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Preparation and properties of the AEO_9/alcohol/alkane/water reverse microemulsion ceramic inks

Ruisong Guo*, Haitao Qi, Zhengfang Yang, Yuru Chen

Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, Tianjin 300072, PR China

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Abstract

Reverse microemulsion method was applied and the AEO_9/alcohol/alkane/water system was chosen to prepare ceramic inks for forming by jet-printing. The ceramic inks were prepared by reaction after mixing the zirconium oxychloride and ammonia reverse microemulsions homogeneously through vigorous stirring. The physicochemical properties of the ZrO_2 ceramic inks were systematically determined and discussed based on the requirements of the ink-jet printers available. They generally met the requirements for the drop on demand printers and were adjusted and improved by adding a small amount of alcohol and inorganic electrolyte to meet the demands for continuous ink-jet printers. It was shown that the ceramic ink with viscosity below 18 mPa s and conductivity close to 100 mS m^{-1} was obtained after modification. Transmission electron microscope observation showed that ZrO_2 nanoparticles in the reverse microemulsion were very well dispersed and the stability of the inks was excellent. Besides, several ceramic ink compositions with bicontinuous structure were specially designed based on the phase diagram, and the changes of water-dissolving amount into the system was investigated aiming to increase the concentration of ZrO_2 ceramic ink.

Keywords: A. Powders: chemical preparation; A. Suspensions; C. Electrical conductivity; D. ZrO_2; Ceramic ink

1. Introduction

Solid freeform fabrication has become one of the new forming technologies of advanced ceramics since the 1990s, mainly because it meets the special design ideas for composite materials and multifunctional materials. Ink-jet printing forming is a novel method for shaping advanced ceramics, especially for multiplayer materials, in virtue of the modern office computer system, in which the ceramic powder to be formed must be well suspended into a liquid to form so-called ceramic ink. Since the ink is printed onto a carrier through an ink-jet printer, just like printing an article on paper, the size and shape of the body can be easily controlled by the computer. The key issue in this forming is to prepare ceramic ink suitable for printing in both aspects which is still very challenging to ceramic researchers: its own physicochemical properties and the match to the hardware of the printer. Therefore, there are two basic requirements for ceramic inks. One is stability, dispersivity and homogeneity of the suspension, and the other is that the physicochemical properties of the ceramic inks should meet the requirements of the commercially available printer because there are no dedicated printers available for this usage at present. There are two types of ink-jet printers: continuous and drop on demand, which have different requirements for ink. So far the preparation methods for ceramic inks include dispersion method [1–5], sol method [6,7] and reverse microemulsion (RM) method [8–11], each of which has its own advantages and disadvantages as mentioned in Ref. [8].

This paper focuses on the RM method, which was widely used to prepare nanoparticles of ceramic powder several years ago [12–22]. Microemulsion is referred to a homogeneous and thermodynamically stable system consisted of oil, water, emulsifier and/or co-emulsifier, which is located in a limited region of the ternary phase diagram of water/oil/emulsifier and/or co-emulsifier, where water is spontaneously suspended into the continuous oil matrix in nanometer size (usually 8–80 nm) with the help of emulsifier and/or co-emulsifier after stirring the mixture intensively. The water particles, also called water pools, provide

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* Corresponding author. Present address: School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China.
E-mail address: rsguo@tju.edu.cn (R. Guo).

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reaction spaces for the formation of ceramic nanoparticles. Due to its high stability and good dispersion in nanometer sizes, this system has superiority to the other two methods with a great potential in preparing ceramic inks. According to these unique characteristics, it is worthy to try this new way to prepare ceramic inks. Generally speaking, there is a limitation for RM in that the water-dissolving amount is usually very low, which results in low solid load in the ceramic inks, because RM only lies in a limited region in a ternary phase diagram of oil–water-surfactant. Also the conductivity is relatively low for continuous ink-jet printer due to the continuous oil phase [2–6]. These become an obstacle for the successful realization of forming by printing. According to the ternary phase diagram of water, oil and surfactant, there is a region called bicontinuous structure [7–10], in which relatively large amount of water can be dissolved into the system. This RM is in a transition stage from ordinary RM to macroemulsion.

In the previous paper [23], the work on the choice of a proper reverse microemulsion system, use of co-surfactant, determination of quasi-ternary phase diagram and the conditions for maximum water-dissolving amount has been reported. The main purpose of this paper is to report the preparation and properties of ceramic inks of AEO_9/*n*-butanol/*n*-octane/water system and to design several compositions corresponding to the bicontinuous structure. Ceramic inks with such a structure are prepared by the same route. Regarding the physicochemical properties, we have found that there are still some shortcomings of these ceramic inks prepared via bicontinuous structure, therefore, a small amount of alcohol and inorganic electrolyte are added into the inks to modify their structure and properties. Their compatibility with the printing forming hardware was discussed and analyzed based on the measured properties.

2. Experiment

Different concentrations of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, Yixing Chemical Factory, China) solution and ammonia ($NH_3 \cdot H_2O$, Tianjin Chemical Reagent Factory, China) solution were separately prepared, and the water in the optimized RM system of AEO_9/*n*-butanol/*n*-octane/water [23] was replaced with equivalent volume by these two solutions respectively, giving rise to two RMs. These two RMs were then mixed homogeneously and the reaction of zirconium oxychloride with ammonia in the water pools took place and $Zr(OH)_4$ nanoparticles formed. The process of the reaction was controlled by adjusting pH value through adding different amounts of ammonia RM. The resulting microemulsion was referred to ZrO_2 ceramic inks listed in Table 1. Its rheological characteristics, surface tension, conductivity, transparency and stability were determined by rheometer (WCR 300 SN 357142), surface tensiometer (self-installed based on the maximum bubble pressure method), conductivity meter (DDS-11A), ultraviolet/visible spectrophotometer (750MC), respectively. Phase separation and stability were determined by centrifugal separation and visual observation after settling in sealed vials for a period of times. Volatility was determined at 25 °C in ambient environment by weight loss after putting a certain amount of ceramic ink onto a plate for different times and comparison with common ink was made under the same conditions. The particle size in the RM was observed by TEM (100CX-II).

Table 1
Composition of ZrO_2 ceramic inks

No.	AEO_9 (wt.%)	*n*-Butanol (wt.%)	*n*-Octane (wt.%)	$ZrOCl_2 \cdot 8H_2O$ (wt.%)	NH_4OH (wt.%)
1	14.4	9.4	31.7	25.0	19.4
2	14.9	9.7	32.6	25.7	17.9
3	14.1	9.2	30.8	27.0	18.9

Alcohol (Tianjin Chemical Reagent Factory, China) and Na_2CO_3 (Tanggu Chemical Reagent Factory, China) were added to the prepared ceramic inks in order to adjust the structures and properties. Several special compositions of inks with bicontinuous structure were designed according to the phase diagram and ceramic inks with such a structure were prepared using the same way as mentioned above, and the changes in water-dissolving amount were investigated. Finally, the physicochemical properties of the modified ceramic inks were determined in the same way also as mentioned above.

3. Results and discussion

3.1. Solubility limit of zirconium oxychloride solution and ammonia solution in the system of AEO_9/n-butanol/n-octane at 25 °C

The effect of different concentrations of zirconium oxychloride solution and ammonia solution on the solubility limit in the system of AEO_9/*n*-butanol/*n*-octane at 25 °C was shown in Fig. 1. It can be seen that a large amount of zirconium oxychloride solution and ammonia solution can be dissolved into the system, with the maximum of about 38% respectively. However, water content decreased with increasing the concentration for both solutions, and the solubility drop was more severe for zirconium oxychloride solution due to the existence of Zr^{4+}. Because non-polar surfactant is much less sensitive to electrolyte than ionic one, the RM system with non-polar surfactant could allow much wider range of salt to be added. That means more kinds and amounts of electrolyte could be dissolved into the system. For example, the dissolving amount of 28.1% could be achieved for zirconium oxychloride solution with the concentration of 1 mol/l. Zirconium oxychloride, being regarded as a electrolyte, will not compress the electric double layer between interface film and water, but destroy the structure of the film, which resulted in debonding of

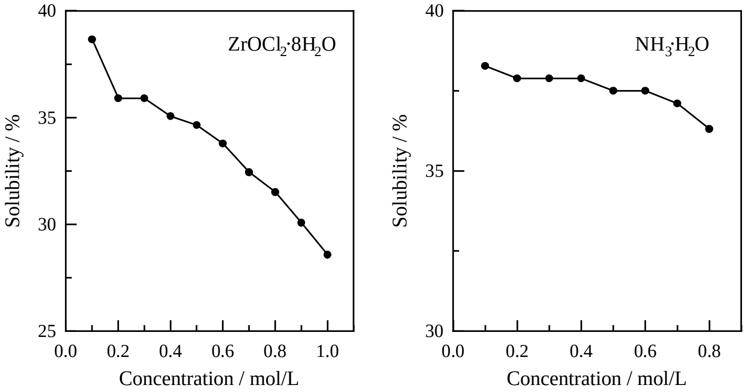


Fig. 1. The maximal solubility of $ZrOCl_2 \cdot 8H_2O$ solution and NH_4OH solution vs. their concentrations in reverse microemulsions at 25 °C. Both solutions were slowly added into oil phase while keeping vigorous stirring.

hydrogen bond formed between oxygen in the ester group and water. Therefore, the hydrophilicity of the surfactant decreased and water dissolving amount reduced as well.

The mixing of the two RMs caused the formation of numerous $Zr(OH)_4$ precipitates, which destroyed the interface of oil–water to some degree, leading to the reduction in transparency and the enhancement in viscosity. Specially, this situation turned to be relatively severe when the concentrations of RMs were high. Therefore, the concentration of zirconium oxychloride solution and ammonia solution should be lowered a little to ensure satisfactory quality. It was found that the most important factors concerning the success of ceramic ink preparation were concentration and amount of zirconium oxychloride solution and ammonia solution added, with concentration being prerequisite. When concentration of zirconium oxychloride solution and ammonia solution was less than 0.5 and 5 mol/l, their dissolving amounts of 33.3 and 25.9% could be reached in the RM solutions, respectively. Good stability of the ceramic ink obtained by mixing these two RM solutions of zirconium oxychloride and ammonia could be obtained when pH value remained below 8.

Three ceramic ink samples prepared at 25 °C for the measurement and analysis of their physicochemical properties were given in Table 1. They all had good comprehensive properties in the pH range of 4–8, and the solid loads in the inks reached 2.2, 2.4 and 2.5 wt.%, respectively.

3.2. Physicochemical properties of the ceramic inks

3.2.1. Conductivity

It can be seen from Fig. 2 that the conductivity of three ceramic inks remained in the range of 20–26 mS m^{-1} at low pH value, but increased sharply when pH was larger than 8 for numbers 1 and 2 samples and pH larger than 6 for number 3 sample, which meant that the RM system was destroyed at those corresponding points. The reason for this could be attributed to breakage of interface film due to fast growth of nucleus of particle in water pools resulting from the saturated concentration of zirconium oxychloride and ammonia.

There was no limitation of conductivity for the drop on demand printer. However, the conductivity of the ceramic ink must lie in a certain range for continuous printers, so that ceramic ink can be manipulated by electric field while printing forming. In general, the conductivity must be larger than 100 mS m^{-1}. The contribution of conductivity of RM mainly came from the permeation of electrolytical ions through the interface film. In addition, migration and impact of liquid drops under electric field caused breakage of interface film

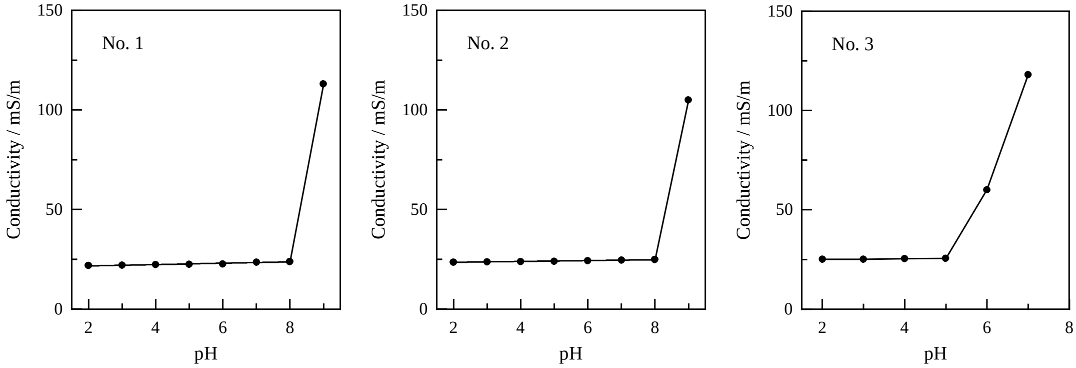


Fig. 2. Relation of conductivity with pH value of three ceramic ink samples shown in Table 1 at 25 °C. The pH value was adjusted by controlling the amount of ammonia RM added into $ZrOCl_2 \cdot 8H_2O$ RM.

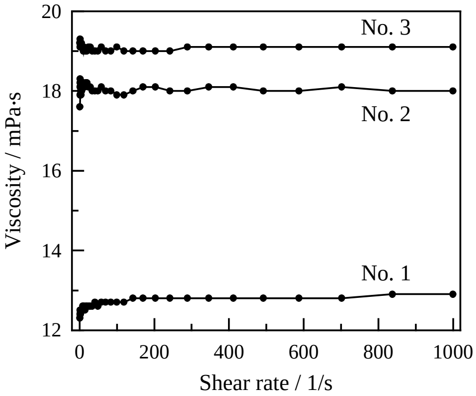


Fig. 3. Hydrodynamics capability of ceramic ink samples at 25 °C, showing their viscosity at different shear rates determined by rheometer.

due to bounce of surfactant molecules, which helped improve the conductivity (effective medium theory [24,25]). The conductivity of RM was basically equal to that of continuous phase, i.e. oil phase, because the dispersion phase was separated. Therefore, it was very difficult for the conductivity to meet the demands for continuous printers because alkane was used in this paper as oil phase, which is a poor conductor. How to enhance the conductivity of ceramic inks will be discussed later.

3.2.2. Rheological behavior

Viscosity of ceramic inks mainly affected the rheological performances through the capillary of the printer's nozzle. High viscosity could led to insufficient jet of inks, on the contrary, too low viscosity could lower the inner friction of the ink, which made the ink drop become crescent, resulting in damped oscillation, so that the ink-jet velocity decreased. It can be seen from Fig. 3 that the viscosity of ceramic inks increased with increasing concentration of ZrO_2 from 12.8 mPa s to 19.1 mPa s which fell into the range required by drop on demand printer, but a little higher than that required by continuous printer. Viscosity of all samples remained almost constant as shear rate increased. No shear thickening or shear thinning was observed, which was helpful to realize ink-jet printing forming. We believe that this phenomenon was attributed to good dispersion of nanoparticles in the inks.

3.2.3. Surface tension

The surface tension of ceramic inks mainly affected two processes of printing forming. One was decomposition into fine drops of ceramic ink efflux through the capillary tube of a printer nozzle, and the other was wettability of ceramic ink onto the forming carrier. The oil phase, as a major phase in the ceramic ink, had a predominant role on the surface tension. The existence of surfactants made a further contribution to lowering the surface tension. *n*-Octane was chosen as oil phase due to its suitable surface tension. It could be seen from Fig. 4 that the surface tension of three ceramic ink samples lie within the range from 37.5 to 45.4 mN m^{-1}, which met the needs of printers.

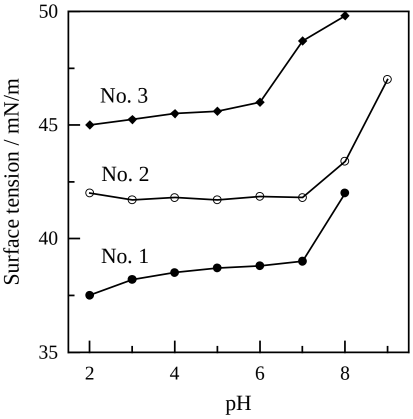


Fig. 4. Surface tension vs. pH value of the ceramic ink samples at 25 °C, which was determined by the maximum bubble pressure method using self-installed surface tensiometer.

3.2.4. Volatility

The volatility of ceramic inks was closely related to drying rate and formability of ceramic inks after jet printing forming. The liquid medium would evaporate quickly during jet printing onto a carrier causing a great mass loss for ceramic inks with good volatility. Therefore, liquid left in the inks was greatly reduced, which was helpful to the close packing of particles and reduction in porosity.

The volatility of ceramic inks, using number 2 sample as an example, was compared with that of common ink under the completely identical conditions, as shown in Fig. 5. It was found that the ceramic ink had a very good volatility through comparison. Alcohol, alkane and water all evaporated fully and AEO_9 evaporated partly, so there were only precipitates and part of AEO_9 left on the carrier, which could ensure close packing of particles during the ink-jet printing forming.

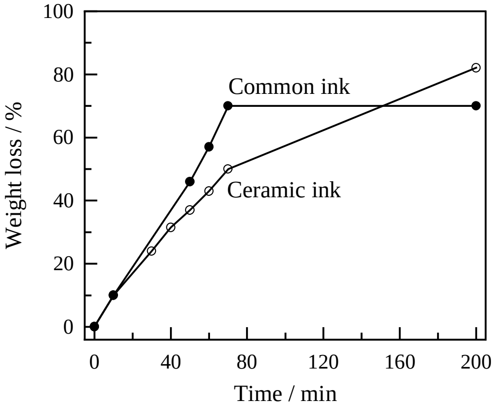


Fig. 5. Comparison of volatility between number 2 ceramic ink and common ink at room temperature. They were put into beakers, evaporated for different times and weighed.

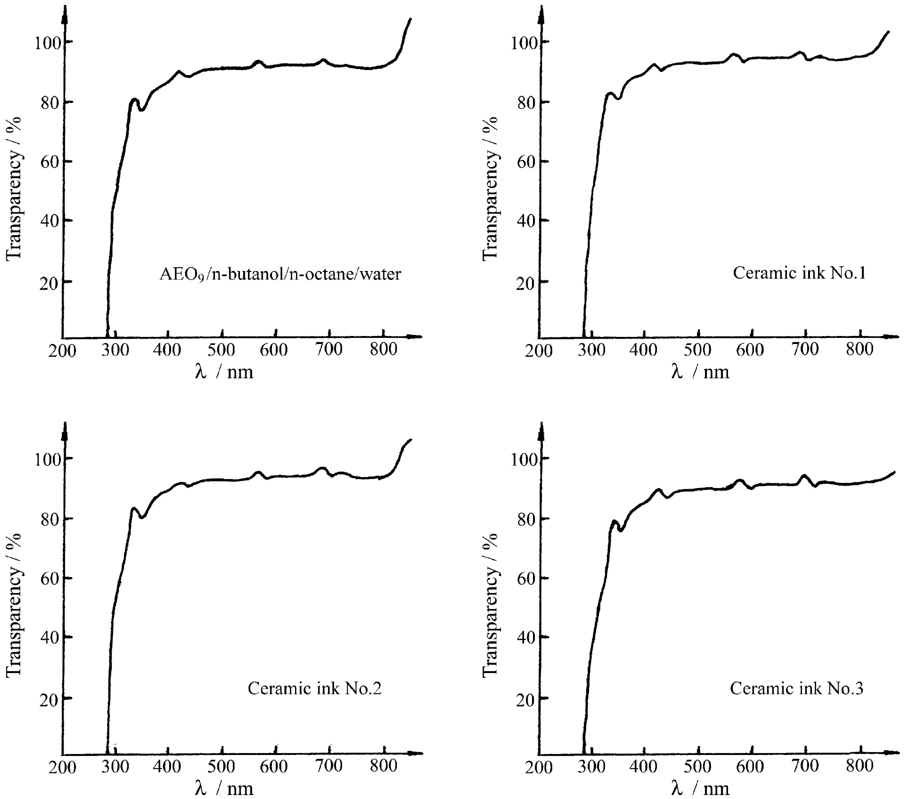


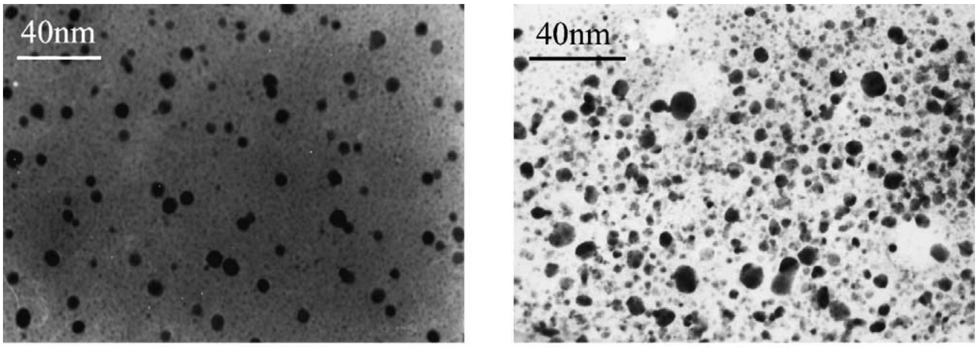
Fig. 6. Comparison of transparency spectra among the pure RM and three ceramic ink samples at 25 °C, showing their transparency change with wavelength λ determined by ultraviolet/visible spectrophotometer.

3.2.5. Transparency

Theoretically, reverse microemulsion systems are thermodynamically stable and transparent or translucent. The transparency of a real system will change a little bit with the suspended particle size, and reflects the inner structure and stability of this RM system. It could be seen from Fig. 6 that the transparency of three ceramic ink samples was almost the same as that of the pure RM system. Peak distribution of these spectra was nearly identical and only difference was that transparency decreased a little with concentration. This meant that they were all the RM systems and their inner structure was basically consistent.

3.2.6. Morphology observation of particles in the ceramic inks

The TEM photographs of particles in the ceramic inks were shown in Fig. 7, which obviously demonstrated extremely well dispersed particles with very narrow size distribution (4–6 nm) in the inks. No agglomerates were found and the particles were almost spherical. These revealed that the interface film was not subjected to destroy while nucleation happened in the water pools. Surfactant and co-surfactant formed a shell around particle surface protecting them from collision and growth while the formation of particles; hence they could exist stably and in isolation.



Ceramic ink No.2 Ceramic ink No.3

Fig. 7. TEM photographs of ceramic ink samples, showing morphology and dispersion of nanometer particles.

3.2.7. Stability of the ceramic ink at different temperatures

The ZrO_2 ceramic inks were sealed and settled at 20, 25 and 30 °C, respectively. The inks settled at 20 and 25 °C remained stable after a long period of times, however separation happened for the inks settled at 30 °C. When temperature decreased to 20 or 25 °C again, the inks resumed their original clearness in a few minutes. It was because the RM system with non-polar surfactants was very sensitive to temperature. The region of RM changed also with temperature notably and phase boundary line of the system drifted as well. It was believed that the RM system began to separate when temperature was about 30 °C and to resume to its original structure and performance when environmental temperature was lowered down again due to its thermodynamic stability. At suitable temperatures, the inks could be kept for more than half a year without any degradation of stability and transparency.

3.2.8. Adjusting the viscosity and surface tension by addition of alcohol

It was found that the addition of small amount of alcohol to number 2 ceramic ink prepared above significantly reduced its viscosity after intensive stirring, as shown in Fig. 8. When the amount of alcohol added was 1–2%, the viscosity decreased to 11 mPa s, very close to the upper limit required by the continuous printers. Meanwhile, the surface tension lowered a little.

It is generally believed that this measure we have taken is feasible for lowering viscosity of ceramic inks. Firstly, the alcohol molecule inlay between the inter-molecules of emulsifier, forming mixed micelles so that the repulse of ions of emulsifier and co-emulsifier was lowered. The surfactant film between oil and water became more integral and its flexibility was increased, therefore, it became to be much easier to bend and therefore improved the stability of micelles. Secondly, the alcohol could change the surface characteristics of matrix oil phase to increase the affinity between surfactant and oil phase. These two factors played a very active role in reducing the viscosity.

3.3. The bicontinuous structure

3.3.1. Composition determination

The concept of bicontinuous structure was firstly given by Scriven [26], who suggested that the particles in a bicontinuous structure emulsion did not distribute in the same pattern as in the ordinary emulsion, but formed a tube type dispersed in the oil matrix, like a network. Talman et al. [27] proved the probabilities of existence of bicontinuous structure when the amounts of oil and water were equivalent according to statistic thermodynamics. In the case of water-in-oil emulsion, water drops, while embedded in the continuous oil phase, connected with each other to form a stereo network, so that they did not keep a perfect spherical shape and did not exist separately. Whether the bicontinuous structure formed or not was judged by the change of conductivity with water content. When water content was low, the emulsion was water-in-oil type, and the continuous phase was oil which was not a good conductor. When water drop migrated in the oil matrix and collided, the electrolyte ions past through the interface film to make the emulsion conductive, but the conductivity remained very low, thus there were nearly no differences in conductivity when changing the type of electrolyte. With increasing water content, the number of water drops was increased and the volume of each drop increased a little as well, then the probability of collision of water drops rose significantly. At the same time, the number of electrolyte ions was increased and their migration became more frequent, giving rise to the enhancement of conductivity to a certain extent, but not remarkably because water drops were still separated. When water was further increased, water drops gradually moved closer and closer and formed a dumbbell type. The molecule density of emulsifier film on the surface of water drop lowered due to expansion of water drop under the condition that emulsifier and co-emulsifier kept constant. Therefore, electrolyte ion became much easier to pass through. When water content reached a certain threshold, the interface film did not keep its perfection any longer. The distance between wa-

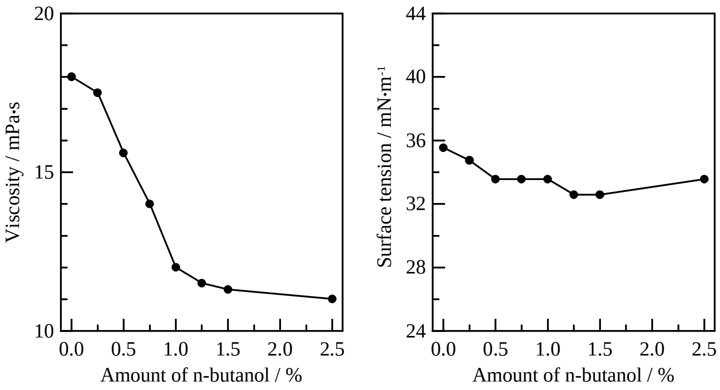


Fig. 8. Influence of *n*-butanol addition on viscosity and surface tension of ceramic ink number 2.

Table 2
Composition of a bicontinuous structure ceramic ink

Temperature (°C)	AEO_9 (wt.%)	*n*-Butanol (wt.%)	*n*-Octane (wt.%)	$ZrOCl_2 \cdot 8H_2O$ (wt.%)	NH_4OH (wt.%)	pH
25	13.9	9.1	30.5	27.8	18.7	6

Table 3
Properties of the bicontinuous structure ceramic ink

Conductivity ($mS\,m^{-1}$)	Viscosity (mPa s)	Surface tension ($mN\,m^{-1}$)	Stability	ZrO_2 content (wt.%)
57.5	31.5	41.8	>60 days	2.54

ter drops became very short, even began to contact. At that moment, the conductivity rose remarkably. From this point, the emulsion became to have a bicontinuous structure and a sharp increase in viscosity was often observed as a result of difficulty in movement of the water drops.

The bicontinuous structure created a new way for preparing ceramic ink in that it provided a high conductivity and more importantly a high water-dissolving amount compared with the ordinary RM. Table 2 showed a ceramic ink composition with ZrO_2 content 2.54 wt.%.

3.3.2. Physicochemical properties of the bicontinuous structure inks

The physicochemical properties of the bicontinuous structure ink were shown in Table 3. The ink was clear and transparent by visual observation, and did not sediment after centrifugal separation. When added to the ink, the water did not diffuse, which revealed it was neither a normal emulsion nor an oil-in-water emulsion. However, the conductivity and viscosity were improved compared with those of ordinary emulsion. There was no big decrease in transparency measured by transparent spectrometer, though its pattern changed a little (Fig. 9), which meant that its inner-structure changed only slightly. The tube type distribution of water drops in the oil phase was obviously observed, demonstrating an intrinsic feature of bicontinuous structure (Fig. 10), and the original particles were shown to be below 10 nm. Regarding the required properties for ink-jet printing forming, the surface tension and stability met the needs quite well. Unfortunately the conductivity was still not sufficiently high and viscosity not low enough.

3.3.3. Modification of the ceramic inks

In order to decrease the viscosity and increase the conductivity so as to meet the conditions for forming by printing, inorganic electrolyte solution of $0.2\,M\,l^{-1}$ Na_2CO_3 was added to the RMs. It was added drop by drop while stirring, then settled for a period, followed by determinations of viscosity and conductivity, which was shown in Fig. 11. It was found that the addition of small amount of Na_2CO_3 significantly increased the conductivity to $100\,mS\,m^{-1}$ and lowered the viscosity to 18 mPa s at the same time. Both were now very close to those required for printing forming.

The measurements of surface tension and transparent spectrum gave nearly no changes compared with the ordinary ceramic inks. We believe that the water drops in the ink with the bicontinuous structure were connective each other. The conductivity mainly depended on the migration of electrolyte ions and did not suffer a restriction by the interface film. Since the freedom of electrolyte ions was large, it would consequently raise the conductivity to the value which is equivalent to that of the electrolyte solution itself.

Meanwhile, the electrolyte destroyed the hydrogen bond in the solution and caused the changes in the interaction between emulsifier and water, making the thickness and flexibility of the film changed, which led to a significant reduction in viscosity. It was proven that the measures taken in this paper were effective. Certainly, it is still needed to further explore new kinds of electrolyte to give better results while lowering the amount used.

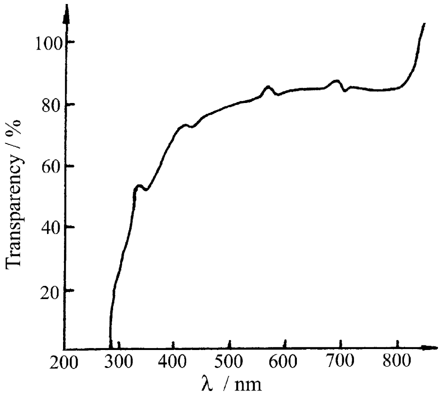


Fig. 9. Transparency spectrum of the bicontinuous structure ceramic ink.

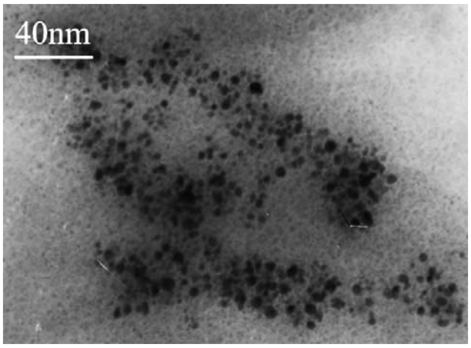


Fig. 10. TEM photograph of the bicontinuous structure ceramic ink.

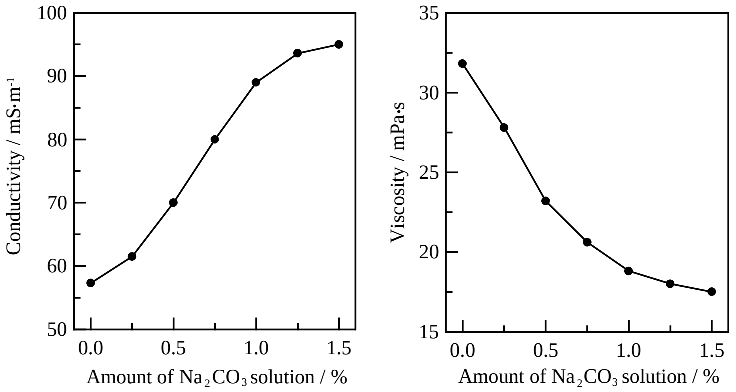


Fig. 11. Influence of Na_2CO_3 addition on conductivity and viscosity of the bicontinuous structure ceramic ink.

4. Conclusions

(1) Zirconium oxychloride and ammonia RMs were prepared by replacement of the water in the system with equivalent volume of zirconium oxychloride solution and ammonia solution, respectively based on the results of [23], and then ceramic inks were obtained by reaction after mixing the both RMs uniformly. The physicochemical properties of the inks were determined and analyzed according to demands of printers for the inks, as listed in Table 4.

(2) A relatively high concentration of ceramic ink was prepared, and it basically met the needs of physicochemical properties regarding to jet-printing forming for the drop on demand printer.

(3) Conductivity should be further increased and viscosity should be lowered for the jet printing forming by continuous printers.

(4) It is still necessary to increase the solid load in the suspension further.

(5) It provided a new way to prepare ceramic inks with enhanced solid load and high conductivity by introduction of bicontinuous structure.

(6) The inner structure of the bicontinuous structure ceramic inks could be modified by addition of small amount of alcohol such as *n*-butanol and inorganic electrolyte such as Na_2CO_3 to the ceramic inks, resulting in the increase of conductivity and decrease of viscosity to a suitable level required by the printing forming.

Table 4
Properties of ceramic ink of AEO_9 system

Item	Property
Particle size and distribution	4–6 nm, well-dispersed
Solid load	2.5 wt.%
Viscosity	12.8–19.1 mPa s
Surface tension	38–50 mN m^{-1}
Conductivity	20–26 mS m^{-1}
Stability	>180 days
Volatility	Good

Acknowledgements

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