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Magnetic and X-Ray Diffraction Studies on Dextran Iron-Oxide Magnetic Fluid

I. Sakamoto, H. Hasegawa, T. Hanaichi, I. Oguro* and S. Maruno

Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466, Japan

** The Institute for Solid State Physics, University of Tokyo, Minato-ku, Tokyo 106, Japan*

Abstract. Two types of dextran iron-oxide complexes (ATDM and CMDM), magnetic fluid applicable to the contrast agent of magnetic resonance imaging of living body, have been synthesized without surfactant. We have measured temperature dependences of magnetization and X-ray diffraction of ATDM, CMDM and also magnetite fine-particles as a reference substance in atmospheres of air and helium up to 840°C. The results are discussed in view of the reaction of magnetite core with the surrounding gas and products formed by thermal decomposition of the dextran molecules which is directly bonded to magnetite core of the complexes.

1. INTRODUCTION

Recently fine-particle iron-oxide magnetic complex has been paid much attention in numerous medical uses. For examples, they can act as a contrast agent in magnetic resonance imaging technology and localized heating agent by an RF generator in hyperthermia medical treatment. To apply the magnetic complex to living body, it is essential that the magnetic complex is non-toxic and is stabilized with biocompatible polymer. Two kinds of iron-oxide complexes with components of dextran, dextran derivatives and nanometer particles of Fe_3O_4 cores, which are expected to meet the above requirements, have been synthesized by the present authors[1-3]. One is the alkaline-treated dextran magnetite (ATDM) and the other is the carboxymethyl dextran magnetite (CMDM). In ATDM alkaline-treated dextran molecules which have the D-gluconic acid residue having $-\text{COO}^-\text{Na}^+$ group at the terminal of dextran are linked to iron ion on magnetite core. On the other hand, in CMDM the magnetite core is linked with dextran derivatives in which the hydroxy group ($-\text{OR}$) on a D-glucitol terminal of the dextran reduced by sodium borohydride is replaced by $-\text{OX}^-\text{Na}^+$ and some of hydroxy groups joined to the carbons 2, 3 and 4 in D-glucopyranose are also replaced, where $\text{X} = -\text{CH}_2\text{COO}^-$, the carboxymethyl group. Because the alkaline-treated dextran and carboxymethyl dextran are bonded to the Fe_3O_4 cores through the carboxyl group $-\text{COO}^-$, the core of CMDM is expected to be more firmly covered with the dextran derivative than that of ATDM with the dextran.

We have intended the systematic investigation of biological, medical, chemical and physical properties of these dextran magnetites to reveal an applicability of them to living body. We have reported the results on chemical, medical properties in previous papers[1-3]. In the present work we report the thermal stability of dextran magnetite in high temperatures in atmospheres of air and He by magnetization and X-ray diffraction measurements.

2. EXPERIMENTAL

Alkaline-treated dextran and carboxymethyl dextran were prepared from dextran molecules with molecular weight of 4200. ATDM and CMDM were synthesized in pH controlled aqueous solution of a mixture of ferrous chloride and ferric chloride and alkaline-treated dextran and carboxymethyl dextran, respectively, using Molday's method [4]. CMDM in which about 20% of the $-\text{OR}$ groups are replaced by $-\text{OX}^-\text{Na}^+$ was used in the present work. The nanometer size dextran magnetite was selected by a successive use of filtration and centrifugation. X-ray diffraction patterns from ATDM and CMDM were measured by a standard powder diffractometry. The particle diameter was determined by Scherrer's equation using (311) plane to be 6-10 nm. Diffraction patterns of ATDM and CMDM were found to agree with that of standard magnetite particles. Magnetization were measured by a vibrating samples magnetometer in atmospheres of air and He. Temperature dependence curve at a field of 5kG was obtained in increasing temperature up to 850°C and in decreasing temperature down to room temperature. The rate of temperature change was 20°C/min.

3. RESULTS AND DISCUSSION

Figure 1 shows the temperature (T) dependence of magnetization (M) of Fe_3O_4 particles(a), ATDM (b) and CMDM (c) measured in an atmosphere of He. Figure 1(a) shows that the two curves of M for the Fe_3O_4 particles in increasing and decreasing temperatures agree and that the Fe_3O_4 particles are quite stable in the atmosphere of He up to a temperature as high as 800°C. Figure 1 (b) shows that the magnetization of ATDM decreases initially, take maxima at 230°C and 370°C and reaches to zero at 580°C with increasing T . As T increases further, the M curve shows a hump at about 700°C and again reaches to zero at 790°C. When T decreases from 840°C, the magnetization increases sharply at 790°C and tend to saturate below 600°C. The value of M at room temperature is $1.9\mu_B/\text{Fe}$, which nearly equals to that of bulk Fe. Figure 1(c) shows that the variation of M for CMDM in increasing T is similar to that of ATDM. But the different temperature dependence of M was

Figure 1: Magnetizations of Fe_3O_4 particles(a), ATDM and CMDM in the atmosphere of He in increasing (the rightward arrow) and decreasing (the leftward arrow) temperatures.

observed in decreasing T ; first the M curve begin to increase at 720 $^{\circ}\text{C}$ lower than that of ATDM by 70 $^{\circ}\text{C}$ and second it again increases drastically at about 200 $^{\circ}\text{C}$.

Dextran is known to dehydrate at about 200 $^{\circ}\text{C}$ and to decompose into a mixture of carbohydrate, carbon oxide and carbon at 300 $^{\circ}\text{C}$ -400 $^{\circ}\text{C}$. If the dextran in DM is dehydrated and decomposed, then the state of Fe ions on the core surface of DM should be affected. Thus we can speculate that the first maximum at $T=230^{\circ}\text{C}$ in the M curve for ATDM is ascribed to the dehydration and the second maximum at $T=370^{\circ}\text{C}$ to the decomposition of the dextran. The hump at $T=700^{\circ}\text{C}$ indicate that the products formed by thermal decomposition of dextran begin to reduce the core state from Fe_3O_4 to $\alpha\text{-Fe}$. Since the reduction is accelerated with increasing T , the concentration of $\alpha\text{-Fe}$ in the core increases in higher temperatures. From this, we can understand that the M curve in decreasing T agree practically with that of bulk Fe. As mentioned above, CMDM contains more carbon atoms in the neighborhood of the core than ATDM. Therefore carbon atoms in CMDM are used not only to reduce the Fe_3O_4 core, but also to react with the reduced $\alpha\text{-Fe}$ core and to make a solid solution of $\text{Fe}(\text{C})$. The phase diagram of Fe-C system shows that the eutectic reaction which divide the $\gamma\text{-Fe}(\text{C})$ phase into a mixture of the $\alpha\text{-Fe}$ and Fe_3C phases occurs at $T=723^{\circ}\text{C}$ and the carbon concentration of 0.08 at%, where the $\gamma\text{-Fe}(\text{C})$ state is nonmagnetic while the Fe_3C state the ferromagnet with the Curie temperature of 210 $^{\circ}\text{C}$. The M curve above 720 $^{\circ}\text{C}$ indicate that the core is in the $\gamma\text{-Fe}(\text{C})$ state. Thus when T reaches to 723 $^{\circ}\text{C}$ from higher temperature, the phases of $\alpha\text{-Fe}(\text{C})$ and Fe_3C are formed by the eutectic reaction. This is the reason why we observed the rapid increase of M at 720 $^{\circ}\text{C}$ and also the drastic increase in M at about 200 $^{\circ}\text{C}$. X-ray diffraction measurements of DM samples used for magnetization measurement supported our view clearly; the diffraction pattern for ATDM contain only the $\alpha\text{-Fe}$ lines and those of CMDM a mixture of $\alpha\text{-Fe}$ and Fe_3C lines.

Figure 2: Magnetizations of Fe_3O_4 particles(a), ATDM and CMDM in the atmosphere of air in increasing (the rightward arrow) and decreasing (the leftward arrow) temperatures.

Figure 2 shows the temperature dependence of M for Fe_3O_4 particles(a), ATDM(b) and CMDM(c) in an atmosphere of air. Figures 2(a) shows that the Fe_3O_4 particle loses its magnetization on exposure to air at a temperature as high as 800 $^{\circ}\text{C}$. This indicates that Fe_3O_4 particles are completely oxidized in air and changed to $\alpha\text{-Fe}_2\text{O}_3$ particles. Figure 2(b) shows that the M curve in increasing T does not show a hump above 700 $^{\circ}\text{C}$. This implies that the oxygen in the atmosphere prevents the Fe_3O_4 core from reducing by the products formed by thermal decomposition of dextran and that it preferably oxidizes these products instead. In fact, when we began to decrease T after arriving at 780 $^{\circ}\text{C}$ in measuring M for ATDM in the atmosphere of air, we found that the M curve agrees qualitatively with that of Fe_3O_4 shown in Fig. 1(a). The M curve in decreasing T shown in Fig. 2(b), which has similar temperature dependence to that of ATDM in the He atmosphere, indicates that Fe_3O_4 in the core are reduced to $\alpha\text{-Fe}$ at temperatures as high as 800 $^{\circ}\text{C}$. Figure 2(c) shows that the core state of CMDM is in the $\gamma\text{-Fe}(\text{C})$ state at the highest temperature and divided into the $\alpha\text{-Fe}(\text{C})$ and Fe_3C states at the eutectic temperature of 723 $^{\circ}\text{C}$. This Fe_3C is oxidized by the oxygen in the atmosphere of air with decreasing temperature from 723 $^{\circ}\text{C}$. This is the reason why the M curve does not have a abrupt increases at 200 $^{\circ}\text{C}$.

4. CONCLUSION

we have found that the dextran and its derivative of DM prevent the core of DM from oxidizing in the environment where Fe_3O_4 particles is easily oxidized. This is the important point for application of DM to the contrast agent of magnetic resonance imaging for living body.

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