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STABILIZATION OF HEAVY METAL PARTICLES IN AL_2O_3-W SUSPENSIONS

Ceramic – metal composites are widely used materials in a whole world. There were invented many fabrication methods for those kind of materials, but still exists some problems which need to be fixed. Stability of high density metal particles (e.g. W, Mo, Nb) in ceramic-metal composite suspensions is one of crucial issues to be solved in order to obtain homogenous composite material with desired properties such as high fracture toughness, mechanical strength, hardness, wear resistance.

In this paper, results of two different methods of stabilizing W particles in Al_2O_3 – W – H_2O system were compared. The zeta potential by laser doppler electrophoresis, stability by static multiple light scattering and rheological behavior of prepared suspensions were analyzed. As a result application of hetero-flocculation effect was consider as a good way to obtain homogeneous dispersion of metal particles with a high density.

Keywords: ceramic matrix composites, alumina, tungsten, hetero-flocculation

1. Introduction

Ceramic materials reinforced with metal particles have many advantages compared to pure ceramics. They have improved mechanical properties such as fracture toughness, frictional wear resistance, thermal fatigue resistance, hardness and others [1]. Improved effect depends on used materials, size of ceramic and metal grains, homogeneity of the composite as well as bonding between metal and ceramic grains. Very important are also properties of interphases on interface between metal and ceramic grains [2,3]. There are numerous methods used for fabrication of this kind of materials. The most popular is simple mixing the ceramic and metal powder, followed by drying, pressing and sintering [4]. Researchers very often use hot isostatic pressing [5] or spark plasma sintering [6,7] which methods ensure high density and minimal grain growth after sintering in obtained material. Other common methods of ceramic-metal composite fabrication are slip casting [8], gel casting [9,10] or infiltration of porous ceramic perform with molten metal [11]. However, in order to obtain homogenously dispersed metal phase in ceramic matrix with submicron/nanosized grains it is necessary to apply more complicated route. Interesting way was proposed by Rodrigez-Suarez et al. [12], who synthesized tungsten nanoparticles (with a diameter around 20 nm) on surface of alumina or spinel powder. Then the composite powder was pressed and sintered.

Analyzing the surface properties and particle-particle interaction plays crucial role in proper preparation of ceramic-metal composites. Particularly when metallic powder is characterized by high density. Very often different kind of dispersing agents are used. Other way to stabilize metallic particles is, for example, playing with distance between ceramic grains in the suspension. It is possible to use this method to obtain functionally graded or homogeneous materials [8].

In the present work authors focus on the interaction between Al_2O_3 and W powders in water based systems. Composite suspensions Al_2O_3-W were stabilized by small particle-particle distance, which blocked sedimentation of heavy metal particles and with use of hetero-flocculation effect between ceramic and metal particles.

2. Materials and methods

Al_2O_3-W composites were obtained by slip casting method. The used materials in powder form were: α-Al_2O_3 – TM-DAR (Tamei Chemical Corporation Co. Ltd., Japan) with purity of 99.99% and density of 3.96 g/cm^3 and tungsten powder monocrystalline (Sigma Aldrich Co.) with purity of 99.9% and theoretical density of 19.3 g/cm^3. As organic additives there were used di-ammonium hydrogen citrate (DAC) delivered by POCH SA, with density of 1.48 g/cm^3 and poly(ethyleneimine) (PEI) from Sigma Aldrich Co. with average molecular weight 2000 and density of 1.08 g/cm. Ultra-pure Mili-Q water with conductivity below 9 mS was used a solvent. The pH of colloidal dispersions was controlled by addition of 0.05 M solutions of NaOH and HCl.

Zeta potential measurements as a function of pH were done by laser doppler electrophoresis LDE and grain size distribution was measured by dynamic light scattering DLS (Zetasizer Nano ZS, Malvern Instruments Ltd). Measurements were performed for 0.01 vol. % colloidal dispersions in 10 mM NaCl solution. Colloidal mixture Al_2O_3 and W was prepared in volume ratio of 88% to 12% respectively. This ratio results from calculation of Al_2O_3 volume which is necessary to surround

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completely W particles in case when hetero-flocculation effect occurs.

Stability analysis of prepared suspensions was carried out by static multiple light scattering (MLS) provided by Turbiscan^{TM} LAB (Formulaction SA). The principle of MLS is to analyze changes occurred in the suspension with passing time. Analyzed substance is placed in a glass bottle and near infrared light source (880 nm) goes to the sample (Fig. 1.). There are two detectors – for transmitted (T - for low concentrations) and backscattered (BS - for higher concentrations) light originate from the sample. For each time point and sample height (duration of experiment and time sequence is defined by operator) full profile of T and BS is registered. For stable sample, no changes in T and BS light profile with passing time occur. In order to obtain destabilization kinetics for each sample, Turbiscan Stability Index (TSI) is calculated according to equation (1). For each time point of measure (*i*) changes in the intensity of light on each sample height (*H*) are calculated. The lower TSI value, the more stable is the sample.

$$TSI = \sum_i \frac{\sum_h |scan_i - scan_{i-1}|}{H} \qquad (1)$$

Investigated suspensions for MSL were prepared with two concentrations: 0.01 vol. % for pure W and Al_2O_3 colloidal dispersions and 5 vol. % for mixture of W and Al_2O_3 (W - 0.1% vol. to 4.9% vol. Al_2O_3) with different dispersing solutions.

Slip casted samples were prepared from two different suspensions with compositions shown in Table 1. All components were mixed in planetary ball mill during 1h with a speed of 300 RPM. After mixing, composite suspensions were degassed in planetary mixer THINKY ARE-250 (THINKY Corporation, Japan) and slip casted into plastic mold with porous bottom. The rheological measurements were conducted on Brookfield DV2TLV viscometer.

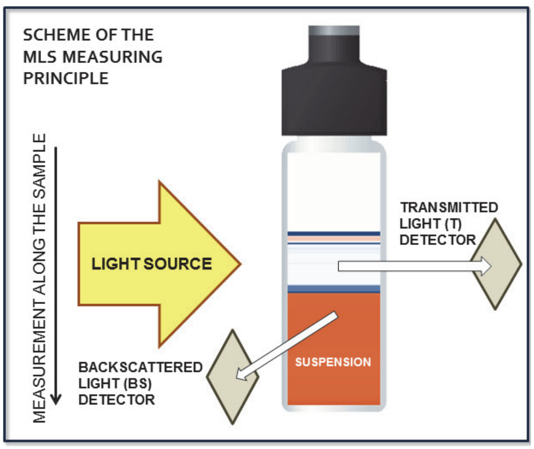

Fig. 1 Scheme of MLS measuring principle

TABLE 1

The composition of prepared ceramic suspensions with the use of Al_2O_3, W and DAC/DAC+PEI as dispersing agents. Concentration of solid phase is 50 vol%, pH 7-8.

Mass	DAC	DAC+PEI
Concentration of Al_2O_3 [vol%]	49.0	49.0
Concentration of Al_2O_3 [wt.%]	73.3	73.3
Concentration of W [vol%]	1.0	1.0
Concentration of W [wt.%]	7.5	7.5
Dispersant DAC content [vol.% wrt Al_2O_3 powder]	0.80	0.80
Dispersant PEI content [vol.% wrt W powder]	/	2.2

For analysis of the arrangement of metal particles in green body samples the fracture surface were observed by scanning electron microscopy (Zeiss Ultra Plus, Germany) and optical microscope (Nikon, Japan).

3. Results and discussion

3.1. Colloidal dispersions analysis

Pure tungsten powder has negative value of zeta potential below -50 mV in all range of investigated pH. At the same time average size of particles/agglomerates (Z-Ave) value is around 500 nm, which is in good correlation with powder specification (0.6 – 1 μm) supported by the producer. Alumina powder has positive charge in pH below 9 and negative charge in pH higher than 9. Designated isoelectric point (IEP) is in pH 9.6 (Fig. 2). Alumina powder has average agglomerate size around 250 nm in pH lower than 6 and higher than 11. In pH close to IEP powder tends to agglomerate average size of agglomerates is around 10 times bigger from original (~3 μm).

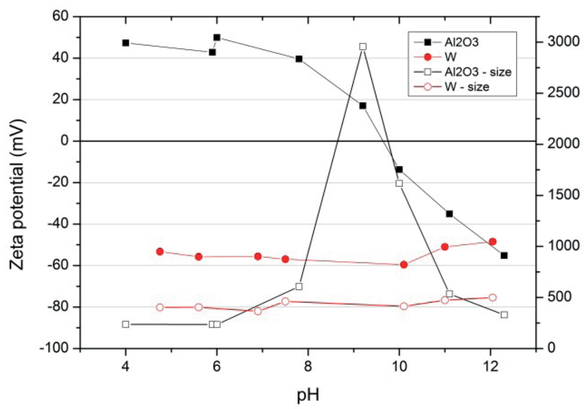

Fig. 2 Zeta-potential and Average Agglomerates Size of pure Al_2O_3 and W powders as a function of pH

Despite high zeta potential value for W particles, its sedimentation rate is much higher than Al_2O_3 particles due to almost 5 times higher density of the metal. Fig. 3 presents the evolution of the T and BS light through cell within 2 hours for diluted (0.01 vol. %) suspensions of Al_2O_3 and W.

For Al_2O_3, on the top of the measured cell there are visible some minor changes (zone Top A). Backscattered light decreases and transmitted light increases with time which indicates change in concentration of particles and slow sedimentation of particles. At the same time, in the middle of the sample the transmitted light slightly increases with time, which suggests slow process of particles agglomeration. For W suspension, the zone where sedimentation occurs is much larger compare to previous suspension (zone Top B in Fig. 3.). To compare the rate of changes in stability with time the TSI index (1) for both suspensions was analyzed. Calculated TSI after 2 hours of measurement was equal to 2,9 for Al_2O_3 and 14,7 for W (Fig. 2c). Considering the differences in densities and measured TSI values of the metal and ceramic, it can be concluded that the main factor that causes lower stability of W is its higher density.

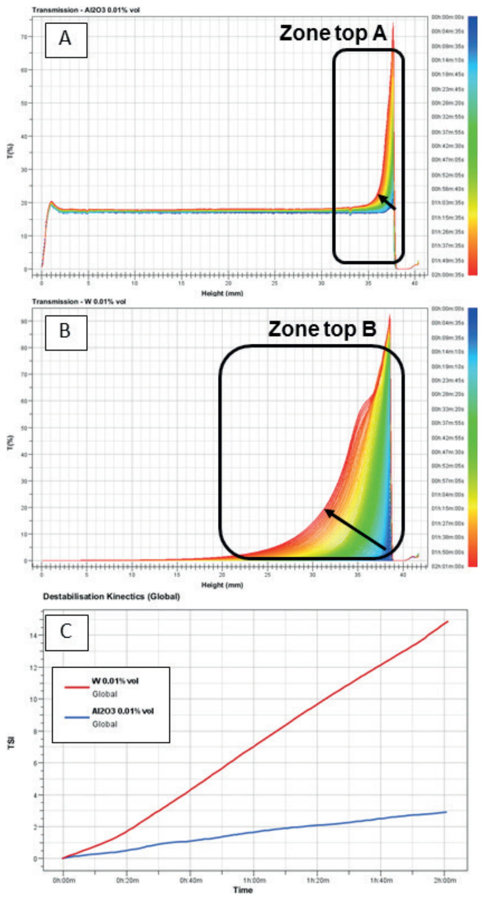

Fig. 3 Transmitted light registered along the sample with time during 2 h for Al_2O_3 (A) and W (B) 0.01 vol. % colloidal suspensions and corresponding change in TSI index with time. Arrows on graph A and B indicate the direction of changes in the samples

3.2. Stabilization of W particles through interparticle distance between Al_2O_3

Despite high value zeta potential for both W and Al_2O_3 which should theoretically ensure stability of the system, it was necessary to use anionic dispersing agent to obtain high loading of solid phase in suspension for slip casting. One of the common dispersing agents for Al_2O_3 material is dibasic ammonium citrate (DAC). In Fig. 4 there are shown zeta potentials in function of pH for Al_2O_3 and W colloidal suspensions with addition of DAC. Designated IEP for Al_2O_3 stabilized with DAC is in pH 3.6. For pH higher than 3.6 both metal and ceramic particles have negative zeta potential but for W values are lower. Black curve (Fig. 4) shows zeta potential of mixture Al_2O_3 and W. Value of the measured potential is an average between values of potentials for Al_2O_3 and W.

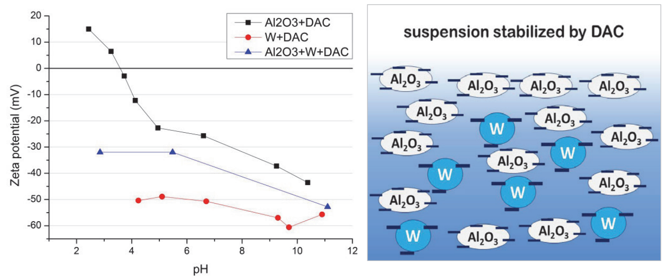

Fig. 4 Values of zeta potential for 0.01 vol. % suspensions Al_2O_3, W and their mixture, stabilized with addition of DAC. On the right scheme of particle distribution in suspension stabilised with DAC at pH 7-8

Results shown in Fig. 5 explain behavior of suspension prepared without hetero-flocculation of W particles. It is possible to distinguish two processes occurring inside the sample. The descent of W particles results in increasing the BS signal and inform about corresponding concentration of particles change (Zone A). Phase separation between Al_2O_3 and W causes decreasing BS signal and corresponds to reduction of particles concentration (Zone B).

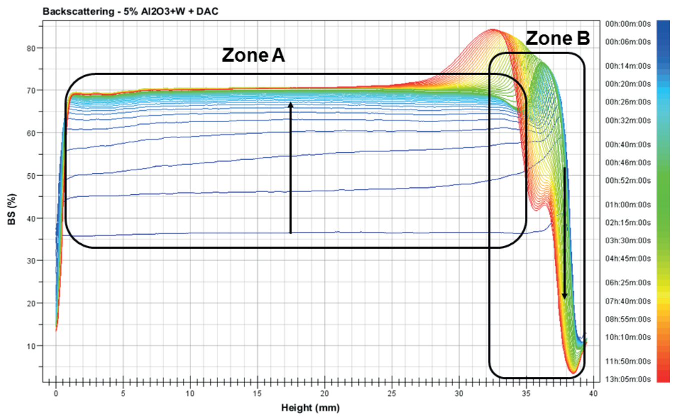

Fig. 5 Backscattered light (BS) registered along the sample with time during 13 h for 5 vol. % mixture of Al_2O_3 and W with addition of DAC as a dispersing agent

3.3. Stabilization of W particles through hetero-flocculation effect

In order to improve stability and homogeneity of W particles dispersion in the investigated suspension, it was necessary to modify surface potential of W. Addition of 2.2 vol. % PEI to colloidal dispersion of W resulted in change its zeta potential to positive at pH values higher than 5. According to paper Andersson and Bergström [13] PEI adsorbs on WO_3 surface and changes zeta potential from negative to positive. In case of W powder immersed in water certainly there is tiny layer of WO_3 on surface of powder. In this case at pH > 6 Al_2O_3 is stabilized with DAC and has negative potential and W is stabilized with PEI and has positive potential (Fig. 6). Due to electrostatic forces between countercharged particles hetero-flocculation effect occurs.

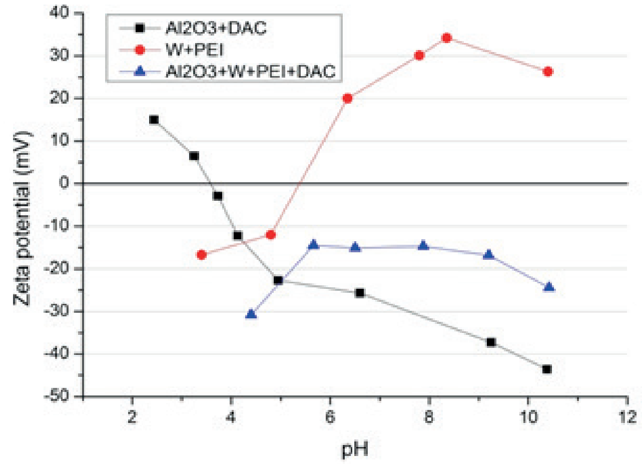

Fig. 6 Values of zeta potential in function of pH for Al_2O_3 with 0.8 vol. % of DAC , W with 2.2% vol. of PEI and their mixture prepared in 0.01 vol. % concentration suspensions. On the right scheme of particle distribution in suspension stabilised with DAC and PEI at pH 7-8

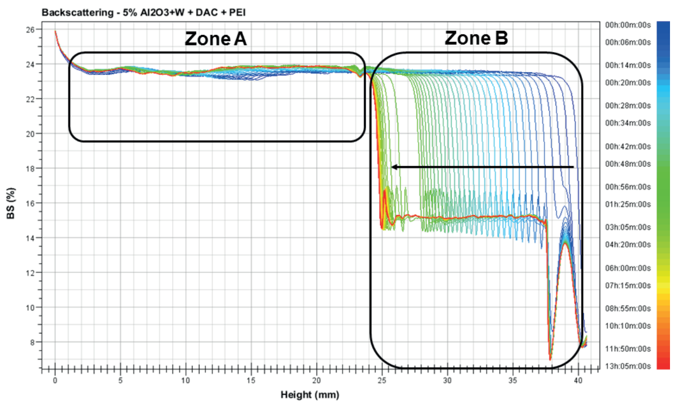

Fig. 7 Backscattered light (BS) registered along the sample with time during 13 h for 5 vol. % mixture of Al_2O_3 and W with addition of DAC and PEI as a dispersing agents

In case of suspension stabilised with addition of DAC and PEI, the results of BS signal change with time (Fig. 7.) differ from those showed in Fig. 5. Although it is possible to recognize sedimentation process, W and Al_2O_3 phase separation with time is not visible. On area pointed as Zone A (Fig. 7.) it can be observed drooping mixture of powders – BS signal almost imperceptible increases what correspons to small growth of concentration. In Zone B descent of particles concentration occurs. Decrease of BS signal from almost 25% to 15% corresponds to signal for nearly pure water.

Lack of phase separation with time proves PEI function as an agent causing hetero-flocculation behaviour.

3.4. Slip casted samples from 50 vol. % suspensions – effect of hetero-flocculation

Composite suspensions stabilized with DAC and DAC+PEI were prepared according to data shown in Table 1. Fig. 8 shows viscosity and flow curves for mentioned suspensions. It can be seen, that addition of PEI results in viscosity increase. This effect is reasonable due to long chain of PEI molecule. Furthermore, electrostatic attraction forces between Al_2O_3 and W (hetero-flocculation) could be responsible for the increase of viscosity. Both of samples shows shear thinning behavior. Higher viscosity of suspension prepared with DAC and PEI could participate in effect of better stabilization.

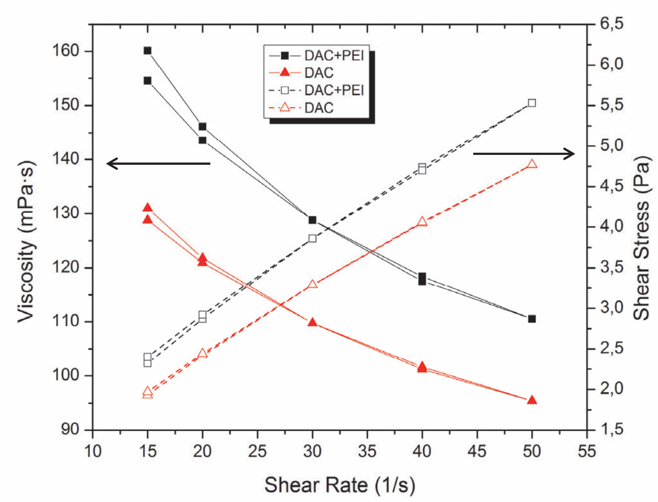

Fig. 8 Flow curves (dashed lines) and viscosity curves (solid lines) for composite suspensions

The presented optical and SEM photographs of green body fracture surface show difference in arrangement of metal particles on top and bottom of slip casted samples obtained from suspension DAC (Fig. 9) and DAC+PEI (Fig. 10). On the top of DAC sample there is visible light gray layer which corresponds to significantly decreased concentration of W particles (Fig. 9A, B). Bottom of the sample contains higher amount of W particles as well as larger Al_2O_3 aggregates (Fig. 9C, D.). This phenomena requires an additional study.

Different microstructure and behavior of composite green body is shown in figure 10. Sample obtained with hetero-flocculation effect is more homogeneous. Top and bottom layer are similar to each other. It is difficult to figure out different zones/layers in the material, as it is in composite DAC. The same as for previous sample Al_2O_3 larger aggregates can be recognized. Presence of this kind of structures may be due to relatively low zeta potential value for Al_2O_3 for this pH (~ -30 mV).

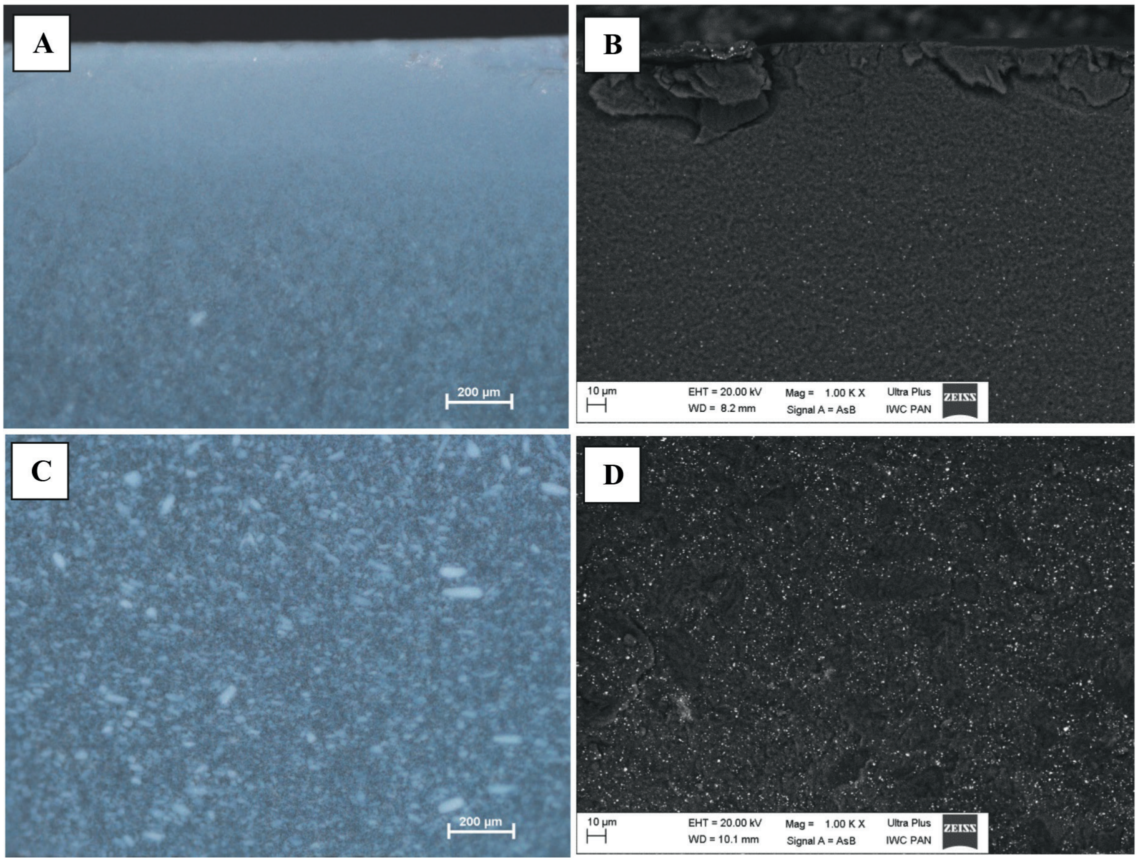

Fig. 9 Optical (A, C) and scanning electron microscope (B, D) microphotographs of top (A, B) and bottom (C, D) slipcasted Al_2O_3-W composite stabilised with DAC. Brighter points on SEM photograph correspond to metal particles

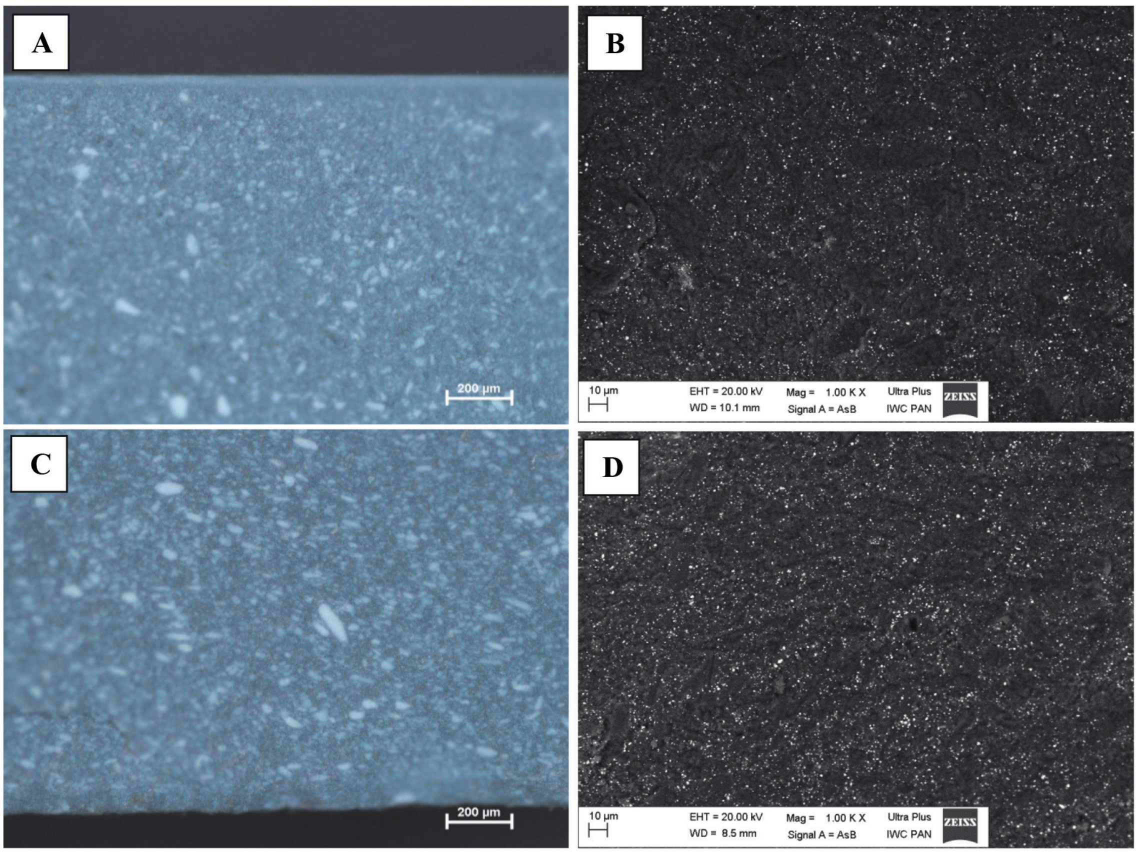

Fig. 10 Optical (A, C) and scanning electron microscope (B, D) microphotographs of top (A, B) and bottom (C, D) slipcasted Al_2O_3-W composite stabilised with DAC and PEI (hetero-flocculation). Brighter points on SEM photographs correspond to metal particles

4. Conclusions

Present work confirmed positive effect of hetero-flocculation on slip casted composite material homogeneity. It is possible to avoid sedimentation particles with high density (e.g. metal particles, in this work W) by playing with surface properties of materials in water based system. As a result homogeneous ceramic-metal composites can be fabricated with simple slip casting method.

Poli(ethyleneimine) is an effective organic additive for modifying surface properties of metal particles, although it increase viscosity of suspension. Proper preparation of composite, ceramic-metal suspension is necessary to obtain homogeneous material with good mechanical properties. Analysis the components zeta potential, grain size distribution, stability is crucial in order to success.

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