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(54) Title: POWDER SUSPENSIONS FOR PLASTIC FORMING AT ROOM TEMPERATURE AND FORMING PROCESSES
FOR SUCH SUSPENSIONS

(57) Abstract: Suspensions of ceramic and/or metal powders according to the invention are characterized in that as liquid phase paraffin oil is used, which is defined as a mixture of aliphatic non-branched hydrocarbons with a chain of 9 to 18 carbon atoms and with solids loading between 35 and 65 vol. %. With the inventive solution the following advantages are achieved: suspensions prepared in accordance with the disclosed procedure may be plastically formed at room temperature and, in addition, the shape imparted to the articles may be retained by cooling or immersing them in water. Moreover, the suspensions of the invention are capable of forming articles with a larger volume. Additionally, suspensions according to the invention enable cellular composites to be obtained by stacking layers of different structures and rolling. The process of preparing the inventive suspensions is not expensive, or technically challenging, or requiring special equipment.



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**Powder Suspensions for Plastic Forming at Room Temperature
and Forming Processes for Such Suspensions**

The object of the invention is to disclose a liquid-phase suspension of ceramic and/or metal powders wherein paraffin oil is used as liquid phase, enabling plastic forming of such suspensions at room temperature, and processes for forming such suspensions which then retain the imparted shape at room temperature.

The technical problem overcome by the invention is plastic forming of suspensions of ceramic and/or metal powders with various processes and subsequent retaining of the desired shape at room temperature. The process of preparing suspensions is very simple and the costs involved are comparable to other methods of forming ceramic or metal powders, while offering new potential for forming ceramic or metal products.

Beside the price, there are two critical factors limiting the practical application of the products of conventional technical ceramics, namely, the capabilities and reliability thereof. The capabilities fundamentally depend on the intrinsic properties of the material, reliability, on the other hand, is mainly affected by flaws imputable to the various stages of fabrication of ceramic articles. One of the critical steps in the fabrication of ceramic articles is the step of forming compacts. One such widely used forming process is dry pressing the powder in a die. The feed powder is generally granulated and comprises between 0.5 and 10 % of organic additives which serve as binders, plasticizers and/or lubricants. The main disadvantage of this process is that it is not capable of

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pressing large compacts, compacts with a relatively high height to base ratio, or intricately shaped compacts. If allowed by the shape of the article, the extrusion method may be used for forming. Forming ceramic compacts by means of extrusion, as opposed to pressing, requires higher amounts of organic substances, which in this case serve as binders and plasticizers. The main disadvantage of the process is that the compacts are limited geometrically, which is why said process is used for forming products presenting a uniform axial cross-section along their length, such as rods, pipes, or supports for catalytic converters in automobile engines.

A further method of forming ceramic compacts known in the art is by injection molding. This technique is commonly used for forming smaller compacts with intricate shapes. For this process an initial suspension of ceramic and/or metal powders of a suitable viscosity as to allow injection into metal molds must be provided. Two processes are known in the art, depending on the pressure applied for injection: a process is called low-pressure injection molding (LPIM) if up to 0.6 mPa of pressure is applied, and high-pressure injection molding (HPIM) if the applied pressure exceeds 0,6 mPa. In low-pressure injection molding paraffin wax is used as the liquid phase, whereas in high-pressure injection molding higher polymer materials are used, such as polyethylene, polypropylene or other. In both cases, compacts are formed by injecting the suspension into a mold with a temperature below the melting point of the liquid phase used to prepare the suspension. Consequently, the suspension solidifies in the model, retaining the shape of the model cavity. Generally, the temperature of the

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suspension ranges from 60 to 80° C for LPIM and from 110 to 160° C for HPIM.

Another known forming technique is by tape casting thin layers. This forming method involves a liquid phase comprising volatile organic liquids which contain binders and plasticizers. The tapes are formed by casting the suspension onto the substrate and heating. When the volatile components of the liquid phase evaporate from the suspension, the solids loading in the layer increases substantially and the suspension loses its fluid characteristics. The residual components of the liquid phase in the layer (binder, plasticizer) enable thus obtained thin layers to be readily handled.

However, none of the techniques discussed above allows suspensions to be plastically formed (clay-like properties) or shape to be retained at room temperature. In the case of pressed and extruded articles, subsequent plastic forming is impossible. LPIM or HPIM suspensions, on the other hand, do exhibit high elasticity, allowing secondary plastic forming of the suspension, but only in a very narrow temperature range, which is situated significantly above room temperature. Thin layers may likewise be plastically formed at high temperatures, which is made possible by the presence of the residual plasticizers and binders.

The object of the invention is to provide suspensions of ceramic and/or metal powders that will allow plastic forming by pressing, extruding, rolling, or manual forming at room temperature, with the possibility to retain the desired shape of the compacts at room temperature, and with a simple, cheap and effective preparation procedure. By repeatedly rolling and stacking layers upon layers of

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various ceramic and/or metal powders, composites with a corrugated layered and cellular structure will be fabricated.

In accordance with the invention the object is fulfilled as set forth in the independent patent claims.

Suspensions of ceramic and/or metal powders with a 35 to 65 vol. % powder content can be formed by extrusion, pressing, rolling, or manual forming at room temperature provided that they exhibit clay-like properties. This requirement is met by employing a liquid phase of a novel formulation, the primary characteristic of the inventive process for preparing suspensions being that paraffin oil, which is fluid at room temperature, is the major component of the liquid phase, and that suspensions with predetermined rheological properties are obtained by adding divers paraffins having a melting point above room temperature in the range of up to 30 vol. % of the liquid phase; the viscoelasticity of the suspension at room temperature may be changed by changing the dosage of added paraffin(s), whereas for retaining the desired shape after forming the compacts from thus prepared suspension the articles must be cooled below the softening temperature of the liquid phase which depends on the composition thereof, or immersed in water, during which preferential adsorption of water on the surface of the ceramic and/or metal particles takes place, resulting in a high increase in the surface elasticity of the suspension and thereby enabling the shape to be retained and the compact to be handled prior to entering the next stage of article fabrication, consisting in the removal of the binder from the compacts.

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The invention shall hereinafter be described with reference to the preferred embodiments thereof and illustrations representing:

Figure 1a: Structure of plastically formed composites with a corrugated structure;

Figure 1b: Structure of plastically formed composites with a cellular structure.

The preparation of suspensions of ceramic and/or metal powders allowing plastic forming by extrusion, rolling, pressing or manual forming, and being capable of retaining the desired shape at room temperature, comprises the following steps:

Prior to preparing the suspension, the optimum quantity of surface agents must be determined for each powder. An example of a surface agent that may be used in this process is stearic acid, comprising a polar head, whereby it is bound to the polar surface of particles, and a non-polar tail allowing the particles to be wetted with a non-polar liquid medium. Other carboxylic acids and silanes are also known in the art that can be used as surfactants. Once the optimal amount of surfactant to be added has been determined, powder, surfactant, and liquid phase must be weighed in the right proportions to allow preparation of the suspension with the desired volumetric ratio of solids loading and with a viscosity that will enable plastic forming. Into the weighed amount of liquid phase the required quantity of surfactant, usually 1 % by weight relative to the solids loading, is added, wherein ceramic and/or metal powder is subsequently dispersed. Dispersion

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may be carried out at room temperature or above by stirring. There is no time limit to the preparation, seeing that once a homogeneous suspension has been obtained, ulterior stirring has no effect on the properties of the suspension. In the case that the suspension is prepared at a higher temperature, it should subsequently be cooled to room temperature. The suspension is then plastically formed at room temperature. Plastic forming may be carried out by pressing, extrusion, rolling, or manual forming. Thus formed articles will preserve their shape if cooled to below the softening temperature of the liquid phase - T_g , which depends on the composition thereof, or immersed in water. The following stage is organic phase removal, taking place in a powder bed at temperatures up to 400° C. Thus obtained compacts are then sintered.

Composites with layered corrugated or cellular structure are fabricated from two or more suspensions, obtained by the above-described process. The final composite structure depends on the rheological properties of the prepared suspensions, which may be controlled by adding the liquid phase with divers paraffins having a melting point above room temperature in the range of up to 30 vol. %, thereby affecting T_g and consequently the rheological properties of the suspensions. First, thin (max. 3 mm thick) layers of single suspensions must be prepared by rolling. Thus obtained layers are then stacked in any order (e. g. AB, ABA, BAB, ABC, ...), whereupon the prepared layered composite is reduced in thickness by an arbitrary amount through rolling. Thus obtained composite is then folded and rolled one more time. The process is

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repeated until a composite with a corrugated layered or cellular structure is obtained.

The invention shall now be further described with reference to the preferred embodiments thereof.

First Embodiment:

A suspension of alumina (Al6, Alcoa, USA) with 60 vol. % of powder in paraffin oil (paraffin oil, Kemika, Croatia) is prepared. Powder dispersion in the liquid medium takes place at 80° C with the aid of a three-roll mill. After preparing the suspension, the same is cooled down to room temperature. From thus obtained suspension, the desired shape of the compact is plastically formed by hand. A plate may be formed by rolling. Thus obtained compacts are then put into water for at least 1 hour, followed by the organic phase removal stage at 200° C for 2 hours, and by sintering at 1600° C for 4 hours.

Second Embodiment:

A suspension of zirconium oxide (TZ-3Y, Tosoh, Japan) with 57 vol. % of powder in paraffin oil (paraffin oil, Kemika, Croatia) containing 5 vol. % of INA 58/62 paraffin (INA, Zagreb, Croatia) is prepared. The procedure for preparing the suspension is analogous to the first embodiment. After forming, the plastically formed article is cooled in a refrigerator at 2° C for 8 hours. After removal of the organic phase the compact is sintered at 1500° C for 2 hours.

Third Embodiment:

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A suspension of alumina (Al6, Alcoa, USA) with 60 vol. % of powder in paraffin oil (paraffin oil, Kemika, Croatia) is prepared. Powder dispersion in the liquid medium takes place at 80° C with the aid of a three-roll mill. After preparing the suspension, the same is cooled down to room temperature. From thus obtained suspension, 1-mm-thick layers are formed by rolling. Eight such layers are stacked together in a pile and rolled to a thickness of 7.8 mm. Subsequently, the organic phase was removed, followed by sintering at 1600° C for 2 hours.

Fourth Embodiment:

A suspension of alumina (Al6, Alcoa, USA) with 60 vol. % of powder in paraffin oil containing 20 vol. % of INA 58/62 paraffin (INA, Zagreb, Croatia) and a suspension of zirconium oxide (TZ-3Y, Tosoh, Japan) with 57 vol. % of powder in paraffin oil containing 5 vol. % of INA 58/62 paraffin (INA, Zagreb, Croatia) are prepared. The two suspensions are prepared separately. Powder dispersion in the liquid medium takes place at 80° C with the aid of a three-roll mill. After preparing the suspension, the same is rolled into 1-mm-thick strata by means of a two-roll rolling device. Thus obtained strata are then piled up in the following order: a stratum of alumina - a stratum of zirconium oxide - a stratum of alumina or zirconium oxide - a stratum of alumina - a stratum of zirconium oxide. Thus obtained composite is then rolled from an initial thickness of 3 mm to a thickness of 1 mm. Thus prepared strata are subsequently stacked two by two and rolled once more from the initial thickness of 2 mm to a final thickness of 1 mm. This procedure is repeated, whereby a transition from a

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layered composite structure to a layered corrugated or cellular structure takes place after a certain number of cycles, as shown in Figs. 1a and 1b. Thus obtained composites are then immersed in water for 1 hour at least, followed by the stage of organic phase removal at 200° C for 2 hours and sintering at 1520° C for 4 hours.

Fifth Embodiment:

The suspensions are prepared according to the procedure of the first embodiment, except that the powders from which the suspensions are prepared are alumina (Al6, Alcoa, USA) and nickel powder ($d_{50} \approx 1 \mu\text{m}$, Ventron, Germany), respectively. Both suspensions contain 60 vol. % of powder. After obtaining the suspensions and the strata, a composite with the following stratum sequence was prepared: Al_2O_3 -Ni- Al_2O_3 . Thus obtained composites are left in water for at least 1 hour to retain their shape.

With the inventive solution the following advantages are achieved: suspensions, prepared by the disclosed procedure may be plastically formed at room temperature and, in addition, the shape imparted to the articles may be retained by cooling or immersing them in water. Furthermore, the suspension according to the invention are capable of forming articles with a larger volume. Additionally, suspensions in accordance with the invention enable cellular composites to be obtained by stacking layers of different structures and rolling. The process of preparing the inventive suspensions is not expensive, or technically challenging, or requiring special equipment.

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Patent Claims

1. Suspensions of ceramic and/or metal powders, characterized in that as liquid phase paraffin oil is used, which is defined as a mixture of aliphatic non-branched hydrocarbons with a chain of 9 to 18 carbon atoms and with solids loading between 35 and 65 vol. %.
2. Process for forming compacts from the suspension of Claim 1, characterized in that forming comprises extruding, pressing, rolling and manual forming, and that the retainment of the shape of the compacts after forming is ensured.
3. Process for forming compacts from the suspension according to Claim 2, characterized in that the shape retainment is ensured by immersing compacts into water or by cooling compacts to a temperature below the softening temperature of the liquid phase.
4. Process for forming compacts from suspensions according to Claims 2 and 3 for the preparation of layered cellular composites and layered composites with a corrugated structure, characterized in that the process comprises stacking and rolling the layers of two or more distinct suspensions of ceramic and/or metal powders repeatedly.

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Figure 1a

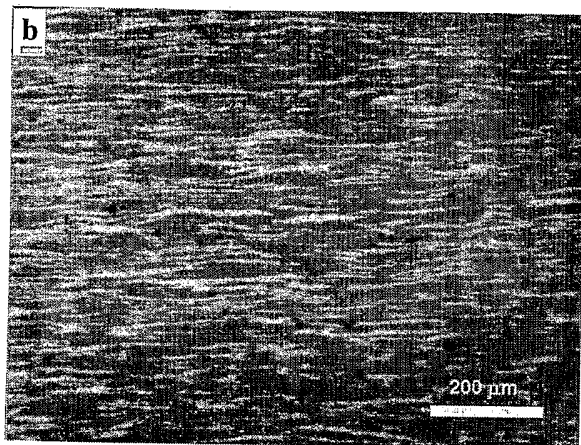


Figure 1b

