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Elucidation of imprint mechanism of Ru-La gels

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1. Background

"Printed Electronics", which can directly pattern electronics devices by using functional inks, has been proposed for the purpose of manufacturing devices at low cost with saving resources. However, existing printing techniques have a limitation in patterning size being limited at around several micro meters, so that they cannot manufacture devices on the order of nanometers. To solve this problem, we developed a new printing method named "nano-Rheology Printing (n-RP)^[1]. In this method, a functional ink is converted to a gel by drying solvent and the gel is imprinted directly to make patterns, which are in turn annealed to be solidified. We previously succeeded to fabricate Ru-La-O line patterns having the width of 30nm, where imprinting ability depended on the ratio of Ru to La. However, the deformation mechanism remained unclear ^[2]. Here, I have investigated rheological properties of Ru-La gels with viscoelastic measurement their thermal behaviors with thermogravimetry-differential thermal analysis (TG-DTA) and their organic structures with Fourier transform infrared spectroscopy (FT-IR) to clarify the formability changing of the gels with various Ru / La ratios. The results were analyzed together with the data from the high energy X Ray diffraction (HE-XRD) to consider the deformation mechanism of Ru-La-O gels at imprinting.

2. Experiments

The solution of Ru-La were prepared by dissolving Ruthenium(III) nitrosyl acetate (Ru-NO-ac), Lanthanum(III) acetate (La-ac) hydrate 1.5H₂O and MEA in propionic acid. The concentration of sum of Ru-NO-ac and La-ac were set to 0.4 mol/L; the mixing ratios of Ru-NO-ac and La-ac were set to 100:0, 75:25, 50:50, 25:75 and 0:100; the concentration of MEA were set to 0.8 mol/L. Ru-La gels were prepared by drying at 150, 175 or 200 °C for 60 minutes in the atmosphere. Viscoelastic properties of the Ru-La gels were measured by the parallel plate rheometer from 50 to 250 °C. Thermal properties of the Ru-La gels were measured by TG-DTA from room temperature to 600 °C. The organic elements contained in Ru-La gels were analyzed by FT-IR at wavenumber ranges from 4000 cm⁻¹ to 350 cm⁻¹. Molecular crystallinity which change with preparation conditions were measured by HE-XRD at BL04B2 in SPring-8.

3. Results and discussions

3.1 Viscoelastic measurement

The result of viscoelastic measurement is shown in Fig.1-3. The La100 gels were too viscous to be measured. The Ru-La gels dried at 150 °C had tan δ peaks or shoulders at approximately 150 and 170 °C. The Ru-La gels dried at 175 °C had weak tan δ peaks at approximately 170 °C. In the case of Ru-La gels dried at 200 °C, only the Ru25La75 gel had a peak. The tan δ peak became larger when the amount of La was larger and the drying temperature was lower. Judging from the result, it was suggested that amount of remaining propionic acid and La-ac component was closely related to the

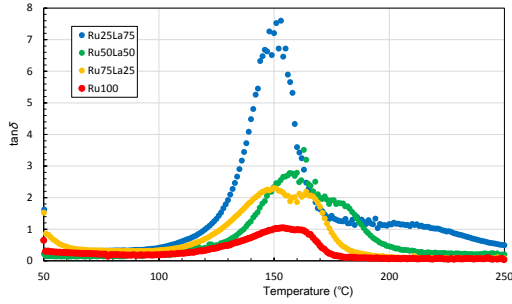


Fig.1 Viscoelastic measurement of Ru-La gels dried at 150 °C

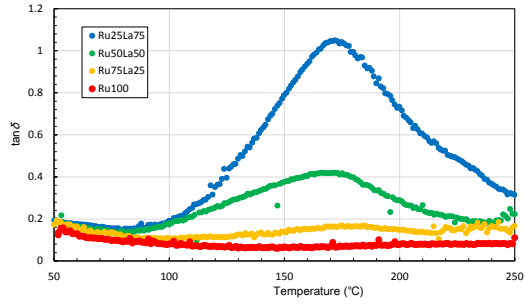


Fig.2 Viscoelastic measurement of Ru-La gels dried at 175 °C

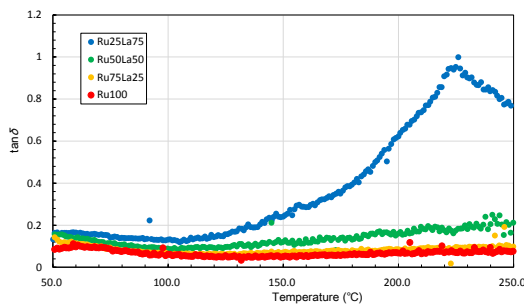


Fig.3 Viscoelastic measurement of Ru-La gels dried at 200 °C

viscoelastic property of a Ru-La gel.

3.2 TG-DTA

The result of TG-DTA measurement is shown in Fig.4-6. The masses of the Ru-La gels dried at 150 °C started to decrease around from 150 °C. The mass of each Ru-La gel dried at 175 and 200 °C also started to decrease from its drying temperature. It was suggested that the mass decrease could correspond to the decomposition of remaining propionic acid. However, the masses of La100 gels started to decrease at the temperature less than the drying temperature. The Ru100 gel had a mass reduction and an exothermal reaction at around 250 °C, which can be estimated to be oxidation of organic elements in Ru compounds. On the other hand, the gels including a La compound showed a small mass reduction from 200 °C to 400°C and their oxidation peaks shifted to a higher temperature. It could be considered that addition of La gave a gel a tolerance for oxidation.

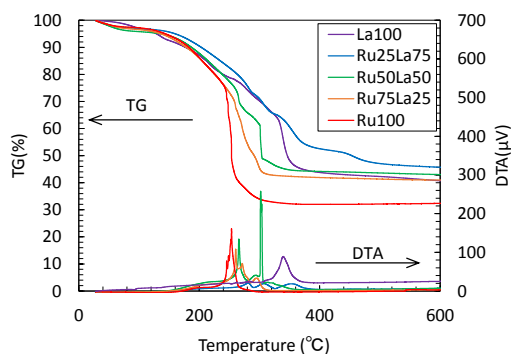


Fig.4 TG-DTA measurement of Ru-La gels dried at 150 °C

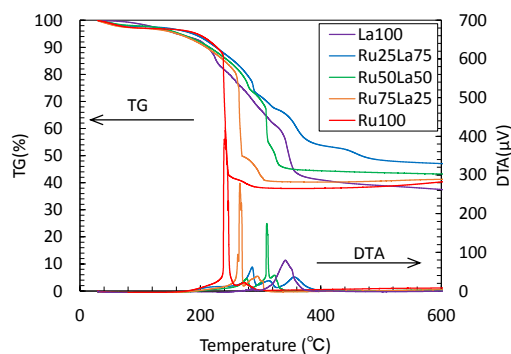


Fig.5 TG-DTA measurement of Ru-La gels dried at 175 °C

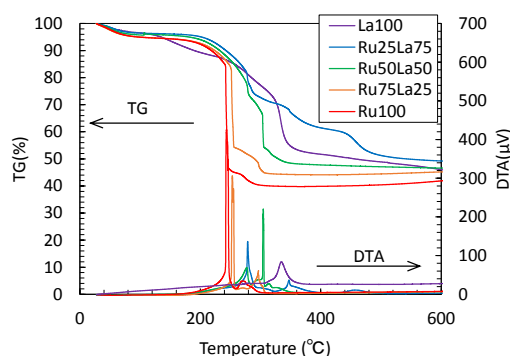


Fig.6 TG-DTA measurement of Ru-La gels dried at 200 °C

3.3 FT-IR

The FT-IR measurements are shown in Fig.7-9. The 1840cm^{-1} peak was observed in all samples containing Ru but not in La100. On the other hand, the samples containing La had peaks at around 1420 and 890cm^{-1} . The height of each peak corresponded to the ratio of Ru/La. That means the Ru component and the La one are supposed to be mechanically mixed without any chemical reactions. As for the 1700cm^{-1} peak, which corresponds to C=O vibration, its maximum was observed in the Ru100 gel dried at $150\text{ }^{\circ}\text{C}$ and it was decreasing with increasing the temperature. Since the peak around 1200cm^{-1} was observed in the Ru100 gel dried at $150\text{ }^{\circ}\text{C}$, the peak should correspond to organic elements in the gel. When heated up to 175 and $200\text{ }^{\circ}\text{C}$, the peak around 1200cm^{-1} disappeared. On the contrary, the peaks originated from La compounds showed small changes against the temperature change, suggesting that the organic elements from La compounds tend to remain at increasing the temperature whereas the organic elements from Ru compounds tend to decompose easily.

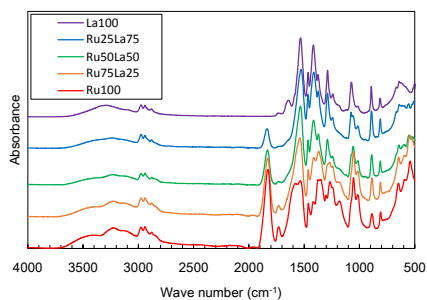


Fig.7 FT-IR measurement of
Ru-La gels dried at 150 °C

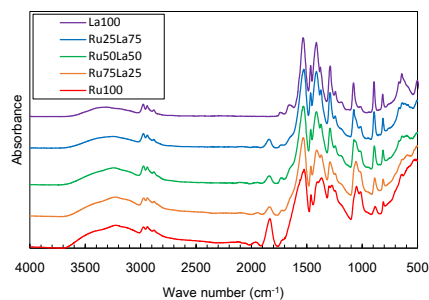


Fig.8 FT-IR measurement of
Ru-La gels dried at 175 °C

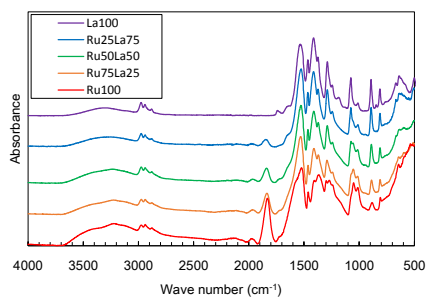


Fig.9 FT-IR measurement of
Ru-La gels dried at 200 °C

3.4 HE-XRD

The measured data of the 200°C dried Ru-La gels with HE-XRD were analyzed by a PDF method. The $S(Q)$ data of them is shown in Fig.10. In the case of the La100 gels dried at 150 or 175 °C decomposed during the HE-XRD measurement. The $S(Q)$ peaks were broad on the whole, but each peak became sharp with increasing the La ratio, which indicated the existence of molecular crystal in La compounds. $T(r)$ is shown in Fig.11-13. The height of peaks around 2 and 3 Å increased with increasing Ru ratio. In the Ru rich gels, the peak around 2.5 Å was getting higher as the drying temperature increased, whereas the peak around 2.5 Å was getting lower. That could be attributed to reduction of the distance between a R atom and an oxygen one with removing of organic elements by the decomposition. The peaks at 2.5 and 4.1 Å in the La rich gels were high and relatively stable when the drying temperature changed. It is considered that the organic elements in La gels don't decompose at the temperature from 150 to 200 °C.

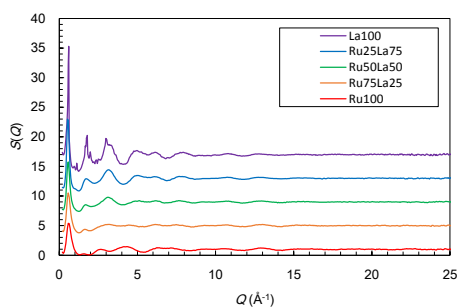


Fig.10 Structure factor $S(Q)$ of
Ru-La gels dried at 200 °C

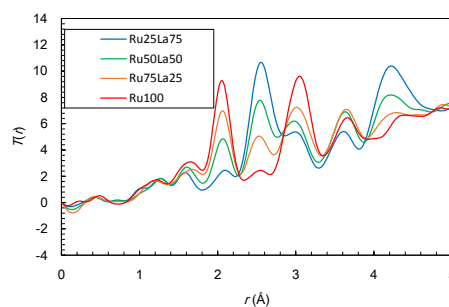


Fig.11 Total correlation $T(r)$ of
Ru-La gels dried at 150 °C

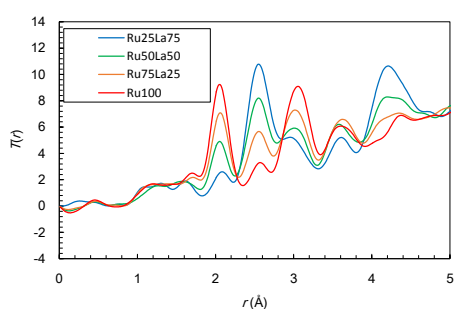


Fig.12 Total correlation $T(r)$ of
Ru-La gels dried at 175 °C

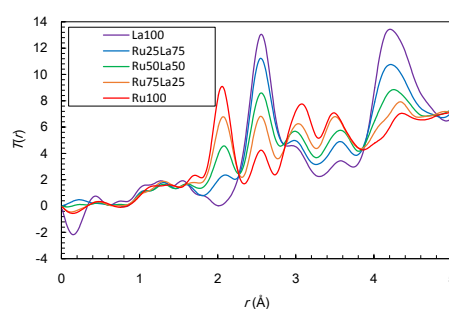


Fig.13 Total correlation $T(r)$ of
Ru-La gels dried at 200 °C

3.5 Summary

I summarize the results. (1) The Ru-La gels dried at 150 or 175 °C had viscous properties at around the individual drying temperature and 170 °C. (2) It was observed that the mass of a gel started to decrease at around each drying temperature. This mass reduction could be attributed to removing of propionic acid from a gel. (3) Organic ligands coordinated to Ru atoms started to decompose at the temperature between 150 and 175 °C, while organic elements in a La gel didn't decompose at least until 200 °C. The removal of coordinated ligands from a Ru compound caused the gels to harden.

4. Conclusion

The objective in this research is to investigate adaptability for Ru-La-O precursor gels for direct imprinting, especially we focused on the compositional effect of a Ru-La binary system on imprinting property. From the viscoelastic measurement, the increase of $\tan\delta$ which is the ratio of a loss elastic modulus G'' to a storage elastic modulus G' was observed in some temperature range. These conditions, where the increase of $\tan\delta$ was observed, coincided with those for good imprinting to form clear patterns. It is suggested that the deformation of a gel is triggered by the removing of propionic acid from a gel. However, the decomposition of Ru ligands, which occurred in the imprinting temperature,

hindered the deformation of a gel because of their stiffening. In order to prevent the Ru gel from being stiffened, addition of La compounds were found very effective, because the La gel is consisted of molecular crystals which strongly hold organic elements to give the Ru-La gels a viscous property under 200 °C.

Based on the result of this work, a general rule which gives an oxide precursor gel the viscous property could be deduced: a gel material, in which the remaining solvent can be removed while keeping organic elements inside it, could be imprinted. I hope this work would play a role to increase imprint competitive materials.

References

- [1] T. Kaneda et al., *J. Mater. Chem. C*, 2014, vol. 2, pp40-49.
- [2] K. Nagahara et al., *Ceramics International* 42, 2016, pp7730-7741.