical milling of metallic powders with MWCNT precedes the conventional production of feedstocks, but with SA addition to improve the nanoreinforced content. The first route impairing its processability by µPIM. The other route revealed to induce homogeneity mixing and torque values suitable to be used as feedstock for µPIM. The route 2 allowed to manufacture with high quality microparts up to 2% of MWCNT addition.

Keywords: MMC; micro PIM; Cu; SS316L; MWCNT; milling; plastograph mixing.

1. Introduction

µPIM is the result of the need to adopt a sustainable production, decreasing dimensions of parts or devices, raw material, time of processing and energy, but maintaining their functionality. One of the great challenges of microworld in engineering structural applications is to decrease the surface areas maintaining the applied load.

The µPIM process is currently being used because it can process a wide variety of materials and near net-shape complex geometries, having dimensional accuracy, replicability, combining high-series production with low cost production of micro components [1,2]. The basic processing steps in µPIM include selection of materials (powder and binder), mixing of powder and a thermoplastic binder system to get feedstock, injection moulding into a required shape, debinding and sintering [1-3]. In order to replicate the micro features, smaller particles powder (< 5 µm) are used in µPIM, which imposes additional and more stringent requirements in the processing conditions [1,3,4]. The powder characteristics, binder composition, powder loading and mixing method are closely related to the quality of the feedstock, and the quality of the µPIM feedstocks is more rigorous than PIM [5]. Inhomogeneity in feedstock can lead to defects in the final parts [5]. The ideal feedstock should be homogeneous and with low viscosity, ensuring complete filling, easy demoulding and good shape retention in debinding and sintering steps [3,4,5]. The thermal and rheological properties of the feedstock are also important because melting and degradation temperatures determine processing conditions for mixing, injection moulding and debinding [5]. The µPIM injection step obliges to higher mould temperature, pressure and lower injection speed when compared with PIM injection

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step [3]. The debinding step should be properly carried out to avoid distortion and give rise to parts/devices with homogeneous shrinkage after sintering [4].

One of the most exciting studies is to adapt μPIM to process nanocomposites, where matrix containing nanoreinforcement (such as MWCNT - multiwalled carbon nanotube) that are incompatible with molten temperatures and hard to be processed via conventional techniques [6]. The MWCNT present outstanding physical properties, such mechanical strength, thermal stability and high electrical and thermal conductivities, becoming them suitable for structural microparts/devices [7]. The most difficult challenge in manufacturing nanocomposites is to attain a homogenous MWCNT dispersion in the metal matrix. This can be attributed to different factors: (i) incompatibility between metal matrix and nanoreinforcement, (ii) large difference in densities (matrix/MWCNT), (iii) unsuitable mixing during the preparation of feedstock and (iv) poor wetting behaviour [6,8].

During last decennia, there are some publications about mixing Cu/CNT nanocomposites by ball milling followed of sintering [6,8]. By these methods, it was possible to reinforce until 3 wt.% [9] or 4 wt.% of MWCNT [8]. However, there is a lack of papers concerning nanocomposites based on steel reinforced by MWCNT.

Many studies concerning PIM of copper and stainless steels powders were published, but there is no impressive publications concerning nanocomposites feesdstocks. A. S. Muhsan *et al*. mixed 10 vol.% of MWCNT with Cu by mechanical milling and after it was mixed with binder to be processed by PIM [6]. And in what concerns preparation of iron powders Shuquan *et al.* prepared by high energy ball milling a 0.2 wt.% CNT and Fe powders, after mixed with binder [10].

The feedstocks preparation of powder mixing (ferrous or non-ferrous powders) with MWCNT reinforcement with the selected content, suitable flowability and low torque for μPIM is not yet overcame.

The main objective of the present study is to optimize feedstocks of nanocomposites based on copper or austenitic stainless steel reinforced with MWCNT for μPIM. An efficient strategy will be outlined to ensure a homogeneous dispersion of MWCNT in metal matrix feedstock with the lowest torque value, suitable to be injected. The procedure selected must minimize the damage of carbon nanotube.

2. Materials and Experimental Procedures

2.1. Raw materials

Copper (Cu) and stainless steel 316L (SS 316L) were used as matrices. Both powders were produced by water atomization and supplied by Epson Atmix Corporation®. A commercial binder (M1), a multi-polymeric system (Atect®), and stearic acid (SA) 97% (Acros Organics) were the binders used. The nanoreinforcement - MWCNT (Nanocyl®) was produced by catalytic carbon vapour deposition, with diameter of 9.5 nm and up to 1.5 μm length.

2.2. MMC feedstocks preparation

For production the feedstocks (powder and binder) is necessary to optimize the powder:binder ratio. The feedstocks optimization was performed using a torque rheometry measuring equipment (Brabender Plastograph mixer). This technique consists in evaluation the critical powder volume concentration (CPVC), by monitoring the torque value during the mixing of powders and binder (is based on resistance that the material opposes to the rotation of blades) [11].

Different procedures were realized until achieve MMC feedstocks homogeneous and with suitable flowability (torque value < 3 N m), containing different percentages of MWCNT reinforcement: 0.5, 1, 1.5 and 2 vol.%. In Table 1 are summarized some details of procedures.

Table 1. Procedures resume.

Preliminary route	Feedstock optimization and production of "master feedstock", i.e., powder and binder with or without SA
Route 1	"Master feedstock" without SA + MWCNT "Master feedstock" with SA + MWCNT
Route 2	Pre-mix (powder and MWCNT) + binder and SA

All mixtures were performed under optimized conditions. In route 2, the mechanical milling between powder and MWCNT was performed in a planetary ball milling machine (Fritsch) with a hardened chromium steel bowl (250 cm^3) and fifteen balls of the same material, with a diameter of 20 mm, under $Ar+H_2$ (5%) atmosphere. The rotation speed of 200 rpm, up to 30 min and ball to powders weight ratio of 20:1 were selected. These pre-mix are then mixed with M1 and SA in a Brabender Plastograph mixer.

2.3. Techniques of characterization

The powders, MWCNT and binders were characterized using the techniques as follows: helium picnometry - Micromeritics AccuPyc 1330 (density), Malvern Mastersizer 2000 (particle size analysis), Scanning Electron Microscopy (SEM) - FEI Quanta 400FEG (morphology, particle distribution), Transmission Electron Microscopy (TEM) – TEM-FEI Tecnai G2 F20 and Thermogravimetric Analysis (TGA) (Setaram Setsys) (weight loss with temperature).

3. Results and Discussion

3.1. Raw materials: powders, binder and nanoreinforcement

The particle powders mean size (d_{50}) of copper is 3.86 µm and SS 316L is 3.48 µm. In Table 2 are resumed the density and specific surface of both materials.

Table 2. Density and specific surface of powders.

Powders	ρ (kg/m^3)	Sw (m^2/kg)
Cu	8642	2405
SS 316L	7544	1913

Fig. 1 shows the shape of powder particles; these are spherical that mean a shape factor close to 1.

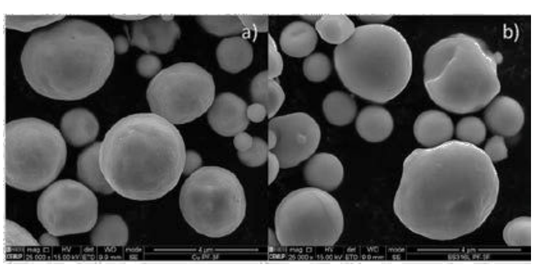

Fig. 1. Morphology of powders Cu (a) and SS 316L (b).

Table 3 resumes the characteristics of binder M1 and SA.

Table 3. Binders' characteristics.

Binders	ρ (kg/m^3)	Composition
M1	969	Polyolefin waxes
SA	983	$C_{18}H_{36}O_2$

The M1 and SA thermal analysis occurred under argon atmosphere until 700ºC, to understand the weight loss (Fig. 2). For the M1, the degradation temperature range is from 275ºC to 475ºC, and for SA is between 275ºC and 525ºC. The two organic components are completely removed at the highest temperature, that is a good binder's characteristic in PIM process.

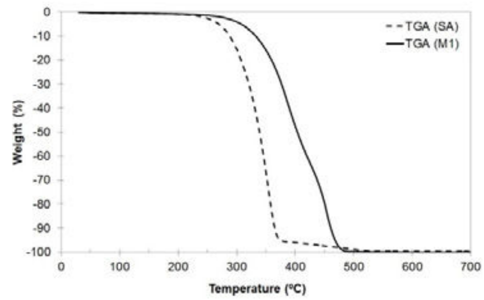

Fig. 2. Thermal gravimetric analysis of binder M1 and SA.

The MWCNT density was 2134 kg/m^3 and is visible the presence of carbon nanotubes in Fig. 3 a). The thermal behaviour of MWCNT was evaluated at different atmospheres (Fig. 3 b)), i.e., air and argon. In air atmosphere, the MWCNT start at 400ºC the degradation process until complete carbonization, which is finished at 950ºC. In argon atmosphere, the weight loss up to 1300ºC is only 4.8%. MWCNT should not be degraded up to the sintering temperature of the metal powders.

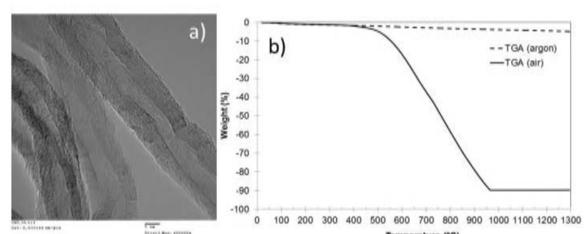

Fig. 3. a) MWCNT micrograph (TEM) and b) TGA of MWCNT in argon and air atmospheres.

3.2. Preliminary route

Before the production of nanoreinforced MMC feedstocks, is essential to make the optimization. All the feedstocks optimized were performed at 180ºC, 30 rpm. Fig. 4 shows the optimization curves for Cu and SS 316L with binder M1. In each case, the critical powder volume concentration (CPVC) selected were 61 and 63 vol.%, respectively.
To produce the "master feedstock", it was selected 60 vol.% of powders and 40 vol.% of binder for both matrices (Cu or SS 316L), for further comparisons.
Fig. 5 shows the behaviour of Cu and SS 316L feedstocks, with and without addition of 10 vol.% SA.

After some minutes of mixing, the torque value stabilizes, revealing homogeneity. The torque value of copper mixture is always higher than SS 316L and the addition of 10 vol.% SA decreases the torque value of both "master feedstocks".

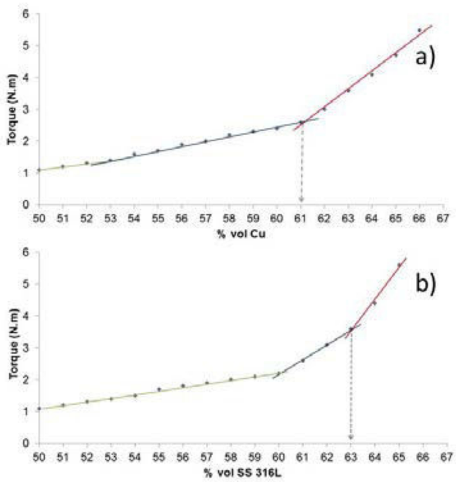

Fig. 4. Optimization curves: Cu (a) and SS 316L (b).

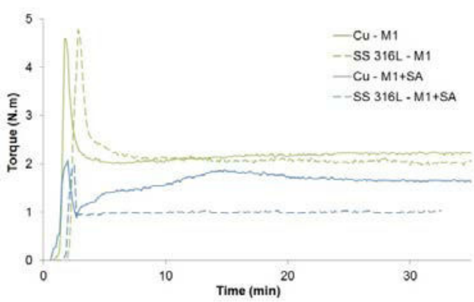

Fig. 5. "Master feedstocks" with or without SA addition - 60:40 vol.% powder:binder.

Fig. 6 shows that the powder particles are involved by binder and there is a good distribution of the powder particle inside the binder, to both feedstocks.

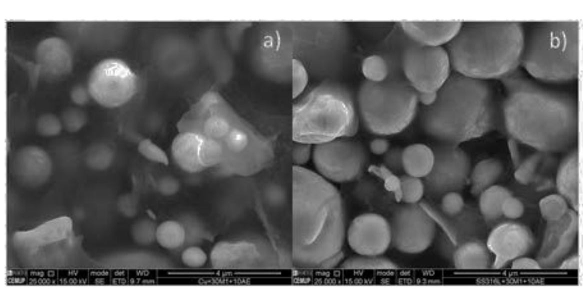

Fig. 6. Feedstocks 60:40 vol.% of powders: M1+SA: Cu (a) and SS 316L (b).

3.3. Route 1

The nanoreinforced MMC feedstocks produced by route 1 are composed by "master feedstock" with or without SA and MWCNT. Different percentages of nanoreinforcement were tested: 0.5, 1, 1.5 and 2 vol.%. Table 4 resumes the torque values for two matrices and with or without SA addition. The addition of different contents of MWCNT changes the behaviour of "master feedstocks" matrices, i.e., increases the torque value. For the same content of MWCNT, the Cu MMC feedstocks reveal always higher torque values than SS 316L, whatever the time of mixing. In copper case, the mixtures become impossible when the content of MWCNT is higher than 1.5 vol.%, with or without SA addition. However, the SS 316L MMC feedstocks reveal a different limit content of MWCNT in mixing (2 vol.%). The MMC feedstocks produced without SA addition become inappropriate to be produced by µPIM because of the higher torque values.

The SA addition contributed to decrease the torque values, in both matrices and with any content of MWCNT, rendering these MMC feedstocks more appropriate for injection moulding step.

Table 4. Route 1: torque values (N m) of nanoreinforced MMC feedstocks with and without SA.

Matrix	Copper matrix		SS 316L matrix	
SA	No	Yes	No	Yes
0 vol.% MWCNT	2.2	1.7	2.0	1.0
0.5 vol.% MWCNT	3.9	2.1	3.0	1.6
1 vol.% MWCNT	6.5	3.1	4.5	2.0
1.5 vol.% MWCNT	7.3	3.6	5.3	2.3
2 vol.% MWCNT	*	*	6.1	2.4

* The reinforced MMC copper feedstock with 2 vol.% MWCNT was not possible.

3.4. Route 2

In order to overcome the high torque values and non-mixture of Cu powder with 2 vol.% MWCNT, a pre-mixing between powder and MWCNT by ball milling was performed. After this, the composite powder is mixed in Plastograph with binder (M1) and SA. The pre-mixing aims to create bonds between powders and MWCNT to prevent the loss of the nanoreinforcement during the removal of binder (debinding).

After 30 min of ball milling, the powders shape presented a slight change in shape factor, particularly for copper based composites powders (Fig. 7).

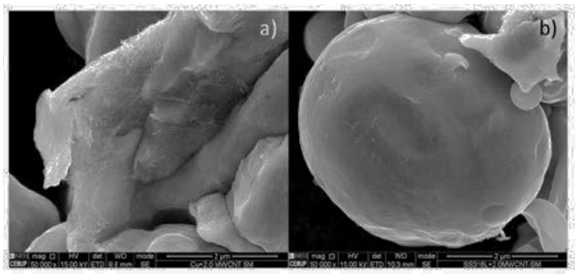

Fig. 7. After mechanical mixing of MWCNT (2 vol.%) with Cu (a) and SS 316L (b).

The feedstocks composite metallic powders after mixed with binder were analysed by SEM to investigate the distribution in feedstock. In both metallic based feedstocks, it was detected that MWCNT are dispersed on powders and not in binder (Fig. 8).

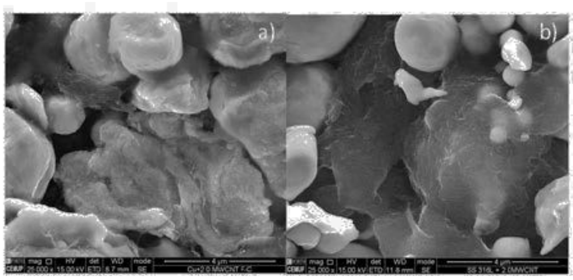

Fig. 8. Route 2 - nanoreinforced MMC feedstocks with pre-mix 2 vol.%: Cu (a), and SS 316L (b)

The route 2 is the best procedure whatever the metallic powder composition. The nanoreinforced MMC feedstocks present low torque values, suitable to be processed by µPIM. The previous mechanical treatment also contributes to increase the content of MWCNT in the copper feedstock up to 2 vol.%, becoming appropriate to be injected (Table 5). Once again, the Cu feedstock presents higher torque values than the SS 316L. This is due to the highest specific surface of Cu powders.

Table 5. Torque (N m) for different MWCNT content (route 2).

Route 2	Copper matrix	SS 316L matrix
0 vol.% MWCNT	2.1	0.9
0.5 vol.% MWCNT	2.8	0.9
1 vol.% MWCNT	3.0	0.9
1.5 vol.% MWCNT	3.7	1.3
2 vol.% MWCNT	4.3	2.2

4. Conclusions

Cu and SS 316L "master feedstocks" for µPIM were successful prepared. The addition of MWCNT increases significantly the torque value of the mixture in contrast with "master feedstock". This fact obliged to a supplementary addition of stearic acid for decrease torque value, improving flowability of feedstock. Premixing let to achieve an effective bonding powder-MWCNT (avoiding its loss in debinding step), without damage of the nanotubes. The nanoreinforced MMC feedstocks produced by route 2 are homogeneous and with flowability suitable to be injected. Feedstocks with MWCNT content > 2 (vol.%) is impossible to be microinjected because feedstocks lost "elasticity" essential to readjust the injection conditions, mainly pressure and temperature.

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