

INFLUENCE OF THE RELATIVE HUMIDITY ON THE “SELF - ASSEMBLY” GROW OF THE SiO₂ FIBRES

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ABSTRACT: The interesting phenomenon of sol - gel transition in silicic acid – NH₃ – HCl – H₂O system is „spontaneous“ origin of fibres on gels' surfaces. In the mentioned system we studied the influence of relative humidity (RH) on the „spontaneous“ fibres' growth. At the RH – point of 52,9 % the growth of fibres reaches its maximum, in the case of high values of RH is the growth practically stopped.

KEY WORDS: sol-gel methods, fibres, silicic acid, spontaneous growth

1. INTRODUCTION

Sol-gel methods based on the use and control of solution-sol-gel-product transition allow preparation of various materials often with unanticipated characteristics [1, 2, 3]. Interesting phenomenon of sol - gel - product transition is „spontaneous“ occurrence of various and often fibrous formations. These „spontaneously“ occurred fibrous formations are measured in dimensions from nanometers to centimeters [4]. Best-known systems, in which „spontaneous“ growth of fibres and fibrous structures occurs, are called chemical gardens but also silicate gardens, colloidal gardens and crystal gardens, mostly because of the similarity to the growth of plants [5]. They occur after addition of grain of soluble salt of metal into solutions containing anions such as silicates, aluminates, borates, carbonates, phosphates, ferricyanides and many others [6]. Nascent crystalline material is in few cases decisive for final shape. This is how inorganic materials are „spontaneously“ created with morphogenesis similar to biological systems in water solution of silicates in the presence of water-soluble baric salts [7]. Driving force of „spontaneous“ growth in this case is crystallization of respective salt that is affected and controlled by present colloid.

2. EXPERIMENTAL

2.1 Preparation of silicic acid sol

We have used freshly prepared solution of sodium silicates in water for preparation of silicic acid. Solution of sodium silicates has been prepared by dissolving of porous SiO₂ (Silica from DEGUSSA company) in calculated quantity of NaOH solution. Solution of sodium silicates had concentration of SiO₂ ~ 1.5 mol.dm⁻³ and molar rate of Na₂O : SiO₂ was 1 : 3. Silicic acid sol has been prepared by ionic exchange of Na⁺ for H⁺ using Amberlite IR cation exchanger – 120H⁺ form 0.3 – 1.2. Created sol had concentration of SiO₂ ~ 1,25 mol.dm⁻³ and pH ~ 2.4.

2.2 Preparation of samples

Samples for observation of fibre spontaneous growth in $\text{KK-H}_2\text{O-HCl-NH}_3$, systems have been prepared by use of hydrochloric acid solution with concentration of 10 mol.dm^{-3} , solution of ammonia, with concentration of 7.5 mol.dm^{-3} . Individual sol samples have been mixed in undermentioned way, to get sol samples with molar rate of $\text{SiO}_2 : \text{HCl} : \text{NH}_3$ according to the Table 1. Prepared samples had concentration of $\text{SiO}_2 \sim 0.75 \text{ mol.dm}^{-3}$.

Tab.1 Molar ratio of individual components

Vzorka	SiO_2	HCl	NH_3
M1	1	0.889	3.333
M2	1	0.889	2.667
M3	1	0.889	2.000

While mixing, we have added required quantity of water and acid solution to required quantity of freshly prepared silicic acid sol into polyethylene bowl. Finally, we have added alkali solution while intense mixing. Prepared samples had concentration of $\text{SiO}_2 \sim 0.75 \text{ mol.dm}^{-3}$. The samples were placing after gelation in environment with constant relative humidity (RV), 0.13, 11.3, 32.8, 52.9, 75.3, 90.0, 97.7 % RV, respectively.

3. RESULTS AND DISCUSSION

Gels of all three composition stayed for the term of two months in containers (see the table no. 1), there were effected the demanded values of relative humidity. After this term each sample was analyzed by the optic microscopy, the results are displayed on the figures 1 to 3.



Fig. 1: Spontaneously growth fibres on SiO_2 gels M1 composition at RV: a - 0.13%, b - 11.3 %, c - 32.8 %, d - 52.9 % a e - 75.3 %



Fig. 2: Spontaneously growth fibres on SiO_2 gels M2 composition at RV: a - 0.13%, b - 11.3 %, c - 32.8 %, d - 52.9 % a e - 75.3 %



Fig. 3: Spontaneously growth fibres on SiO_2 gels M3 composition at RV: a - 0.13%, b - 11.3 %, c - 32.8 %, d - 52.9 % a e - 75.3 %

It has shown that the relative humidity is the influential factor that influences „spontaneous” growth of fibric products on the surfaces of observed gels. According to the figures 1 to 3 we can point out, that with increasing value of the RH also increase amount and length of originated fibres. The maximum is reached at the RH value of 52.9 %. By the RH value of 75.3 % we observed decrease of amount and length of originated fibres and the sample with M3 composition did not even create the fibres. For the RH values 90.0 % and 97.7 % we did not observe creation of fibres in any of samples. Samples of all three compositions create the fibres at the RH value 0.13 %.



Fig. 4: The shape of spontaneously growth fibres on SiO_2 gels. Magnification: a - 500x, b - 125x, c - 1000x

The influence of primary sols composition is obvious when talking about amount of originated fibres (the biggest one is for the M3 composition), but mainly it influences the way of the fibres creation, this means that from the composition M1 to M3 the originating fibres tend more and more to create the bunches. Originating bunches we can see on the figure 4. On the figure 4a it is noticeable the fission of fibres bunches. On the figure 4b we can see coiled bunch of fibres and on the figure 4c we can see the inner structure of observed fibres. According to these figures we are able to state that originating fibres are in the most cases bunches of very soft fibres and they are filled as well. The filling is probably a crystalline NH_4Cl mixed with amorphous SiO_2 .

4. CONCLUSION

In the silicon acid – HCl – NH_3 – H_2O system we studied three samples of compositions which were different in the SiO_2 : NH_3 ratio to find out how the „spontaneous” growth of fibres on the gels’ surfaces is influenced by the relative humidity. With the increasing value of RH from the beginning it also increases the amount and length of originated fibres. The maximum is reached by the RH value of 52.9 %. We did not observe the origin of fibres in any of samples by the RH values of 90.0 and 97.7 %. The change of composition is obvious mainly by the fact, that with increasing ratio SiO_2 – NH_3 the creation of bunches of fibres is preferred.

5. REFERENCES

- [1] SAKKA, S.: *Treatise on Materials Science and Technology*, 22, 1982, 129.
- [2] BRINKER, C.J., SCHERER, G.W.: *Sol-Gel Science - The Physics and Chemistry of Sol-Gel Processing*, Academic Press, Boston 1990.
- [3] RAHAMAN, M.N.: *Ceramic Processing and Sintering*, Marcel Dekker, New York 2003.
- [4] MIYAJI, F., WATANABE, Y., SUYAMA, Y.: *Materials Research Bulletin*, 38, 2003, 1669.
- [5] CARTWRIGHT, J.H.E., GARCÍA-RUIZ, J.M., NOVELLA, M.L., OTÁLORA, F.: *Journal of Colloid and Interface Science*, 256, 2002, 351.
- [6] BALKÖSE, D., ÖZKAN, F., KÖKTÜRK, U., ULUTAN, S., ÜLKÜ, S., NIŞLI, G.: *Journal of Sol-Gel Science and Technology*, 23, 2002, 253.
- [7] GAECÍA-RUIZ, J.M., HYDE, S.T., CARNERUP, A.M., CHRISTY, A.G., VAN KRANENDONK, M.J., WELHAM, N.J.: *Science*, 302, 2003, 1194.