The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

A Study on the Fabrication of Fe-Co Magnetic Fluid from the Waste Pickling Liquor of Steel

Young Sam Kim[1] , Jong Heon Lee[2]

[1), 2)]Department of Metallurgical Engineering Dong-A University, Pusan, Korea

yskim@daunet.donga.ac.kr

ABSTRACT

This paper describes on the fabrication of Fe-Co hydrophilic magnetic fluids from the waste pickling liquor of steel. By adding with HNO_3 in the waste liquor oxidation is proceeded from Fe^{2+}ion to Fe^{3+}ion at 60℃ with air blowing. Ultra-fine Co-ferrite particles with the mean particle size of 50 Å were produced at pH 12 after adjusting the ratio of Fe^{3+}/Co^{2+} = 7/3(wt%) and Fe-Co particles with the mean particle size of 94Å were produced by reducing the Co-ferrite particle with H_2 at the temperature of 500 ℃. After triple adsorption of oleic acid dodecyl benzene sulfonate(D.B.S.) and tetra methyl ammonium(T.M.A.) ions on the surface of Fe-Co particles Fe-Co hydrophilic magnetic fluid was produced by dispersing the Fe-Co particles in ethylene glycol solution. The magnetization of the Fe-Co hydrophilic magnetic fluid increased with increasing the Fe-Co concentration. The magnetic fluid containing 70 % (g/cc) Fe-Co showed 73 emu/g in magnetization at the magnetic intensity of 10 kOe.

1. INTRODUCTION

A steel generally react with oxygen in the atmosphere to form oxides, usually found on the surface of steel. When the oxides is embedded in steel products during processing, the oxides act as inclusion. Tensile strength decreases with stress concentration at steel-inclusion interface, it is subject to failure[1]. As the countermeasure, in process of cold working, in order to descale the oxides on the surface of steel, pickling is one of main way to remove the oxides. The pickling is widely used to descale the oxides on the surface of steel in the steel shaping industries before shaping. However, in the process of pickling, the waste pickling liquor of steel mainly enriched with iron and other heavy metal ions is produced. If the waste pickling liquor of steel is discharged, problems with water pollution take place. In a way of solution to the problems mentioned over, we tried to make Fe-Co[2] having the highest magnetic susceptibility among magnetic fluids repoted until now from the waste pickling liquor of steel.

2. MATERIALS AND METHOD

Fig.1. shows the flow chart for the fabrication of Fe-Co magnetic fluid. The waste pickling liquor of steel was mainly composed of Fe^{2+}ion, Fe^{3+}ion and Clion. Table.1 shows chemical compositions of the waste pickling liquor. Supposing that the other heavy metal ions is ignored in their extremely small quantities, about 8.6wt% of excessive chlorine is soluble in the

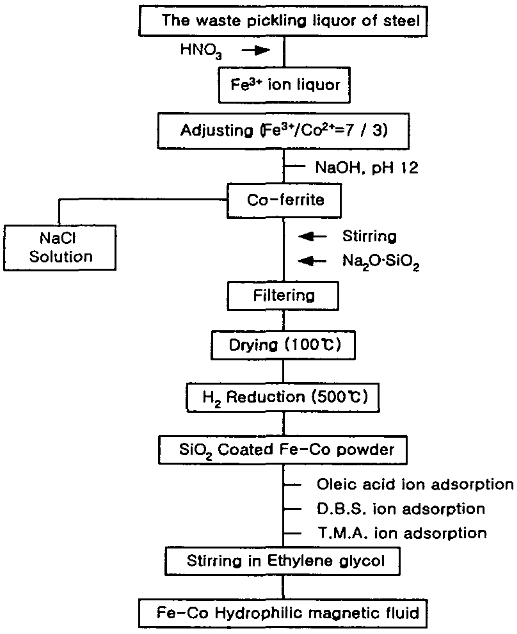

Fig. 1. Flow chart of experimental process

waste pickling liquor of steel by adding HNO_3 and air blowing in the waste liquor, oxidation can proceeded from Fe^{2+}ion to Fe^{3+}ion.

Table.1.Chemical compositions of the waste pickling liquor(wt%) Kuk Dong Metal Co (Pusan, Korea)

Fe^{2+}	Fe^{3+}	Cl	Mn	Al	Cr	SiO_2	Ni	Mg
8.58	0.32	20.1	0.04	0.0025	0.0050	0.0033	0.0010	0.004

Ultra-fine Co-ferrite particles[3)] were produced at pH 12 after mixing Co^{2+} ion of the ratio of Fe^{3+} /Co^{2+} = 7/3 in the oxidized pickling liquor (Fe^{3+}). The Co-ferrite particles are coated with silica in order to inhibit sinter growth of the particles at reduction temperature. We used Fe-Co power as dispersed particles in liquid; it is well known as the material having a largest saturation magnetization among ferromagnetic materials. Magnetic fluid is not separated of liquid and solid from slurry state. The size of ferromagnetic super ultra fine particles is 100 times bigger than that of solvent molecle dia so that they prevented themselves a flocculation as to keep a proper distance from each other due to Brown motion caused by random collisions and elastic repulsive power of the absorbed surfactant.

Table 2. Typical ferromagnetic materials and its theoretical saturation magnetization

Ferromagnetic materials	Fe_3O_4	Fe	Co	Fe-Co[2)]
Saturation magnetization (emu/g)	92	218	161	240

Eventually magnetic field affects the whole fluid in macroscopic view, and thus the magnetic fluid has property of attractive and magnetic force even though it is a slurry. In order to maintain a magnetic characteristic, the particles must exist as a dispersed state without cohesive reaction. The surface activator act as safely dispersed the particles. Surfactants coated Fe-Co powders are stirred by a shaker(American, Red devil co., Model 5400-02, 1030rpm) in ethylene glycol medium for 2 hours. We examined the dispersing stability by measuring the height of sinked particles in the mass cylinder (vol.100cc, height 16cm). Fe-Co particles having the mean particle size of 94Å with the distribution of 30~290Å3), were triple adsorbed oleic acid , dodecyl benzene sulfonate (D.B.S) and tetra methyl ammonium(T.M.A.) ions and thereby hydrophilic magnetic fluid with high boiling point and low vapor pressure could be made by dispersing them into the ethylene glycol by shaking for 2 hours with Shaker(Red Devil company, U.S.A, Model 5400-02, 1032rpm). The magnetic property was measured by Gauss meter (Yokogawa company, Japan, Model 3251) and VSM (Vibrating Sample Magnetometer, U.S.A, Model LDJ-

9600), and the particle size was measured by SEM(Hitachi, S-2400), respectively.

3. DISCUSSION AND RESULTS

3-1 The oxidation of waste pickling liquor of steel.

Influence of the oxidation of waste pickling liquor with temperature is shown in Fig.2. By adding with 1% HNO_3 in 200g of waste liquor, oxidation is proceeded from Fe^{2+}ion to Fe^{3+}ion at 60℃ with air blowing rate of 100cc/sec. for 1 hr. The reaction equation[4] is as follows.

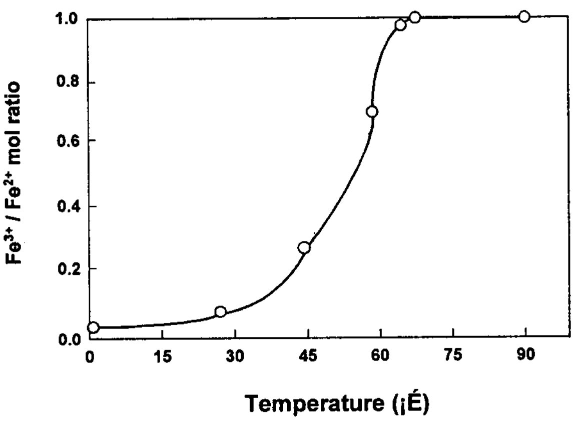

Fig.2. Effect on the oxidation of the waste pickling liquor with temperature

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + 2H_2O + NO \text{ ---- } (1)$$

Co-ferrite particles were produced at pH 12, after adding Co ion to Fe^{+3}/Co^{+2} =7/3 (wt) into the oxidized waste pickling liquor of steel. The fabrication of ultra fine Fe-Co particles is as follow.

$$Fe^{3+} + Co^{2+} + 2(OH)^- = \text{Co-ferrite} + H_2O \text{ ------- } (2)$$

$$Na_2O{\cdot}SiO_2 + 3H_2O \rightarrow 2NaOH + Si(OH)_4 \text{ ---- } (3)$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \text{ ------------------ } (4)$$

$$\text{Silica coated Co-ferrite} + H_2 = \text{Silica coated Fe-Co} + H_2O \text{ --------------------------------- } (5)$$

Ultra-fine Co-ferrite particles, with the mean particle size of 50 Å, were produced at pH 12 after mixing Co^{2+} ion of the ratio of Fe^{3+}/Co^{2+} = 7/3 in the oxidized pickling liquor (Fe^{3+}).

Co-ferrite was deposited and separated from the waste pickling liquor.

Table.3. Residual metal content in the filtrate. (ppm)

Fe	Mn	Cu	Cr	Zn	Co
1.52	0.24	0.12	0.08	0.32	1.30
*Tolerance limit of the Water Pollution Prevent Act.(korea)					
*10	*10	*3	*2	*5	-

Table.3 shows the residual metal content in the filtrate, the content of heavy metal in the filtrate remained is less than the tolerance limit of the Water Pollution Prevent Act. So, the filtrate makes clean excellently. The Co-ferrite particles is coated with silica in order to inhibit sinter growth of the particles at reduction temperature of 500℃ as eq.(5). We used Fe-Co(30%)[2] power as dispersed particles in liquid; it is well known as the material having the largest saturation magnetization among ferromagnetic materials. The Fe-Co(Co;30%) exhibits saturation magnetization 154 emu/g at the magnetic field strength of 10 kOe. (the mean particle size of 94 Å).

3-2. The properties of ethylene glycol-based magnetic fluid.

Table 4. Properties of magnetic fluid medium[5]

Item / Medium	Chemical formula	Specific gravity	Viscosity (cp, 25℃)	Vapor Pressure (20, mmHg)	Boiling point (℃)
Water	H_2O	1	0.8904	17.535	100
Ethylene	$C_2H_6O_2$	1.1155	17.6	0.05	197.85

Due to the higher boiling point and lower vapor pressure of ethylene glycol than water, the ethylene glycol base magnetic fluid prevented the evaporation of medium and hydrophilic. The life span of the circomference apparatus composed of mild steel components was remarkably extended due to the high corrosion resistance of ethylene glycol.

Fig.4 shows the dispersing stability of Fe-Co magnetic fluid against the holding time.

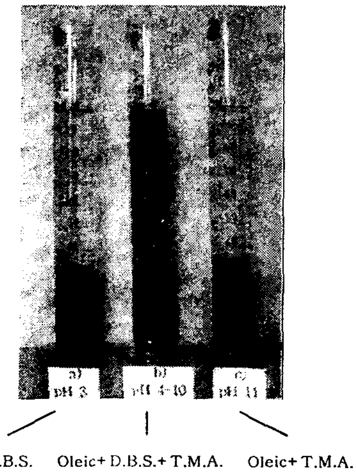

Photo. 1. Effect of surfactants on dispersion stability of Fe-Co suspension. (white: ethylene glycol, black: Fe-Co)

It reveals that the suspension of Fe-Co ultra fine particle surface coated with Oleic acid and D.B.S ions is separated into two phases of liquid and solid with time. On the o:her hand the particle surfaces coated with triple layers of Oleic acid , D.B.S. and T.M.A. ions as a surface activator kept permanently stable dispersion under the atmosphere.

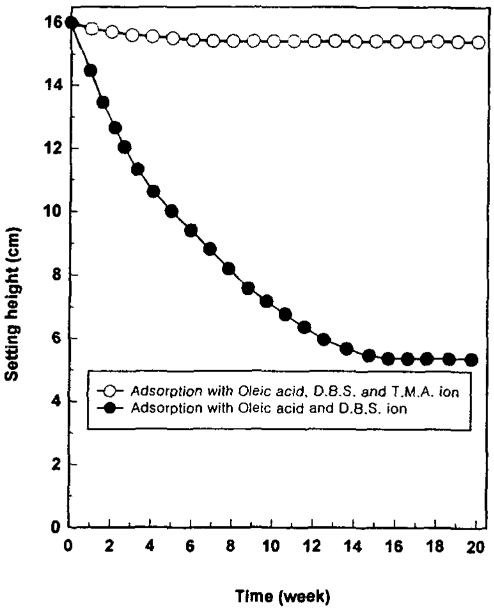

Fig. 4. Effect of surfactant on dispersing property of magnetic fluid.

Here, the concentration ratio of Oleic acid and D.B.S. are 1 mole against 1 kg of Fe-Co particles respectively and that of T.M.A is 0.15 against 1mole of D.B.S[6].

Fig.5 shows the change of magnetic susceptibility of magnetic fluid according to Fe-Co content. The magnetic susceptibility increases with increasing Fe-Co content. When Fe-Co concentration is 70%(g/cc), magnetization shows 73 emu/g (at 10 kOe). This result may be expressed by Eq.(6)

$$\sigma = \rho_2(\sigma_s/\rho)(\rho-\rho_1)/(\rho_2-\rho_1) \quad (6)$$

ρ, ρ_1 and ρ_2 are densities of magnetic fluid, medium, and dispersion particle respectively and σ_s is magnetization of dispersion particle. This is very similar to the Shimoiizaka's result[7] using Kerosene base magnetic fluid.

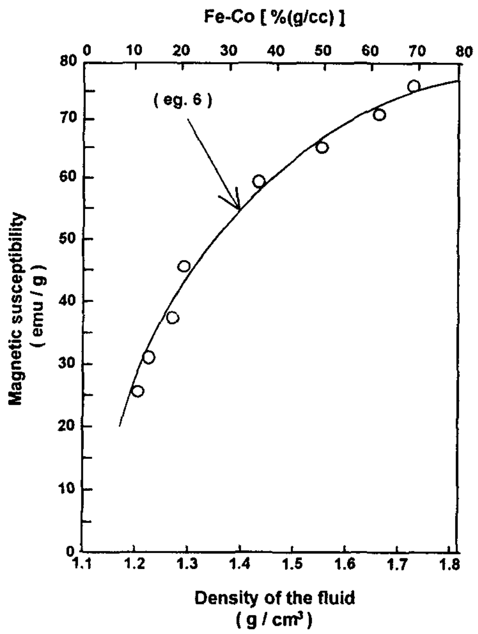

Fig.5. Magnetic susceptibility of the Fluid versus Fe-Co content.

4. SUMMARY

This study describes the fabrication of the Fe-Co hydrophilic magnetic fluid from the waste pickling liquor of steel.

The results are as follows:

1) The waste pickling liquor was oxidized from Fe^{+2} to Fe^{+3} by HNO_3 and Air(O_2) reaction. Ultra-fine Co-ferrite particles, with the mean particle size of 50 Å[2], were produced at pH 12 after mixing Co^{2+} ion of the ratio of $Fe^{3+}/Co^{2+} = 7/3$ in the oxidized pickling liquor (Fe^{3+}) . The Co-ferrite particles is coated with silica in order to inhibit sinter growth of the particles at reduction temperature.

2) When the silica coated Co-ferrite particle was reduced in H_2 at 500℃ for 6 hrs, the magnetization value of reduced Fe-Co particle decreased with increasing the quantity of the silica. The silica coated Fe-Co particle(SiO_2/Fe-Co=3.6wt%) showed following properties, e.g., high oxidation resistance below 150℃, magnetization value of 154.4 emu/g at 10 kOe and the size range between 30 and 290Å.(mean particle size of 94Å)

3) Ultrafine Fe-Co particles, mean particle size of 93Å in diameter, are adsorpted triple layers of oleic acid, D.B.S. and T.M.A ions, thereby anti-evaporable hydrophilic magnetic fluid with high magnetic susceptibility could be made by dispersing them into the ethylene glycol.

4) The magnetization of the Fe-Co hydrophilic magnetic fluid increased with increasing the Fe-Co concentration. The magnetic susceptibility of the fluid [70 % (g/cc) of Fe-Co] is 73 emu/g at the magnetic intensity of 10 kOe(room temperature).

References

1) Y.S.Kim;International Journal of The Society of Materials Engineering for Resources, Vol.7, No.1, (1999), P130

2) Cullity: Introduction to Magnetic Materials, Addison-Wesley Publishing Com. (1972), P146

3) Im Jae Sung, Kang Shin Woo, Kim Young Sam; Industrial Technology Research Center College of Engineering, Dong-A Univ. Vol.3, No.2, (1998), P229

4) Young Sam Kim et al.: J. of the Korean Inst. of Metals. Vol.27No.9, P801 (1989)

5) Ki-soo Kim et al.; Encyclopaedia Physica Chemic, Chang-josa Korea (1976) P750

6) Fujita, B.Jeyadevan et al.; Powder and Powder Metallurgy, Japan, 38, (1991) P695

7) Shmoiizaka et al.; New Magnetic Materials, Kogyo Chosakai Tokyo Japan (1981) P303