The structure rearrangement in mixed and binary Zr-Ti sol-xerogel

Yurii GAPONOV*[1], Yoshiyuki AMEMIYA[3], Kazuki ITO[2], Hironari KAMIKUBO[2], Lembit KARAKCHIEV[1], Nikolai LYAKHOV[1]
[1]ISSC SB RAS, Novosibirsk, 6300128, Rossia
[2]KEK-PF, Tsukuba, Ibaraki, 305-0801, Japan
[3] The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan

Introduction

The sol-xerogel study is performed for simulation of the structure rearrangement during solid-state reaction [1]. To provide investigation of the structure rearrangement during a solid state reaction, it was proposed to simulate the phase formation using the sol-xerogel model system during gelation and thermal decomposition of the sol-xerogels of the same content but prepared by different methods.

Experimental

The diffraction experiments were carried out at BL15A using IP and CCD-based X-ray detectors [2] for WAXD and SAXS experiments. Zr-Ti sols with mole content Zr/Ti=1 were prepared by mechanical mixing of initial sols of hydrated zirconium dioxide and hydrated titanium dioxide (mixed sol) and by electrolysis of water mixture of zirconium oxichloride and titanium chloride (binary sol). In the water dilution experiment the sample set was prepared by adding water to decrease current sol concentration by factor 2. Then, initial sols of both xerogels were gelated to gel-xerogel state and after that both xerogels thermally decomposed at different temperatures (150-900°C) during 1 hour for every temperature (gel-xerogel of mixed/binary Zr-Ti systems).

Results and discussion

Fig. 1 shows the WAXD curves of dehydrated xerogels of mixed Zr-Ti. Analysis of the diffraction curves allows one to conclude that for both systems there are three stages of the structure transformation. At the first stage (20-150ºC) bulk water is evaporating from interstices of anatase (TiO_2) structure and from pores of amorphous zirconium oxide. At the second stage (150-450ºC), probably, hydrated water is dehydrated from zirconium oxide forming amorphous oxide. At the last stage (600-900ºC), probably, water in hydroxyl form (and/or hydrated water) is dehydrated from zirconium oxide. Titanium oxide, probably, transforms from anatase form to another one (Fig.1) that stimulates formation of zirconium titanium oxide. An estimated crystallite size is about 10-15nm and 30-35nm for mixed and binary Zr-Ti systems correspondingly. The reason of the different size of crystallites is that final product starts to form at different stages. In both cases at final stage, probably, metal atoms start to pack into hexagonal closed packed array (occupying the half of the octahedral interstices) forming the plane (111) of the final crystal structure. Fig. 2 shows scattering curve and a table with radius of gyration *Rg* and particle size of the mixed Zr-Ti system at the different concentration. The particle size and *Rg* are increasing with dissolving, probably, due to a process of formation of a secondary particle with a lamella type form. In the experiment with different density of a solvent, it was shown that in mixed system, probably, a nuclear of a particle consists of Ti atoms and a shell consists of Zr atoms, but in binary system a particle has inverse structure.

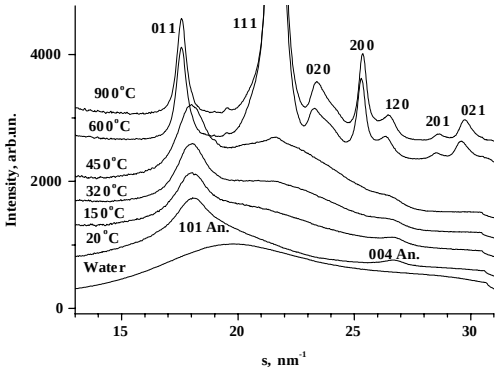
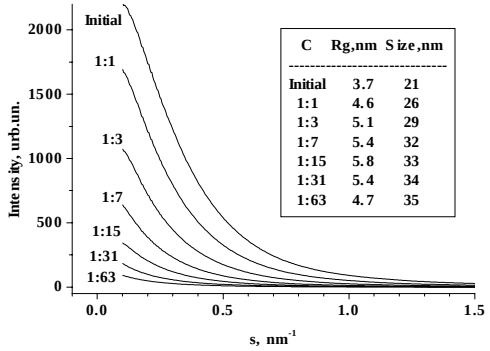


Fig.1 WAXD curves of the mixed Zr-Ti system



C	Rg,nm	Size,nm
Initial	3.7	21
1:1	4.6	26
1:3	5.1	29
1:7	5.4	32
1:15	5.8	33
1:31	5.4	34
1:63	4.7	35

Fig.2 SAXS curves and a table with radius of gyration *Rg* and particle size of the mixed Zr-Ti system at different concentrations (initial sol – initial concentration)

References

[1] Yu.A.Gaponov et al., J. Synchrotron. Rad., V5, 962 (1998).
[2] Y.Amemiya et al., Rev. Sci. Instrum. 66, 2290 (1995)