SELF-LUBRICATING COPPER MATRIX COMPOSITES WITH HIGH CONTENTS OF LUBRICANTS

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SUMMARY

Copper matrix composites reinforced with particles having solid lubrication properties were processed using a non-conventional powder metallurgy technique. With this processing, based on deposition of a copper shell onto particle surface, volume fractions of carbon based reinforcement up to 60 vol.% were achieved, keeping residual porosity to an acceptable level. Moreover, these composites have a homogeneous microstructure without particle-free or matrix-free zones. This process has also been derived to manufacture successfully composites containing MoS_2 particles. Friction behaviour of both kinds of composites has been studied using the pin-on-disk method. Trends in friction behaviour of graphite based composites with respect to the composite composition are pointed out. In the case of MoS_2 reinforcement, first evaluation of the high potential of this new class of materials for space applications is demonstrated.

Keywords: MMC, friction, processing, mechanical, particles

1 INTRODUCTION

In selected applications, where solid lubrication is required, several ways can be chosen for manufacturing pieces having the adequate properties.

In bearings for instance, races maybe coated with solid lubricants [1]. Hence, the lifetime of the component is limited and depends on the coating thickness, which is chosen as a trade off among the part's requirements.

For larger parts, macroscopic drilled holes are stuffed with the lubricant . This method allows having "bulk" lubricant properties, hence no limited lifetime, but is restricted to simple shapes, and large dimension.

Powder metallurgy is another means of achieving the desired properties by mixing particles having different properties. This composite fabrication method is currently employed for low lubricant content and coarse particles. For higher content or fine particles, clustering starts being of concern, particles agglomerate and the final material has an inhomogeneous microstructure, with zones depleted of lubricant, others of matrix.

The ideal solid lubricant material should have bulk lubrication properties, be homogeneous and its fabrication process suitable for any size or shape. This paper describes a copper-based matrix composite processing method, which was developed for achieving homogeneous composite microstructure together with a high volume fraction of reinforcement.

2 RAW MATERIALS AND PROCESSES

2.1 Reinforcement particles

Two types of particles known for their solid lubricant properties have been selected, i.e. graphite (coke as reference) and molybdenum-di-sulphide (MoS_2). The former is of interest for in-air [2], the later for in-vacuum applications [3]. They both have a strongly bonded hexagonal layered structure where layers are stacked, maintained together by Van-der-Waals forces. Shearing separation of layers allows building-up of a solid lubricant film (also on the counterface). This process might require a minimum size of the particles, e.g. shown for MoS_2 [4].

2.1.1 Graphite and coke

Graphite and coke is available in several grades, from natural ores or synthesised by pyrolysis. For each grade, particle sizes are separated by sieving. They can range from few up to few hundreds of microns. Three different grades from Timcal™, with particle size ranging from 6 up to 600 μm, have been used to demonstrate the process versatility. Only most relevant results, mainly related to particle size and graphitization, are presented in this paper. Graphite and coke properties are summarised in Table 1

Grade/size	Shape	E* (GPa)
KS 15	Irregular spheroids	6
KS 150-600		
T 150-600	Angular flakes	5.5
Coke CF 250	Irregular	12

* average value from 25 depth-sensing nanoindents experiments

Table 1: Carbon based particle properties

Graphite is produced at higher temperature than coke and hexagonal planes are better aligned. The two graphite grades are obtained from different precursors.

2.1.2 MoS₂

MoS_2 particle providers are fewer and there is less information about the product. Two different particle size distributions have been used, fine (few μm) and coarse (about 50μm). Results are focussed on coarse MoS_2 particles.

2.2 Processes

The underlined idea for manufacturing is to ensure that in the material each particle is surrounded by a matrix shell. Therefore, prior to further steps, an electroless coppering of powder is performed in aqueous solution.

2.2.1 Surface preparation

For enhancing the copper deposition, particle surfaces were treated using the following steps:

- **Surface cleaning**: process depends on the nature of the particle to be coated. It can consist in just dipping particles into solvent or perform a complex degreasing treatment. Afterwards particles have to be rinsed carefully to avoid contamination of the next treatment bath.
- **Surface activation**: aims at "depositing" a palladium atom on particle surfaces that can act as the first bonding between deposit and surface to coat.
- **Surface generation**: where a tin solution is used to create a chemical bounding between the palladium and a tin complex.
- **Surface stabilisation**: consisting in removing the excess of species from the surface.

2.2.2 Copper electroless deposition

Afterward, the particles to be coated are dipped in an aqueous copper salt solution containing also a reducing agent. Thus, copper is reduced according to [Eq1] and metal deposits on the particle surface. Particle surface preparation and stirring facilitate copper germination and particle separation, respectively. The method ensures a good interface intimacy, copper germinating everywhere on surface. Therefore, before pressing, particles are distant of at least twice the copper coating thickness. Even if copper squeezes during pressing a thin copper layer remains around each particle.

$$CuSO_4 + 2HCHO + 4NaOH \rightarrow Cu + 2NaCOO + Na_2SO_4 + 2H_2O + 2\overline{H_2} \text{ [Eq1]}$$
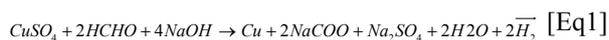
As illustrated on Figure 1, coppering can be successfully applied even on particles having a very small diameter.

Moreover, a uniform thickness copper layer is deposited on each particle as illustrated on Figure 2. The main constrain is that the copper shell shall be thick enough for sustaining the stresses induced during the following processing steps, and as thin as possible to reduce cost. Experiments show that few tenths of a micron is a satisfactory compromise.
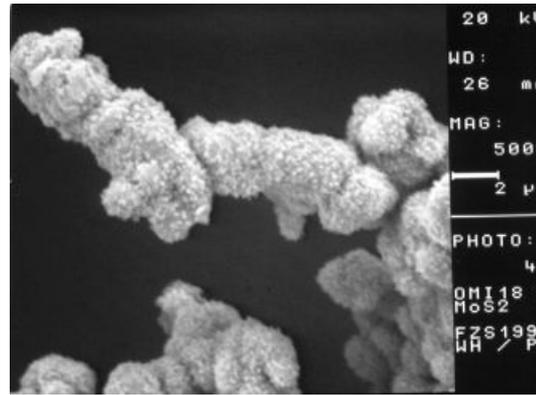

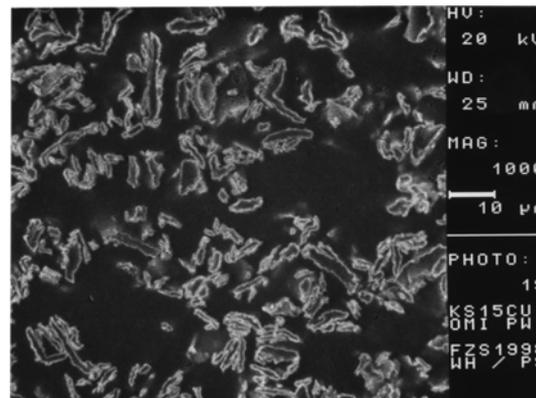*Figure 1: Cu coated fine MoS₂ particles*

Figure 2: Coppered KS15 particles, cross section

2.2.3 Mixing

Taking into account the former step, final reinforcement volume fraction has been adjusted using classical powder-metallurgical processes. Coppered particles were blended with matrix powder, which composition was adjusted to the one desired. Powders targeting[1] different particle volume fraction in the range from 25 to 60% were blended this way.

2.2.4 Pressing

After mixing, the powder was poured into a graphite die and cold pressed. Afterward the die was positioned into a hotpress. Copper oxide, if any present, was removed during the hotpressing cycle by using a hydrogen flux.

The typical parameters for hot-pressing are 20 MPa, 850°C. Some modifications in the cycle parameters were done to take into account composite's specificity.

3 MATERIAL PROPERTIES

3.1 Graphite and coke reinforced

The manufactured composites are summarised in table 2. With this set of composite, influence of particle size, grade and content can be pointed out.

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[1] The amount of copper deposited is estimated by weighing powder before and after coating, assuming that no powder is lost during coppering. This may lead to slightly underestimate the amount of deposited copper.

Grade/size	Vol. fraction %
KS 15	30 / 50
KS 150-600	40 / 50 / 60
T 150-600	40 / 50 / 60
Coke CF 250	50 (4 mixing processes)

Table 2: Carbon based composite pressed.

After pressing material density was measured by Archimedean method to estimate residual porosity. This later remains bellow 6% for volume fraction of particle of 60%. Figure 3 and Figure 4 illustrate the particle distribution and the intimate particle-matrix interface respectively.
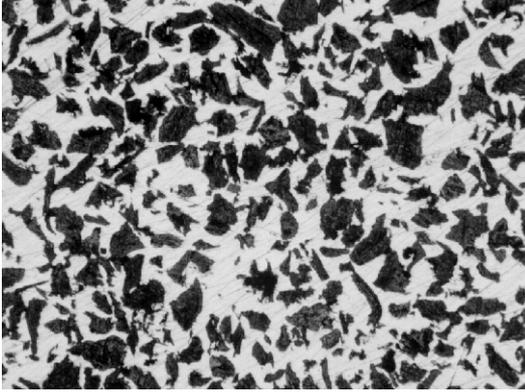

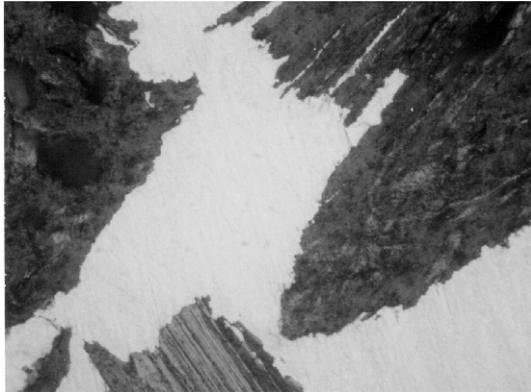*Figure 3: Microstructure of 50% CF 250 composite*

Figure 4: Interfaces in 50% CF 250 composite

3.2   MoS$_2$ reinforced composites

Copper and MoS$_2$ react at elevated temperatures, to form a copper sulphite whose properties are detrimental for the foreseen application. Lowering pressing temperature has a poor compaction, as expected draw back. Therefor, the matrix composition and the overall process have been adapted, for manufacturing dense composite. With 25% volume fraction of MoS$_2$ particles, whose average diameter is 50μm, the achieved residual porosity can be less than 3%. Only this reinforcement volume fraction has been studied until now.

4   TESTING AND RESULTS

Samples have been tested on a vacuum-pin-on-disk equipment developed at ARCS. A cast iron GG25 disk was used as counterpart, the pin being made of the composite. The graphite and coke reinforced composite, were tested in air, with a relative humidity of about 60%, the MoS$_2$ reinforced composite were tested under vacuum, at 10^{-6} mbar pressure. The applied contact pressure was adjusted to material behaviour. The friction coefficient was recorded continuously and the wear rate determined from sample weight loss. Sliding distance was in the range 1000 to 15000 metres, adjusted for having a weight loss of, at least, few milligrams.

4.1   Graphite and coke reinforced composites

The sliding speed was fixed at 0.5 m/s for all specimens. Results obtained on the different carbon reinforced composites are illustrated in Table 3.

4.1.1   Influence of graphite grade

Expected and noticeable differences exist between graphite reinforced and coke reinforced composites, very likely related to graphitisation. Indeed, with graphite particles, the easily shearable layers promote an easy sliding, due to rapid building up of solid lubricant layer. The friction coefficient of graphite reinforced composites is in the range 0.18 up to 0.25, about half of that of coke reinforced composites.

Type of graphite and size	Vol. fract.	Wear rate		Friction Coefficient	
		Mean	StdDev	Mean	StdDev
	v%	x10^{-6} mm³/Nm			
CF 250	50	1.4	0.5	0.43	0.08
T 150-600	60	1.6	0.3	0.23	0.02
T 150-600	50	3.4	1.5	0.22	0.01
T 150-600	40	1.3	0.4	0.21	0.01
KS 150-600	60	4.1	2.4	0.23	0.00
KS 150-600	50	1.3	0.3	0.23	0.00
KS 150-600	40	1.5	0.1	0.18	0.00
KS 15	50	81.7	34.2	0.19	0.01
KS 15	30	206.7	9.4	0.17	0.00

Table 3: Results (Wear rate and friction coefficient) dependent on type and size of graphite particles and their volume fraction.

4.1.2   Influence of particle size

The KS 15 reinforced composites have a slightly lower friction coefficient than the KS 150-600 reinforced composites, but their wear rate is about 100 times higher. Microscopic observations (Figures 5 and 6) show that it is hardly possible to find KS 15 particles on pin's tribo-surface. They are probably rubbed out of the tribo-surface as soon as they come into contact with the disc instead of being sheared . On the other hand, large KS 150-600 particles seem to contribute during a longer time to lubrication, lowering material wear rate.
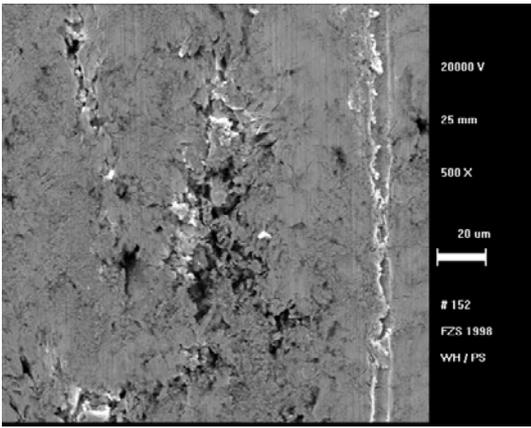
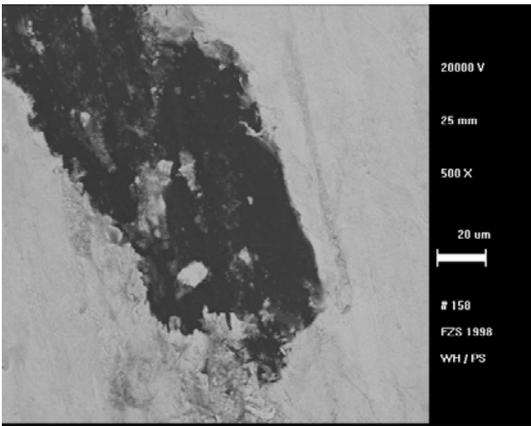*Figure 5: Tribo-surface of KS15 reinforced composite.*

Figure 6: Tribo-surface of KS150-600 reinforced composite

No explanation has been found for the difference in friction coefficient between KS15 and KS 150-600 reinforced composites.

4.1.3 *Influence of reinforcement volume fraction*

For the composites with big particles (T, KS150-600) no significant influence of volume fraction on friction coefficient and wear rate is visible. However, a slight tendency is visible, that the lowest friction coefficient corresponds to the lowest particle volume fraction. These results are in accordance to e.g. [5], or [6], who found an increase of wear rate and friction coefficient if volume fractions are decreased from 20 v% to zero. Only in case of small particles (Table 3: KS15, 15 μm) a strong influence is visible. But herein the poor lubrication efficiency of small particles might superimpose the effect of volume fraction. (See above.)

4.2 MoS$_2$ reinforced composites

With these composites, sliding speed was fixed at 0.1 m/s, the applied pressure was 1.56 MPa. The friction coefficient of such composite is illustrated in Figure 7. One can see that after few meters running distance a steady state is reached where the friction coefficient is stable, with a mean value of about 0.025. This result is very promising, friction being close to that of pure MoS$_2$ films generally used in space applications. Moreover, the wear resistance of these composite is satisfying,
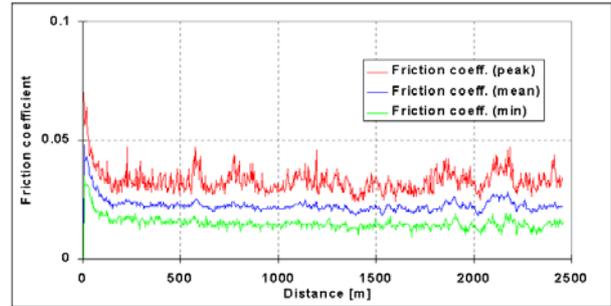
wear rate being close to 10^{-5} mm/Nm.

Figure 7: Friction coefficient Vs running distance of MoS$_2$ reinforced composite.

5 CONCLUSIONS AND OUTLOOKS

This study was conducted for assessing a manufacturing route for copper based matrix composites. The composites thus manufactured have been investigated in terms of microstructure and friction behaviour. The main conclusions that can be drawn are the following:

This route (Cu coated particles) allows manufacturing composites containing up to 60% volume particles. The material presents a low residual porosity together with a uniform particle distribution and a satisfactory interface intimacy. This method can be used for particle size down to few microns.

In addition to the chemical nature of particles, the friction behaviour of such composite depends on particle size and volume content. A minimum size seems to be required for lowering wear rate (150μm). With this size of particles no significant influence of volume fraction (30-60v%) on wear rate and friction coefficient is visible.

The materials manufactured are promising for applications where an important amount of lubricant is needed, i.e. bearing cages. Anyhow, still several points have to be considered before thinking of industrial applications: influence of residual porosity, mechanical behaviour, influence of particle orientation etc. These points will be assessed during the coming years.

6 REFERENCES

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