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Nanotechnology in machining processes: recent advances

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Abstract

In this brief survey, the use of nanoparticle dispersions in machining processes is discussed and the relevant applicational performances are analysed and related to the structural and chemical composition of the embedded nanophase. The paper is divided in two basic parts. In the former, the metalworking nanofluids are classified with respect to the physico-chemical properties of the nanostructured phase suspended in the base fluid. In the latter, some aspects concerning the production of metalworking nanofluids are analysed and a new green and economically viable technique based on a cementation process for metal nanoparticle synthesis is proposed as an alternative approach to the conventional manufacturing techniques.

Keywords: nanoparticle; nanofluid; machining; green synthesis; wet chemical method

1. Introduction

The use of nanofluids has attracted a great attention owing to their multipurpose functions in metalworking processes. In particular, nanofluids proved to be efficient for their unusual properties in heat transfer and lubrication. Singh et al. pointed out that these two aspects account for approximately 15-18% on the total manufacturing cost of a product. However, it should be noted that nanofluids have a considerably higher production costs with respect to conventional cutting fluids, owing to the complex manufacturing steps related to the sinthesis of the nanoparticles embedded in metalworking fluids. According to the definition usually accepted in the physics community, nanoparticles should be objects having at least one linear dimension ≤100 nm. As well known, the production of such materials poses some problems of risk management and safety control [1], deriving from their easy dispersibility in the environment and in living organisms. In particular, such issues are strengthened by a relatively poor literature data on long-term toxicological effects on cells. Recent studies seem to confirm that the noxious action of a nanostructured material on tissues do not depend only by its chemical composition, but it is more strictly related to its dimension and shape and it grows for decreasing values or the nanoparticle size. A typical example is offered by zinc and titanium oxide, which have been proposed as a nanosized additive for cutting fluids for their beneficial effects as friction modifiers. Despite they have a customary use as a cosmetic in microsized particles with good tolerability, they may act in a very different way when they are confined in nanosized form. For these reasons, the synthesis, storage and handling of such materials requires careful precautions [2], raising their production costs. In this context, the technique of minimum amount lubrication (MQL) seems to be a multipurpose optimization choice [3], as the minimization of a metalworking nanofluid flow rate may help reducing the health risk of the workers. Nevertheless, in many cases, the aforementioned drawbacks are more than offset by a sum of

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positive effects in drilling, grinding, turning and milling [4]. Yu et al. [5] discussed the heat transfer enhancements offered by nanofluids in aqueous and organic dispersions and they pointed out the role of several variables tuning their thermal conductivity. In particular, the particle volume concentration, base fluid material, temperature, nanoparticle size/shape and chemical composition were taken into account. Follow-up studies seem to confirm that the chemical composition has a key role in enhancing the heat transfer, as nanofluids containing dispersions of nanoparticles having high conductivity proved to be good candidates whenever the need of heat dissipation prevails on lubricity in machining.

In the present paper, the properties of nanofluids for metalworking applications are briefly reviewed with respect to the physico-chemical properties of the dispersed solid. The paper is divided as follows. In section 2, the types of nanoparticle are grouped in subsets according to their chemical composition. In Section 3, several production techniques are presented, with particular attention to their impact on the environment. Additionally, a new process for the synthesis of metal nanoparticles as basic ingredient of metalworking nanofluids is proposed and its strengths and weaknesses are analysed and compared with the ones typical of traditional techniques. Finally, in Section 4 we present the conclusions and we trace the direction for future works.

2. Nanofluids recipes and properties.

As a general trend, metalworking fluids in liquid state not containing nanoparticles are classified according to the polarity of the prevailing component [6]. Oil-based cutting fluids are made of non-polar or slightly polar compounds having good characteristics of lubricity, like mineral oils and oils of animal or vegetable origin [7]. The latter are gaining an increasing attention for several aspects related to their typical triglyceride structure, giving a good adhesivity with metal surfaces thus reducing friction and wear. Their strengths consist of a high flash point and viscosity coefficient, together with a low toxicity and a satisfactory biodegradability. These positive aspects balance the weaknesses deriving from their poor thermal and oxidative stability, often triggering corrosion processes [8]. Water-based cutting fluids comprises dispersions of oils in water and true solution of synthetic compounds, with applications preferably addressed to those operations where an intense heat removal is required, as in grinding processes [9].

Nanofluids for machining are usually grouped according to two different classification schemes . The former is based on their thermophysical and tribological properties [10], while the latter gives a major emphasis to the chemical composition of the dispersed nanoparticles [11]. Whatever the analysis, most authors seem to agree in recognizing that the enhancement in heat transfer of nanofluids depends on the composition [12] and on the surface-volume ratio of the suspended nanoparticles [13]. In Fig. 1, the values of thermal conductivities of bulk solids have been reported for comparison. It is interesting to observe that carbon nanotubes and diamond, having a considerable higher values of conductivity with respect to metals and their oxides, give

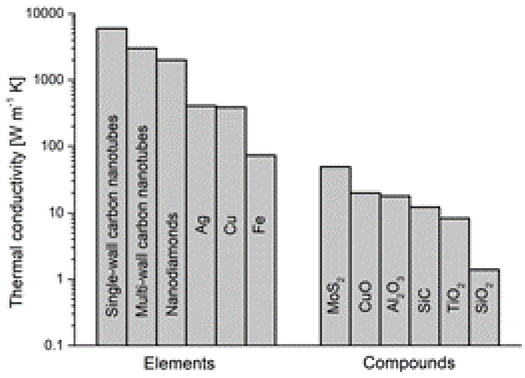

Fig. 1. Thermal conductivity values of some elements and compounds entering the composition of cutting nanofluids

excellent results in relative enhancement of thermal conductivity with respect to the value of the base fluid.

The advantages offered by nanofluids in terms of lubrication performance have been extensively analysed in the tribological literature [14]. In the absence of nanoparticles, the mechanism by which organic friction modifiers act has been identified and discussed in detail [15]. According to Tang and Li [16], a decrease in friction coefficient may be ascribed to three different processes, namely:

- Friction modifiers may be physically or chemically adsorbed on sites of the sliding surfaces with formation of a monolayer preventing a direct contact between moving surfaces;
- Friction modifiers ensure a gap between sliding surfaces by means of a layer made of several superposed molecules with a thickness of several nanometers;
- A layer of sliding liquid may be formed between molecules adhering to the surface of the moving planes. Despite this theory is dated back to 1930 [17], it has been recently revamped by results proving the effectiveness of a surface pretreatment [18].

In the presence of nanoparticles, other mechanisms superpose to the aforementioned ones, according to the scheme proposed by Lee et al. [19]. More recently, other tribological processes have been postulated to account for new phenomena occurring in the presence of particular nanostructures, as in case of nanotube dispersions [20]. In its essence, the process governing the mechanical action of nanoparticles entrapped between two sliding metal surfaces can be described by four different phenomena, namely polishing, mending, filming and rolling effect. The latter is also associated with more complex exfoliating phenomena in the presence of multi-walled nanotubes of carbon or of other nanosized materials.

2.1 Classification of nanofluids with respect to the nanosized phase composition.

The nanosized solid embedded in a nanofluid may have different tribological and thermophysical properties according to its chemical composition, as it may condition both heat and momentum transfer at the interface between sliding metal surfaces [21]. Fig. 2 gives a simple representation of the main subgroups, whose basic difference stems from their belonging to the field of inorganic or organic composition. At present, inorganic nanoparticles seem to dominate the scenario, owing to a large number of investigations concerning solid dispersions in the pure state or in multicomponent molecular structure [22]. The exhaustive review paper by Kulkarni et al. [11] shows that organic nanoparticles, namely carbon nanostructures with different lattice arrangements like carbon dots [23], carbon nanotubes [24], graphene [25], graphite [26] and nanodiamonds [27] have different functionalities according to their dimensionality, but most of them show a remarkable enhancement in thermal conductivity, surface quality of the work piece, tool wear and coefficient of friction with respect to the properties of the pure solvent. The main drawback affecting organic nanoparticle dispersions is the relative instability of the nanofluid, whose solid phase tends to agglomerate and settle for long times even in the presence of surfactants. This phenomenon can be related to a relatively low affinity towards the polar groups of the modifiers [28]. To overcome this obstacle, some researchers are currently investigating hybrid organic/inorganic nanofluids as a challenging trend in this topic. By the way, Azizi et al [29] synthesized hybrid copper/carbon nanodots by chemical reduction of copper salts by means of a disproportionation reaction. The copper/carbon nanodots dispersion remained stable for more than one month, thus solving one of the most crucial problems affecting the nanofluids in real industrial applications. Intriguingly, such results have been obtained in the absence of stabilizers. The thermal conductivity ratio was increased by 25% with respect to the value typical of the pure solvent even for small concentrations of the nanosized phase (0.5%).

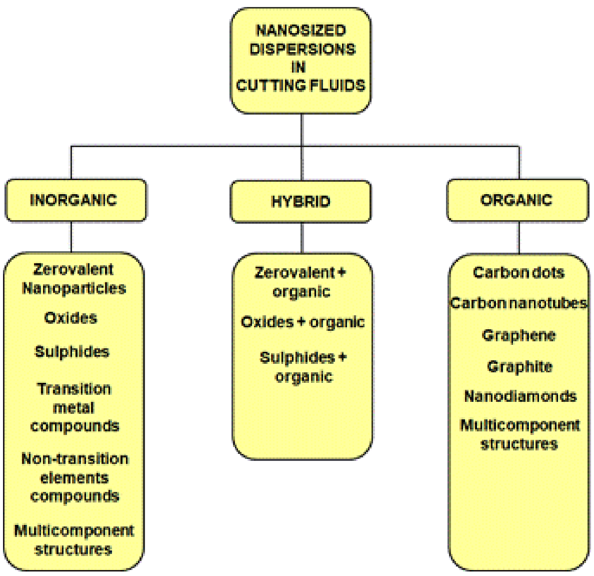

Fig.2. Classification of metalworking nanofluids according to the chemical composition of the dispersed nanophase

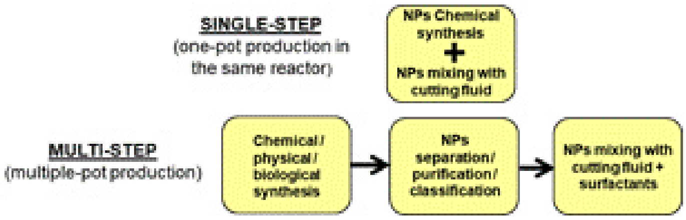

Fig.3. Simplified scheme describing two different classes of processes for the manufacture of cutting nanofluids

3. Synthesis of metalworking nanofluids

3.1 Single- and multiple-step processes

In Fig. 3, two basic schemes for the manufacture of cutting nanofluids are reported.

In a single-step process, the dispersion of the nanophase in the cutting fluid occurs in the same reactor where the relevant nanosized solid phase is synthesized. This technique offers the advantage of requiring a single unit operation, but it is affected by significant drawbacks as it does not allow a satisfactory process control. Even worse, the by-products of the chemical reactions remain dispersed in the metalworking fluid, leading to unwanted residues on the work piece triggering likely corrosion phenomena. These constraints restrict the applicability of a single-step scheme to a very limited number of chemical processes. That is why this approach is usually proposed in the synthesis of metal nanoparticles by wet chemical methods adopting the Capek's reverse micelle scheme [30], requiring specific reducing agent, like the toxic and environmentally unfriendly hydrazine, which do not leave solid residues but only produces gaseous nitrogen according to the reaction [31]:

$$4Me^{n+} + nN_2H_5OH + 4nOH^- \rightarrow 4Me^{(0)} + nN_2 + 5nH_2O \quad (1)$$

The zerovalent metal ($Me^{(0)}$) at the right-hand side of Eq.(1) separates out in form of nanoparticles and it is extracted by the cutting fluid without intermediate treatments.

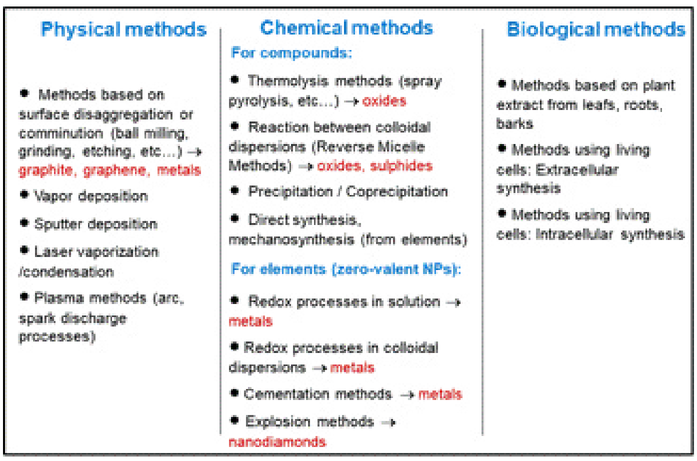

Fig.4. Examples of methods adopted for the synthesis of nanomaterials used in the production of metalworking nanofluids

Multi-step processes allow overcoming such constraints and limitations, at a price of a greater complexity of the manufacturing scheme made of several and often expensive unit operations downstream the chemical reactor. Hovewer, such procedure represents the only option in some specific cases, namely when reaction by- products cannot be avoided [32]. Examples of multi-step processes are given by:

- redox synthesis and bio-synthesis carried out in liquid medium by chemical or bio-chemical eco-friendly reagents, like organic reductants of plant origin for the production of metal nanoparticles [33];
- non-redox reactions in liquid medium of type A+B→C+D, where A is the precursor, B is a reactant, C is the desired nanosized product and D is the unwanted by-product. Such scheme is typically adopted in the synthesis of chalcogenides and other binary compounds separated from the liquid phase by precipitation/centrifugation.
- All other physico-chemical synthesis processes carried out in dry state, like detonation, mechanosynthesis and related processes reported in Fig.4.

In the following paragraph, some non-conventional techniques aiming at improving a multi-step technique for the manufacture of cutting nanofluids will be discussed.

3.2 Some non-conventional techniques for the manufacture of metallic nanoparticle dispersion in cutting fluids.

As reported in Section 2, metal nanoparticles in nanofluids have attracting properties as far as heat removal and wear minimization are concerned. Hence, the current research is focused on finding the most cost-effective, eco-friendly and industrially scalable methods aiming at producing such nanodispersions for metalworking fluids.

Conventional wet-chemical processes for the synthesis of metal (zerovalent) nanoparticles require suitable reducing agents whose strenght has to be tailored with the redox potential of the element undergoing reduction. This amount to saying that strongly electropositive cations need powerful electro-donors (reducing agents) like hydrazine compounds, borohydrides and other chemicals often having noxious properties on the environment and on living organisms.

Following the paradigm of substitution in view of a cleaner production strategy [34], some authors have proposed alternative reductants of vegetal and animal origin which proved to be successful in the synthesis of weak electropositive metals (noble metals) like Au, Ag, Pt, Pd and few others [35]. Regretfully, such reagents have a very limited effectiveness when more electropositive metal nanoparticle are to be produced, like Fe. For this reason, other researchers focused on the synthesis of "difficult" metal nanoparticles using microorganisms as biological nanofactories where the reduction process is carried out in living cells by enzymatic reactions [36].

To the best of our knowledge, despite these biosynthesis processes have a good reaction yield, none of them has been adopted yet in the production of nanoparticles to be used in the production of metalworking fluids. One possible reason can be ascribed to the multiple and complex unit operations following the nanoparticle synthesis in living organisms [37], requiring a mechanical crushing of the biomass, a further separation, purification and mixing with the base oil containing additives and capping agents to ensure a time stability of the cutting nanofluid.

Cementation reactions [38] may represent a sustainable and practical alternative both to a traditional chemical reduction and to the latter procedure based on reagents of natural origin. Such processes are customarily adopted in hydrometallurgy, when a solution containing salts of a metal needs to be purificated eliminating unwanted cations [39]. The corresponding reaction scheme can be written as:

$$nA^{m+}X_m^- + mB^{(0)} \rightarrow mB^{n+}X_n^- + nA^{(0)} \quad (2)$$

where $A^{(0)}$ is the zerovalent element released in form of nanoparticles, whose cation was formerly present as soluble salt in the precursor $A^{m+}X_m^-$. *B(0)* represents a sacrificial metal, namely a metal acting as an electron-donor capable of reducing A^{m+} with formation of the corresponding nanoparticles *A(0)*. Of course, as a result of reaction (2), soluble salts of the sacrificial metal $B^{(0)}$ are formed and they have to be separated from the solid nanosized phase, together with the remaining sacrificial metal, with unit operations only feasible in a multi-step process, as depicted in Fig.5. Additionally, eq.(2) calls for an use of a non-toxic element $B^{(0)}$. As an example, aluminium has been satisfactorily used with good results in the production of bismuth nanoparticles [40], whose positive effect in metalworking nanofluids have been ascertained by Flores-Castañeda et al. [41]. They investigated the tribological properties of a nanobismuth dispersion in light and heavy base oils free of additives.

A four ball test machine allowed to determine the coefficient of friction and the wear scar diameter using the base oil with and withouth suspended nanoparticles. At a Bi-nanoparticle concentration of only 0.31 g/L, 15.1% and 35.1% reduction of wear scar and coefficient of friction with respect to the values corresponding to the light oil without nanoparticles were reported, respectively.

In summary, a comparison between biochemical methods and cementation processes as a basic chemical step for the synthesis of nano-cutting fluids is reported in Table 1 .

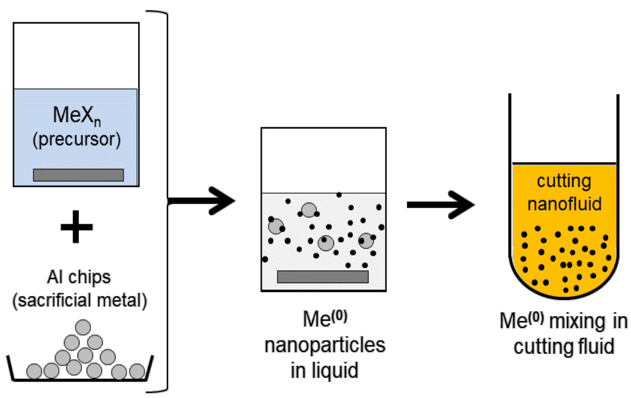

Fig.5. Cementation-based multi-step method for the production of a cutting nanofluid

Table 1. Comparison between three different types of multi-step methods for the synthesis of cutting nanofluids.

Type of multi-step process	Strengths	Weaknesses
Chemical synthesis by plant/ animal extracts	Sustainability Process safety	Low reaction yield Product contamination
Biochemical synthesis by living cells	Sustainability High reaction yield	Poor reaction contol Product contamination
Chemical synthesis by cementation processes	Sustainability High reaction yield High product purity	Kinetic sensitivity Cost of reactants

4. Conclusions

Some aspects concerning the physico-chemical and tribological properties of metalworking nanofluids have been concisely reviewed. In particular, some recent multi-step sustainable methods for the manufacture of such nanofluids have been discussed and compared according to the last trends in nanoparticle synthesis by wet chemical and biochemical processes.

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