Wet processing of mullite/molybdenum composites

M. Diaz, J.F. Bartolomé, J. Requena, J.S. Moya *

Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049-Madrid, Spain

Abstract

The main objective of this work is to show that the difficulties involving substantial differences in particle size and density of commercial molybdenum and mullite powders, when attempts are made to produce homogeneous and/or functionally graded materials, can be overcome by intelligent choice of processing parameters. The flocculant effect of an anionic polyelectrolyte on Mo particles in water and in alcohol media has been shown. On this basis, an appropriate selection of solids loading and surfactant addition allows us to achieve the processing of mullite/molybdenum composites with a controlled metal distribution and microstructure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Mixing; Mullite/molybdenum; Powders; Suspensions

1. Introduction

Ceramic–metal composites have been receiving significant attention in recent years, particularly in the area of processing techniques. New technologies often require that components perform multiple functions or exhibit characteristics not attainable by any single phase material currently available. In this sense, disimilar materials, like metals and ceramics, can be used together to obtain an optimum combination of their properties, but the difficulty in producing these kind of composites has prohibited widespread commercial use. Of the many potential ceramic–metal systems, mullite/molybdenum can be considered adequate to be used in a large number of possible applications, e.g. high temperature structural components, electronics and microelectronics, as thermal barrier coatings or as an electrical conductor/insulator component. This is due to the very similar thermal expansion coefficients of mullite and molybdenum ($\alpha_{Mo} = 5.75 \times 10^{-6}\,^{\circ}C^{-1}$ at 1000°C, $\alpha_{Mull} = 5.13 \times 10^{-6}\,^{\circ}C^{-1}$ at 1000°C), thus, the residual thermal stresses are expected to be very small. On the other hand, Mo is a good electrical and thermal conductor ($\rho_{Mo} = 5.6 \times 10^{-6}\,\Omega cm$, $\kappa_{Mo} = 138\,Wm^{-1}K^{-1}$, respectively) at room temperature whereas mullite is an electrical insulator with a very low thermal conductivity ($\kappa_{Mull} = 2.5\,Wm^{-1}K^{-1}$).

One of the main difficulties encountered in incorporating metal particles into ceramic matrix composites has been the adequate dispersion of the particle within the composite when using traditional dry mixing/milling and pressing routes.[1–4] The poor dispersion of the particles leads heterogeneity in the composites.[5] An approach that has been successful in producing homogeneous microstructures for ceramic–metal composites is by using wet milling in the processing routes.[6–11] The main drawback with the ceramic–metal composites prepared by this route is the presence of hard agglomerates, formed during drying. In a two-component powder system, the two powders will differ on the basis of their respective densities and particle size/shape characteristics. Therefore, they both will have different sedimentation rates, which will lead to time-dependent segregation of a powder mixture with the denser powder gravitating toward the bottom of the sedimentation column. Although generally viewed as a problem in the processing of homogeneous materials, these are naturally segregative phenomena which can be used to create tailored gradients within a component. In this sense, transport processes like sedimentation may be used to produce functionally graded materials (FGMs) at low cost. These materials are characterized by a continuous change in composition, microstructure and properties within the bulk of the material. The gradation methods

* Corresponding author. Tel.: +34-91-334-9000; fax: +34-91-372-0623.

E-mail address: jsmoya@icmm.csic.es (J.S. Moya).

can be divided into dry and wet processes. In the latter case powders are dispersed in a liquid medium,[12] while in the former process powder compacts are usually prepared by stacking dry powders.[13–17] The dry processes are fast, but in general, with these processes only components having a stepwise change in composition through the part can be produced. While such a profile is sometimes preferred, there are applications for which a continuous smoothly varying transition in composition would result in enhanced performance. In wet processes an additional processing step is required for the removal of the liquid phase, but continuous mixing is facilitated and smoother gradients may be produced. Gradient materials have been prepared by sedimentation in a column[18] or in a suitable mould (slip casting method).[19,20] FGM obtained in this way has a continuously varying composition between opposite faces unlike the layers of distinct different compositions found in FGM produced by stacking dry powders or sequential slip casting methods. This latter method, is a widespread technique for ceramic/ceramic gradient materials where slips of different composition are cast one on top of the other.[21–23] However, the production of metal–ceramic FGMs is difficult because the differences in shrinkage between layers can present problems during the drying stage.[24] In a continuous FGM, problems associated with interfaces between the layers of different compositions, common in almost conventional FGM, are eliminated.

The use of pressure slip casting results in a characteristic rapid set, involving movement of the "leather hard" drying front from the top to the mold/casting interface. The level of dewatering required to attain the "leather hard" state is faster than in the case of slip casting without pressure, where the setting rate is relatively slow and ocurring in a matter of hours, rather than minutes as is the case in pressure slip casting. Therefore, this is a desired method, where homogeneous segregation can occur across the entire cross-section of the FGM during casting. Since material characteristics, such as thermal, electrical and mechanical properties, are strongly dependent on microstructure, it is extremely important to control the microstructural transition to improve and optimize a FGM's performance.

Initial processing studies[25] were performed in distilled water, and ethanol absolute alcohol as liquid medium with fine molybdenum powders (1.5 μm). After these early experiments, we decided the more adaptable route would be to use molybdenum powders with larger particle size to form homogeneous and gradient composites. This larger particle size primarily affects the rapid decanting of the heavier molybdenum powder. Using water as the liquid medium and adjusting the liquid–solid ratio ensures a certain degree of coagulation (non segregation) of the powders. The objective of this research is: (a) to optimize the slip formulation to obtain homogeneous or FGM mullite/molybdenum composites, (b) to study the rheological behavior of the suspensions in order to determine the effect of rheological parameters, such as viscosity, (c) to study the relationship between the slurry homogeneity and the microstructure of obtained compacts.

2. Experimental procedure

2.1. Starting materials

The following starting materials have been used: (1) 99.9% pure Mo metal (Goodfellow Cambridge Ltd., UK) with an average particle size of 5 μm and a specific surface area of 0.5 m^2/g; (2) Mullite (Scimarek Ltd., Japan) with an average particle size of 1.5 μm, specific surface area of 7 m^2/g, and with chemical analysis (wt%) Al_2O_3 (71.5), SiO_2 (27.3), Na_2O (0.02), MgO (0.04), CaO (0.07) and Fe_2O_3 (0.05).

2.2. Processing of mullite/Mo composites

The mullite/Mo composition (in vol%) was fixed to 68/32. The liquid medium, solid loading and deflocculant addition employed for the preparation of the different suspensions are summarized in Table 1. All suspensions were homogenized by milling with zirconia balls in polyethylene containers at 150 rpm for 24 h. The sedimentation behavior of water and ethanol-based slurries in glass test tubes was studied at room temperature for times up to 24 h.

The slurries used to obtain the monolithic composites were dried at 90 and 65°C, respectively, for 24 h. The resulting powders were crushed in an agate morter and then passed through a 100 μm sieve. Finally, the powders were pressed isostatically at 138 MPa and the resulting cylindrical rods were sintered in vacuum (5×10^{-3} Pa) at 1650°C for 1 h with a heating and cooling rate of 10°C/min.

The FGM composites were fabricated by the pressure slip casting method. The slip casting was made in cylindrical PMMA tubes placed on plaster of Paris blocks. The pressure has been kept constant at 0.15 MPa for 2 h. Subsequently, the cylindrical green samples were dried at 40°C in air for 48 h. After drying, the specimens were sintered in vacuum (5×10^{-3} Pa) at 1650°C for 1 h.

2.3. Characterization

The particle size distribution of the molybdenum and mullite powders was determined using a particle size analyzer, Coulter LS 130, equipped with a laser source ($\lambda = 750$ nm) and a tungsten lamp to measure particle sizes lower than 0.5 μm.

Table 1
Formulation of the suspensions used in this study

Suspension	Liquid medium	Solids loading (wt%)	Deflocculant addition (wt%)
W501	Distilled water	50	–
W502	Distilled water	50	1
W70	Distilled water	70	1
ET501	Ethanol absolute	50	–
ET502	Ethanol absolute	50	1
ET70	Ethanol absolute	70	1

Viscosity measurements have been performed on mullite/Mo powder suspensions for the mentioned solid loading. The rheological characterization was made using a rheometer Haake RS50 interfaced to a PC. The temperature was maintained constant at 23°C. A double gap cylinder sensor DG41 for the Haake rheometer was used. The general flow behaviour of the suspensions was measured following a cycle in three steps:

1. Up sweep increasing the shear stress (τ) continuously until a maximum value between 7 and 20 Pa, depending on the kind of suspension, for 120 or 60 s.
2. Maintenance of the maximum shear stress reached in step 1.
3. Down sweep decreasing continuously from the maximum value to near 0 for 120 or 60 s.

This procedure provides useful information on thixotropic responses of the suspensions and can reveal whether the structural recovery is appreciable or not.

The bulk densities of green and fired specimens were measured by the Archimedes method using mercury as the immersion medium.

The microstructures of fired specimens were studied on diamond polished surfaces down to 1 µm by reflected light optical microscopy (Leica, DMR model).

The constitutional phases of the mixed powders and the composites were determined by X-ray diffraction using Cu K radiation.

3. Results and discussion

The results obtained from the rheological and sedimentation studies of the suspensions as well as the microstructural aspects of the final composites are summarized in Table 2. The results indicate that a total segregation of mullite and Mo powders leads to final sintered composites with heterogeneous microstructures. Only the water-based suspension with highest solid loading (W70) is adequate to obtain composites after sintering without heterogeneities. On the other hand, the ethanol-based slurry without defloculant (ET501) is appropriated for FGM fabrication.

The relative densities of green and sintered monolithic compacts were found to be ∼56 and >98 th%, respectively.

Fig. 1A shows the flow curve of the W70 suspension. This slurry has a clear pseudoplastic behaviour due to the formation of networks inside the slip by interaction between Mo and mullite particles which avoid the segregation of them (Fig. 1B) and give rise to final sintered composites with microstructures free of mullite or Mo agglomerates, as Fig. 1C shows.

In contrast, all suspensions prepared using ethanol with defloculant addition, possess a rheological behavior close to Newtonian flow and a clear thixotropic effect. In Fig. 2A the flow curve corresponding to ET70 slurry is shown. In this case, no networks inside the slip are formed, even if the solid loading is increased up 70 %. Therefore, the segregation of the powders cannot be avoided (Fig. 2B). In Fig. 2C, the microstructure of the ET70 fired specimen are shown. The presence of large mullite agglomerates can be clearly observed. These are probably formed from the fraction of fine mullite particles which do not sediment as quickly as the fraction of larger mullite and molybdenum particles during the time spent in drying the ball-milled slurry.

Fig. 3A shows the flow curve of the ethanol-based suspension without deflocculant addition (ET501). As can be observed the rheological behavior is basically Newtonian flow with a clear thixotropy. The Newtonian flow behavior and the low viscosity indicate the absence of significant interparticle interactions between mullite and molybdenum particles and that they settle at different

Table 2
Summary of the experimental results

Suspension	Rheological behaviour	Sedimentation	Microstructure
W501	Slightly pseudoplastic thixotropic	No segregation of powders	Mullite and Mo agglomerates (⩽50 µm)
W502	Slightly pseudoplastic thixotropic	Segregation of powders	Large mullite agglomerates (⩽100 µm)
W70	Pseudoplastic slightly thixotropic	No segregation of powders	Homogeneous
ET501	Newtonian thixotropic	Gradual segregation of powders	FGM without heterogeneities
ET502	Newtonian thixotropic	Segregation of powders	Large mullite agglomerates
ET70	Newtonian thixotropic	Segregation of powders	Large mullite agglomerates

velocities as dictate by their density (10.2 g/cm^3 for Mo and 3.16 g/cm^3) for mullite and size. In this particular case, the suspension showed a gradual segregation (Fig. 3B). No heterogeneities are observed in the microstructure of the fired specimen which presents a continuous gradient in Mo content from top to bottom, as can be seen in the Fig. 3C. The cross-section of the cylindrical compact and a plot of fraction of Mo versus length fraction of specimen, as well as reflected light optical micrographs at different distances from the top are shown.

The most striking result is the significant differences in the sedimentation behaviour of the water-based suspensions W501 and W502. The former flocculates giving rise to a homogeneous sediment similar to the one shown in Fig. 1B. In the case of W502 (with a deflocculant addition of 1 wt%) a complete segregation of the mullite and molybdenum powders (as in Fig. 2B) takes place.

To clarify the sedimentation behaviour of the W501 and W502 suspensions the sedimentation study of mullite and molybdenum powders was carry out separately. In order to obtain reliable results the water-mullite and water-molybdenum ratios as well as the deflocculant addition were adjusted to be the same as in the case of the water-based suspensions with a solid loading of 50 wt%. The mullite particles can be stabilized in water with 1 wt% of deflocculant addition, but flocculate in the absence of this. However, the deflocculant addition of 1 wt% drastically increases the sedimentation velocity of molybdenum particles in comparison with the
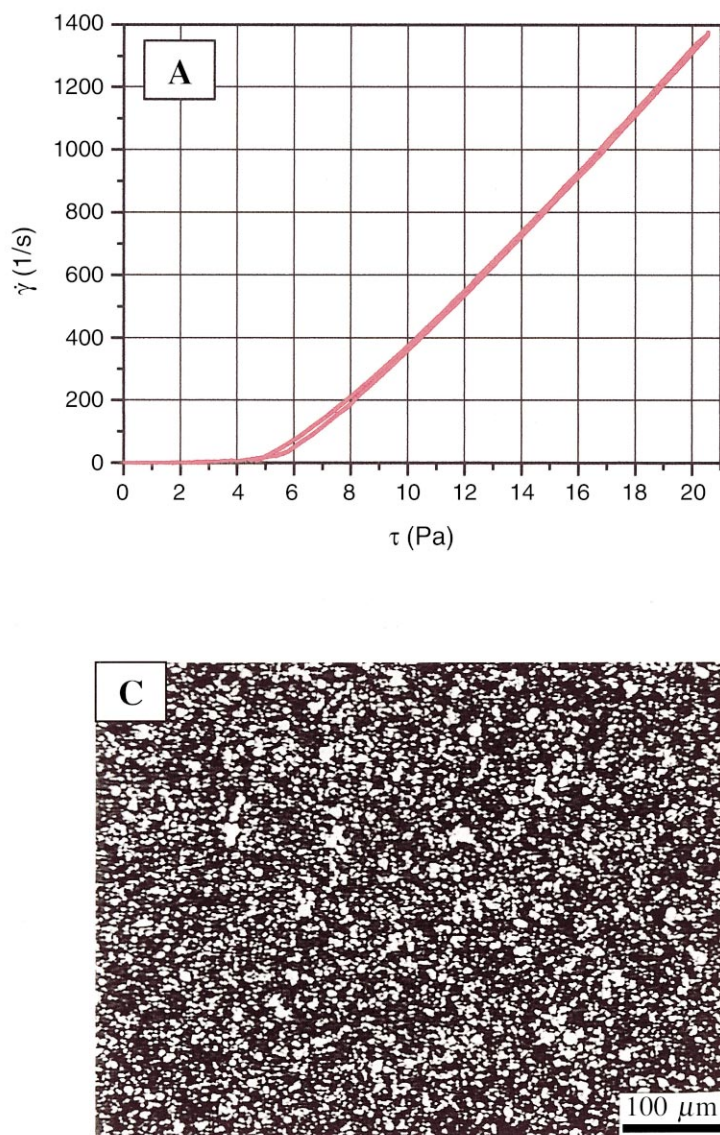

Fig. 1. (A) Flow curve of the W70 suspension showing pseudoplastic behaviour. (B) Sedimentation behaviour of W70 slurries in a glass tube where the resulting sediment is homogeneous. (C) Reflected light optical micrograph of W70 sintered composite showing a homogeneous microstructure.
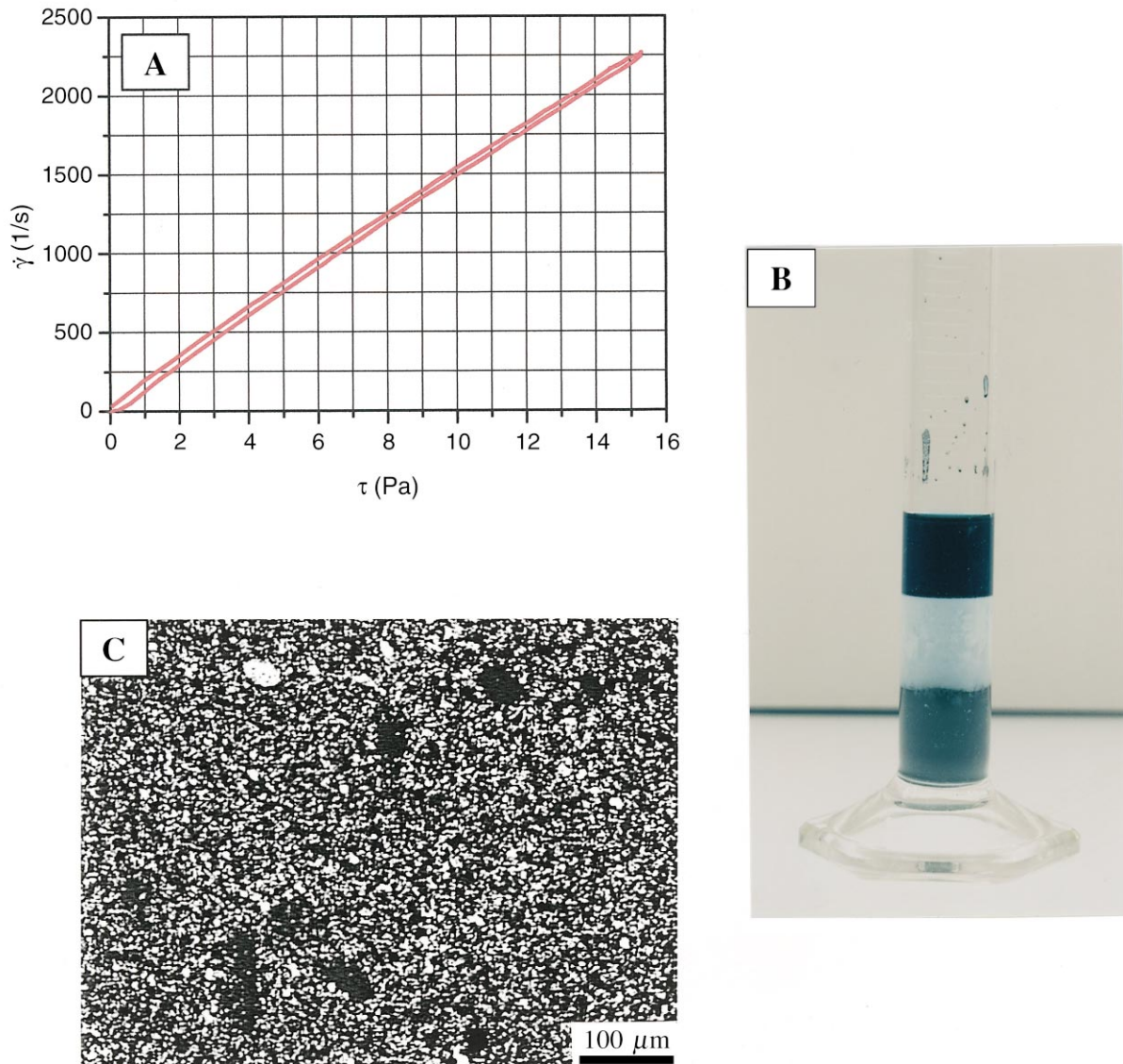
Fig. 2. (A) Flow curve of the ET70 suspension showing Newtonian behaviour. (B) Sedimentation behaviour of ET70 slurries in a glass tube. The segregation of the powders is evident. (C) Reflected light optical micrograph of ET70 fired composite where the presence of large mullite agglomerates can be clearly observed.

molybdenum suspension free of deflocculant (Fig. 4). This is a consequence of the formation of large particle agglomerates which settle very fast. The addition of 1 wt% of the deflocculant used, which consists of a basic solution of an ammonium polyelectrolyte (pH≈9), increases the pH of the molybdenum suspension (pH≈3) approximately one unit. In order to determine if changes in pH cause agglomeration and flocculation of molybdenum particles, some drops of concentrated solutions of ammonium hydroxide and sodium hydroxide were added to molybdenum suspensions. In both cases, flocculation and fast sedimentation of molybdenum particles were observed.

The same experiments were carried out on the ethanol absolute-based suspensions and similar results were found in the case of Mo slurries, i.e. the presence of deflocculant or bases accelerates the sedimentation velocity (Fig. 4) of molybdenum particles as in the case of water-based suspensions. In contrast to the latter, the mullite particles appear to be nearly stable in ethanol absolute having a very low sedimentation velocity which remains unchanged after addition of 1 wt% of the anionic deflocculant.

These results indicate that, contrary to mullite particles, the anionic surfactant is not absorbed on the surface of the molybdenum particles as DSC measurement confirms (data not shown). The partial stabilization of Mo particles in water may be explained considering the possible absorption of H^+ ions on particle surface. Then the addition of an anionic polyelectrolyte or any
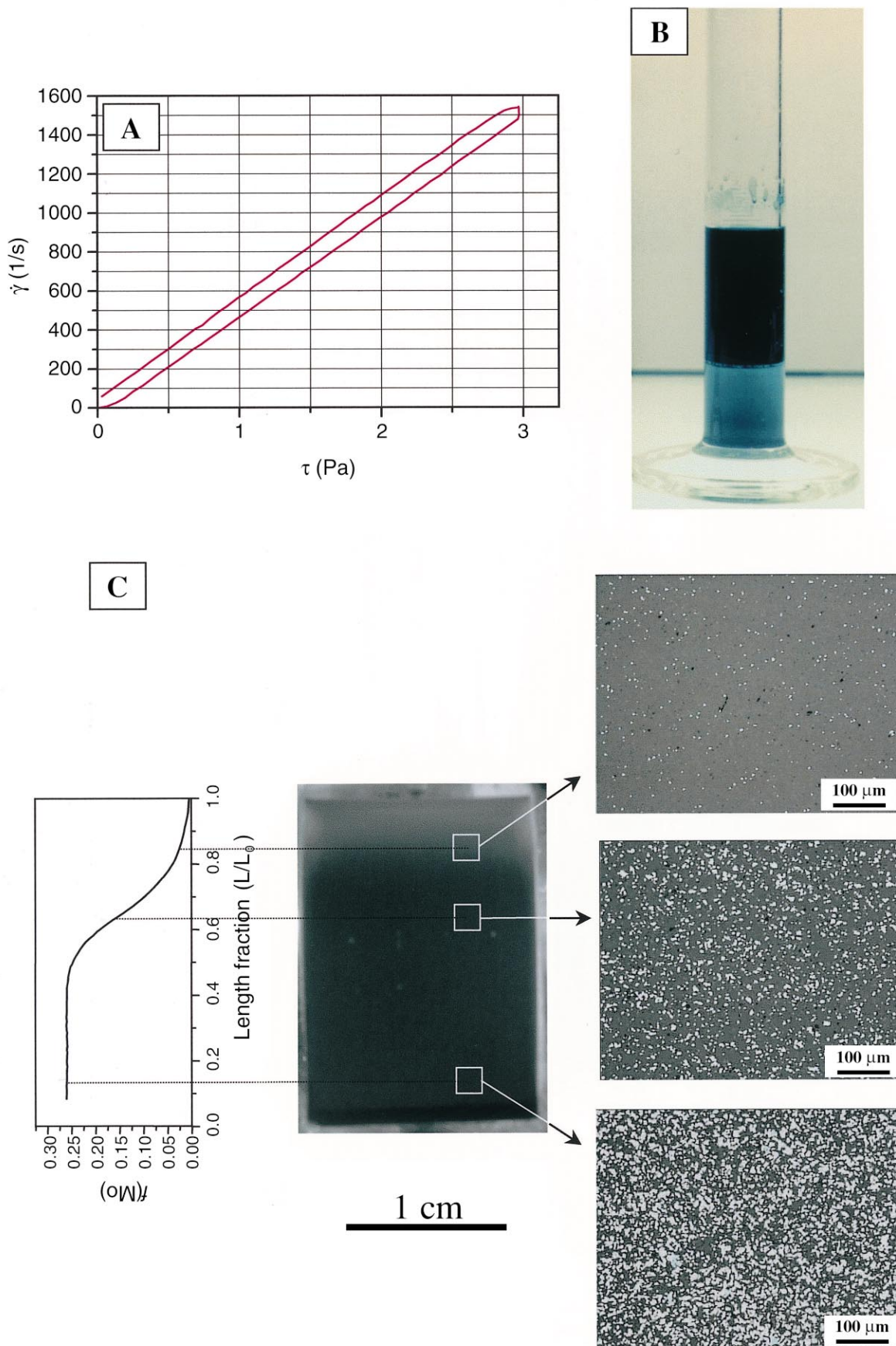
Fig. 3. (A) Flow curve of the ET501 suspension showing Newtonian behaviour. (B) Sedimentation behaviour of ET501 slurries in a glass tube showing a gradual segregation. (C) The cross-section of the sintered cylindrical FGM compact as well as reflected light optical micrographs at different distance from the top are shown, together with a plot of the fraction of Mo vs the length fraction of the FGM specimen.
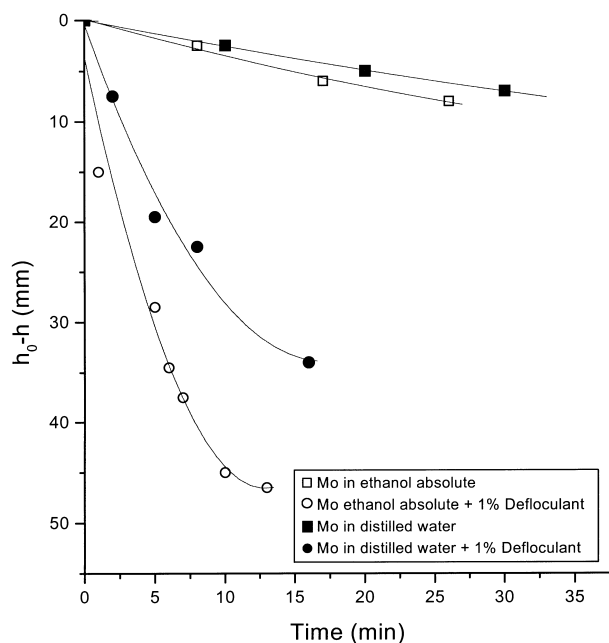
Fig. 4. Height of Mo particles–surnactant liquid interface vs time in distilled water and ethanol absolute slurries with and without deflocculant addition (h_0 = initial height).

base i.e. NaOH, NH_4OH, shifts the pH to higher values inducing a depletion of the positive charges on the molybdenum particles surface and its subsequent flocculation.

In the case of ethanol absolute the molybdenum particles surface can absorbs the H^+ resulting from the alcohol partial dissociation: $CH_3-CH_2OH \rightarrow CH_3-CH_2O^- + H^+$

In this particular case, the disposibility of H^+ is sensibly lower than in water media. In this regard the surfactant addition produces a higher flocculation effect in alcohol than in water as observed by comparing the particle setting rate in water 4.8×10^{-5} m s^{-1} and alcohol 5.7×10^{-5} m s^{-1}.

It is worthy to mention that the molybdenum particle is not stable in water in the studied pH range $(3–4)$[26] producing soluble Mo^{n+} species, i.e. Molybdenum Blues (see the blue color of surnactant liquid in Figs. 1B, 2B and 3B), which also may affect the particles stability.

To avoid the formation of agglomerates, an anionic deflocculant is needed in order to stabilize the mullite particles. The preparation of mullite/Mo composites from water-based suspensions involves the optimization of the solid concentration to obtain slips showing a clear pseudoplastic or nearly plastic rheological behaviour (Fig. 1A), which prevents the segregation of the powders during the drying step. The inter-particle forces depend on the distance between particles, and this distance is dependent on the number of particles per unit volume. A high solid concentration minimizes the possibility of

segregation of the different constituents of the suspension by formation of networks inside the slip which sustain both mullite and molybdenum particles due to the increase of the interactions between them. In the case of the ethanol-based suspensions the segregation of the powders cannot be avoided by increasing the solid concentration of the suspensions due to the absence of any networks inside the slip by interaction between particles, as the Newtonian behaviour of ET502 and ET70 suspensions indicates.

In the case of ET501 the absence of deflocculant allows the sedimentation of mullite and non agglomerate molybdenum particles without strong interactions between them following the trend dictate by the Stoke's law. The resulting composite shows a continuous gradient in Mo content from one side to another.

The mechanism of molybdenum flocculation cannot be completely explained in terms of DVLO theory because Mo is not thermodynamically stable in water suffering an oxidation process that is changing continuously the surface of molybdenum particles and is strongly dependent on pH. Therefore, in order to reach a complete understanding of the charge distribution on the surface of molybdenum particles further investigation is needed.

4. Conclusions

The following conclusions can be drawn:

(1) Through a careful control of particle processing conditions, we have shown that either homogeneous or functionally gradient mullite/molybdenum materials close to theoretical density can be obtained.
(2) The flocculant effect of an anionic polyelectrolite on Mo particles in water and alcohol media by depletion of the surface charges has been shown.
(3) Significant improvement in the homogeneity of the ceramic–metal monolithic composite was observed due to the optimization of: (a) the deflocculant content (1 wt%), (b) solids loading (70 wt%) and (c) appropriate selection of suspension media.
(4) A continuous mullite/Mo FGM was obtained using ethanol as a liquid media free of deflocculant and a solid loading of 50 wt%.

References

1. Sun, X. and Yeomans, J. A., Optimization of a Ductile-particle-toughened ceramic. *J. Am. Ceram. Soc.*, 1996, **79**, 2705–2717.
2. Khan, A. A. and Labbe, J. C., Aluminium nitride–molybdenum ceramic matrix composites: influence of molybdenum concentration on the mechanical properties. *J. Mater. Sci.*, 1997, **32**, 3829–3833.
3. Khan, A. A. and Labbe, J. C., Aluminium nitride–molybdenum ceramic matrix composites: characterization of ceramic–metal interface. *J. Eur. Ceram. Soc.*, 1996, **16**, 739–744.
4. Kotec, V., Metal ceramic Al_2O_3–Tungsten composites. *Euro-Ceramics II*, 1991, **2**, 1685–1690.
5. Trusty, P. A. and Yeomans, J. A., Crack-particle interactions in alumina–iron composites. *Ceram. Eng. Sci. Proc.*, 1993, **11**, 908–913.
6. Nawa, M., Sekino, T. and Niihara, K., Fabrication and mechanical behaviour of Al_2O_3/Mo nanocomposites. *J. Mater. Sci.*, 1994, **29**, 3185–3192.
7. Tuan, W. H. and Brook, R. J., Processing of alumina/nickel composites. *J. Eur. Ceram. Soc.*, 1992, **10**, 95–100.
8. Waku, Y., Suzuki, M., Oda, Y. and Kohtoku, Y., Improvement of fracture toughness of Al_2O_3 composites by micro-dispersion flaky refractory metals Mo, Ta and Nb. *J. Ceram. Soc. Jap.*, 1995, **103**, 702–708.
9. Nawa, M., Yamazaki, K., Sekino, T. and Niihara, K., Micro-structure and mechanical properties of interpenetrated ZrO_2–Mo nanocomposites. *Proc. 4th Japan International SAMPE*, 1995, 357–362.
10. Tuan, W. H., Wu, H. H. and Yang, T. J., The preparation of Al_2O_3/Ni composites by a powder coating technique. *J. Mater. Sci.*, 1995, **30**, 855–859.
11. Tuan, W. H. and Chen, W. R., Mechanical properties of alumina–zirconia–silver composites. *J. Am. Ceram. Soc.*, 1995, **78**, 465–469.
12. Neubrand, A. and Rödel, J., Gradient materials: an overview of a novel concept. *Z. Metallkd*, 1997, **88**, 358–371.
13. Rabin, B. H. and Heaps, R. J., Powder processing of Ni–Al_2O_3 FGM. *Ceram. Trans.*, 1993, **34**, 176–180.
14. Kawakasi, A. and Watanabe, R., Fabrication of disk-shaped functionally gradient materials by hot pressing and their thermo-mechanical performance. *Ceram. Trans.*, 1993, **34**, 160–164.
15. Zhu, J. C., Yin, Z. D. and Lai, Z. H., Fabrication and micro-structure of ZrO_2–Ni functionally gradient material by powder metallurgy. *J. Mater. Sci.*, 1996, **31**, 5829–5834.
16. Kawakasi, A., Tanaka, M. and Watanabe, R., Powder metallurgical fabrication of SiC–AlN/Mo functionally graded material. *Ceram. Trans.*, 1993, **34**, 189–196.
17. Hülsmann, S. and Bunk, W., Functionally graded metal–ceramic materials by powder processing. *Ceram. Trans.*, 1993, **34**, 197–202.
18. Miller, D. P. and Lannutti, J. J., Fabrication and properties of functionally graded NiAl/Al_2O_3 composites. *J. Mater. Res.*, 1993, **8**, 2004–2013.
19. Chu, J., Ishibashi, H., Hayashi, K., Takebe, H. and Morinaga, K., Slip casting of continuous functionally gradient material. *J. Ceram. Soc. Jap.*, 1993, **101**(7), 841–844.
20. Masuda, H., Hayashi, K. and Morinaga K., Fabrication of continuous functionally graded materials (FGMs) by slip casting method. *Ceramic Materials and Components for Engines*, 1997, 341–346.
21. Moya, J. S., Layered ceramics. *Adv. Mater.*, 1995, **7**, 185–189.
22. Requena, J., Moya, J. S. and Pena, P., Al_2TiO_5–Al_2O_3 functionally gradient materials obtained by sequential slip casting. *Ceram. Trans.*, 1993, **34**, 203–210.
23. Bartolomé, J. F., Moya, J. S., Requena, J., Llorca, J. and Anglada, M., Fatigue crack growth behavior in mullite/alumina functionally graded ceramics. *J. Am. Ceram. Soc.*, 1998, **81**, 1502–1508.
24. Takebe, H., Teshima, T., Nakashima, M. and Morinaga, K., Powder processing technique for development of zirconia–nickel functionally gradient materials. *J. Ceram. Soc. Jap.*, 1992, **100**, 396–400.
25. Tomsia, A. P., Saiz, E., Ishibashi, H., Diaz, M., Requena, J. and Moya, J. S., Powder processing of mullite/MO functionally graded materials. *J. Eur. Ceram.*, 1999, **18**, 1365–1371.
26. Burriel Martí, F., Lucena Conde, F., Arribas Jimeno, S. and Hernández Mendez, J. *Química Analítica Cualitativa*, 15th edn., Paraninfo, Madrid, 1994, p. 544.