Floating Zone Refining of Iron under Reduced Pressure with Dynamic Hydrogen Flow

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High purity iron was prepared by floating zone refining under reduced hydrogen pressure with dynamic hydrogen flow. Commercial 99.999% iron was used as the starting material. The residual resistivity ratio and glow discharge mass spectrometry were used for purity evaluation of zone-refined iron. The residual resistivity of the starting material was 1000 and that of zone refined iron was 11000. The floating zone refining under dynamic hydrogen flow is efficient in removing gaseous elements and for the preparation of ultra high purity iron. The residual resistivity ratio values show good correspondence with the chemical purity.

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1. Introduction

Floating zone refining has been widely used as a purification method of high purity iron on a laboratory scale.¹⁾ For example, Isshiki and Igaki^{2,3)} prepared ultra high purity iron which had residual resistivity ratio (hereafter *RRR*) larger than 10^4 by an anion exchange method followed by floating zone refining. In general, static reduced pressure hydrogen, atmospheric hydrogen flow or ultra high vacuum atmosphere have been used for the floating zone refining of iron to prevent contamination and/or to eliminate gaseous impurities. Some interstitial impurities have significant effect on physical properties of iron, therefore, elimination of them is one of the most important factor to study inherent properties of high purity iron.

Recently, we have developed an apparatus for floating zone refining under reduced pressure hydrogen atmosphere by supplying fresh purified hydrogen, expecting that the dynamic process is probably effective to remove gaseous elements. Copper has been successfully purified by floating zone refining under a continuous flow of hydrogen at a reduced pressure, and the *RRR* value of the refined Copper, 36000, is the highest reported value for polycrystals annealed in hydrogen.⁴⁾

In this study, we have applied the floating zone refining under a continuous flow of hydrogen at a reduced pressure for the preparation of ultra high purity iron, and then estimated the purification effect. Recently, a glow discharge mass spectrometry (hereafter GDMS) has widely been used for purity evaluation of high purity materials, which is capable to analyze almost all elements simultaneously. Comparison between the GDMS results and the *RRR* is also valuable to examine validity of purity evaluation by *RRR*.

2. Experimental

Commercial high purity iron with nominal purity of 99.999 mass% was used as a starting material for floating zone refining. The sample rod of 7 mm in diameter was elec-

trochemically polished prior to floating zone refining. The length of the molten zone was the same as the rod diameter and the length of zone pass was 150 mm. The rate of the zone pass was 2 mm/min and 5 mm/min under hydrogen and vacuum, respectively. A schematic diagram of the apparatus for floating zone refining was shown in a previous paper.⁴⁾ Induction heating with a 400 kHz and 20 kW power supply was used, and the turbo-molecular pump was applied as a main pump and the base pressure before melting was typically 10^{-4} Pa. Hydrogen pressure was kept at 20 kPa for the first and second passes, and 0.7 Pa for 3rd to 5th passes, then zone refined under vacuum for 6th to 10th passes. The reason for the step under 20 kPa hydrogen was to suppress splash of melt and evaporation loss of matrix. Melting under 0.7 Pa hydrogen was adopted to remove metallic impurities with high vapor pressure where evaporation loss of matrix was much smaller than melting under vacuum condition.

Specimens for $RRR_{H,4.2K}$ measurements were 0.5 mm wires formed by cold drawing, electrochemically polished before annealing. The wires were placed in a quartz tube with an inner diameter of 5 mm during annealing, and electrochemically polished again to eliminating Si contamination by the dry hydrogen treatment.³⁾ Platinum wires with diameter of 0.1 mm were welded to the annealed wire specimen as electrode. Distance between the voltage electrodes was typically 100 mm.

Resistance of the refined iron was measured both at 4.2 K and at room temperature by a four-point probe method. A digital voltmeter with sensibility of 10 nV and a stabilized dc current source with a maximum current of 2 A were used. A longitudinal magnetic field of 60 kA/m was applied to minimize the magneto-resistance effect, and the measured resistances at 4.2 K were extrapolated to 0 K to eliminate T^2 term of the temperature dependence of resistance³⁾ to evaluate $RRR_{H,0K}$ values.

Glow discharge mass spectrometry (hereafter GDMS) was used for analysis of metallic impurities. Three different sections of zone-refined iron, which were taken from the refined rod for $RRR_{H,0K}$ profile measurements, were used to evalu-

uate the chemical purity and the refining effect. The starting material 5N iron was also analyzed by GDMS to compare the refining effect and to examine the possibility of contamination during floating zone refining procedure.

For oxygen analysis by the inert gas fusion method, a 5N iron rod with initial oxygen content of 98 mass ppm was refined for two passes under a continuous flow of hydrogen at a reduced pressure of 20 kPa for the leveling of oxygen content, and then zone refined for 10 mm with at a velocity of 2 mm/min under various hydrogen pressures with and without dynamic flow. An activation analysis of oxygen⁵⁾ was also carried out for comparison. Samples for activation analysis were cold rolled and electrochemically polished before analysis. Bombardment with ³He particles at 20 MeV for 3.6 ks was used for activation analysis and the ¹⁸F decay curve was measured and compared with that of the standard sample. The procedure of activation analysis was fundamentally the same as in Ref. 5).

3. Results and Discussion

3.1 Floating zone refining of iron under reduced hydrogen atmosphere at a reduced pressure

Figure 1 shows the RRR profile of the floating zone refined iron. The RRR values of refined iron are plotted against the normalized position of the sample, X/L where L is the zone refined length and X the distance from the starting point of the zone melting. The open marks are the measured values at 4.2 K under longitudinal magnetic fields ($RRR_{H,4.2K}$). The solid marks are the extrapolated values to 0 K to eliminate the T^2 term of the temperature dependence of resistance.³⁾ The RRR of the annealed starting material is shown by an arrow for comparison.

Purification by segregation of impurities is clearly demonstrated by Fig. 1. The highest $RRR_{H,0K}$ value of 11000 is obtained in a range of $X/L = 0.15$ to 0.4 . Most metallic impurities have equilibrium distribution coefficients, k_0 , smaller than unity,⁶⁾ therefore, the measured $RRR_{H,0K}$ profile as shown in Fig. 1 is reasonable. In addition, the $RRR_{H,0K}$ of the end side of the sample ($X/L = 0.9$) is still much higher than that of the starting material, which indicates that the melting under reduced pressure and vacuum is effective to remove relatively high vapor pressure impurities for example Cl compared with iron.

Table 1 shows GDMS results of starting material and refined iron. Chlorine content of starting material is relatively high, however, that of refined iron is extremely low even at $X/L = 0.9$. Elimination of Cl by the floating zone refining process is clearly seen in Table 1, corresponding to the RRR profile in Fig. 1. Elimination of volatile elements, for example S, Cl, Cr, Cu, Zn, As, Se, In, Te and Pb, are clearly demonstrated. The equilibrium distribution coefficient of Cr is also close to unity, however, Cr content of the zone refined iron is significantly lower than that of starting 5N iron even in the near end part, $X/L = 0.9$, which is due to refining by vapor pressure difference between iron and Cr.

Segregation of Co and Ni are not clearly seen in Table 1, indicating that the equilibrium distribution coefficients of Co and Ni are close to unity ($0.7 \sim 0.8$).⁶⁾ In addition, vapor

Fig. 1 Residual resistivity ratio profile of floating zone refined iron. Specimens were cold worked and annealed in dry hydrogen at 1073 K for 86.4 ks. Open marks: measured at 4.2 K, Solid marks: extrapolated values to 0 K.

Table 1 GDMS analysis results of floating zone refined iron (mass ppm).

Elements	Starting material	$X/L = 0.2$	$X/L = 0.5$	$X/L = 0.9$
B	0.005	0.002	0.003	0.1
C	0.3	0.2	0.1	0.1
Na	0.01	0.004	0.003	0.02
Al	0.006	0.06	0.2	1.8
Si	<0.08	<0.005	<0.003	<0.01
P	0.013	0.012	0.003	0.004
S	0.3	0.003	0.004	0.005
Cl	60	0.001	0.003	0.4
Ti	0.25	0.17	0.07	0.5
Cr	0.04	0.005	<0.003	0.008
Co	0.6	0.6	0.7	0.7
Ni	0.1	0.08	0.08	0.1
Cu	0.6	<0.006	0.006	0.01
Zn	0.8	<0.02	<0.01	0.01
As	1.3	<0.004	<0.005	<0.07
Se	3.6	<0.04	<0.05	<0.04
Sr	0.28	0.25	0.08	0.22
Zr	0.05	<0.006	<0.008	0.03
Mo	0.2	0.4	0.6	3
Ag	0.3	0.1	0.04	0.05
In	0.04	<0.006	<0.009	<0.009
Te	0.1	<0.01	<0.01	<0.01
W	<0.003	<0.003	0.004	0.01
Ir	0.08	0.09	0.1	0.15
Pt	0.02	0.01	0.004	0.005
Pb	3	<0.008	<0.01	<0.01
Purity (mass%)	99.993	99.9998	99.9998	99.9992
$RRR_{H,0K}$	1000	11000	10000	4000

F, Na, Mg, K, Sc, V, Br, Rb, Y, Rh, Pd, Sn, Sb, Ru, I, Au, Th, U: not detected for all samples. Mn < 0.02 mass ppm, Cd < 0.5 mass ppm, Ga < 0.06 mass ppm and N < 0.1 mass ppm for all samples.

pressure difference between these elements and Fe are small, therefore, purification by evaporation is not effective. The initial concentrations of Co and Ni are among the most important factors to prepare ultra high purity iron by this floating zone refining process.

The evaporation of matrix causes enrichment of refractory metals, such as Mo which has much lower vapor pressure than Fe. Although Al has much higher vapor pressure than Fe at the same temperature, concentration of Al is higher than that of starting material, as seen in Table 1. It suggests that there is a possibility of Al contamination during refining or following the procedure.

Near the bottom line of Table 1, chemical purity of analyzed samples for almost all impurities are summarized and compared with $RRR_{H,0K}$. Chemical purity is qualitatively in good agreement with the $RRR_{H,0K}$ values. Quantitative comparison between electrical purity and chemical purity by GDMS will be discussed in §3.3.

3.2 Removal of oxygen

Table 2 shows the summary of oxygen analysis by the inert gas fusion method and activation analysis. The average of two samples for each condition is shown in Table 2. The oxygen content obtained by dynamic conditions is almost the same as that resulting from the static conditions at the same hydrogen pressure. In addition, almost all sample show relatively low oxygen content, and there is little effect of hydrogen pressure.

The oxygen detection limit of the inert gas fusion method is about 1 mass ppm, which is mainly limited by the surface oxide.⁷⁾ Thickness of native oxide layer formed on the surface of ultra high purity iron by air exposure was characterized by angle resolved XPS,⁸⁾ and the thickness was evaluated to 2.5 to 3 nm. We evaluated the effect of surface oxide on oxygen concentration of fusion method under the assumption that Fe_2O_3 is a surface oxide and typical dimension of the sample is 0.5 mm in diameter, 5 mm in length. When the surface oxide thickness is 3 nm, oxygen increment by the surface oxide layer is 0.7 mass ppm even if there is no oxygen inside the sample, and that is 0.6 mass ppm when surface oxide layer is 2.5 nm.

The activation analysis can eliminate the interference of surface oxide, and the results of the dynamic conditions show lower oxygen content for all samples. Although surface treatment of specimen for the fusion method was not the same as that for the angle resolved XPS, the estimated oxygen content increment was somewhat similar to the difference of oxy-

gen content among fusion method and activation analysis, 0.2 to 1 mass ppm. Further study is needed for detailed qualitative analysis, however, advantage of activation analysis in low oxygen range (<1 mass ppm) and the oxygen removal effect of the floating zone refining under hydrogen has become evident.

Almost all samples have very low oxygen content even under static hydrogen atmosphere, therefore, the difference of purification efficiency in removing oxygen between static and dynamic conditions is not clearly seen. Agitation of molten zone by electromagnetic force probably assists removing oxygen, therefore, two passes refining under 20 kPa for leveling of initial oxygen content was enough to eliminate oxygen. In general, removal of oxygen from iron by vacuum melting is difficult without the existence of carbon. However, the oxygen content of sample melted in vacuum following initial two passes in 20 kPa hydrogen shows no oxygen increment compare to the sample melted in hydrogen. Therefore, no oxygen contamination during vacuum melting by the floating zone refining apparatus is confirmed.

3.3 Comparison of measured residual resistivity and evaluated resistivity values

Figure 2 shows the relationship between chemical purity analyzed by GDMS and the $RRR_{H,0K}$ values. Although the kind of dominant residual impurity affects the relationship, the $RRR_{H,0K}$ values show qualitatively good correspondence with chemical purity. When almost all impurities have similar resistivity contribution per unit concentration, the relationship between chemical purity and $RRR_{H,0K}$ values is represented by a straight line with the same slope as the dashed line in Fig. 2. A solid line was fitted to the experimental results using the same slope as the dashed line, and the solid line does not show always a good fitting. When the dominant impurity has relatively large resistivity contribution per unit concentration, the slope of the chemical purity— $RRR_{H,0K}$ relationship is not the same as that of dashed line in Fig. 2. For example, the main impurities of iron refined by solvent extraction followed by ion exchange,⁹⁾ (~5N) in Fig. 2, is phosphorous which has relatively high resistivity contribution, therefore, the $RRR_{H,0K}$ value is not as high as expected from chemical purity. In addition, resistivity increase by oxygen on resistivity for high purity samples whose $RRR_{H,0K}$ values are close to 10^4 is not negligible compared to metallic impurities. It is difficult to estimate the absolute value of oxygen concentration, and/or solubility of oxygen in iron at extremely low temperatures.

The effect of the types of dominant impurities on the relationship between chemical purity and $RRR_{H,0K}$ in Fig. 2 can be examined by plotting the measured resistivity against resistivity calculated from GDMS results and resistivity contribution per unit concentration. The resistivity increase per unit concentration ($\Delta\rho_i$) of some impurities in iron are reported,^{10,11)} and almost all impurities are analyzed by GDMS in the study, therefore, resistivity can be estimated:

$$\rho_{cal} = \sum \Delta\rho_i \times C_i \quad (1)$$

Detection limits of the GDMS analysis were used for the not detected elements. Measured residual resistivity ratios

Table 2 Oxygen analysis results (mass ppm).

	Inert gas fusion method		Activation Dynamic
	Static	Dynamic	
H ₂ 101 kPa	1.3	1.0	0.8
H ₂ 20 kPa	1.0	1.5	0.4
H ₂ 3 kPa	1.3	1.1	~0.1
H ₂ 0.7 Pa	0.8	0.8	<0.1
Vacuum (10^{-4} Pa)		0.8	<0.1
Starting material		98	—

Fusion method: LECO TC-436, degas: 5500 W, analyzed by 5000 W, electrochemically polished before analysis.

Fig. 2 Chemical purity analyzed by GDMS and $RRR_{H,0K}$ for floating zone-refined iron. Results of Song⁹⁾ are plotted as a comparison.

Fig. 3 Relation between $\rho_{H,0K}$ and evaluated ρ_{CAL} from impurity content detected by GDMS. Error bars of evaluated resistivity are caused by difference of interstitial content used estimation; The left side: resistivity caused by O, C, N are neglected. The right side: GDMS results of O, C, N are used for estimation. Solid marks: GDMS results for C, N and assume that O is 0.1 mass ppm.

($RRR_{H,0K}$) can be converted into resistivities ($\rho_{H,0K}$) by the following equation, which is based on definition of the RRR

$$\rho_{H,0K} = \rho_{298K} / RRR_{H,0K}. \quad (2)$$

where ρ_{298K} of iron is $9.7 \mu\Omega\text{m}$. Figure 3 shows the relationship between the measured residual resistivity $\rho_{H,0K}$ and ρ_{CAL} , and almost all marks lie on the solid line labeled $y = x$. A good correspondence is clearly seen in Fig. 3 not only for the present study but also the study by Song.⁹⁾ The dominant reason for deviation between solid marks and open marks in Fig. 2 is provided by the difference in the kinds of main residual impurities.

To evaluate the effect of interstitial impurities on resistivity, error bars for solid marks are shown as a range of resistivity

caused by the different assumption for oxygen content. The highest values of the error bar were calculated by GDMS values for O, C, N, which were probably overestimated. The lowest values of the error bar were calculated by neglecting the resistivity increment due to O, C and N, which implies underestimation. It is clearly seen that the estimated resistivity range becomes wider with decreasing estimated resistivity, in particular, resistivity is smaller than $1 \times 10^{-11} \Omega\text{m}$ which corresponds to $RRR_{H,0K}$ values larger than 10000. Solid marks were calculated using GDMS results for C and N, 0.1 mass ppm for O that obtained by the activation analysis. GDMS results and RRR values of iron refined by solvent extraction and anion exchange followed by plasma arc melting, and electron beam melting⁹⁾ are plotted as open marks (O, C, N = 0.1 mass ppm are used as assumption). Although the main impurities are different in the iron prepared in Ref. 9) (P and Al) and in the iron of the present study, the correspondence of measured and calculated resistivities is relatively good.

In a RRR range of 1000 to 10000, calculated resistivities ρ_{CAL} correspond to measured resistivities $\rho_{H,0K}$. In a range where RRR is larger than 10000, further detailed characterization based on oxygen solubility and/or resistivity due to grain boundary segregation is needed in order to apply residual resistivity for purity evaluation.

4. Summary

The effect of hydrogen flow on purification efficiency of the floating zone refining of iron has been examined by $RRR_{H,0K}$ measurements, GDMS and oxygen analyses. The $RRR_{H,0K}$ profile shows fairly good correspondence with GDMS analysis results in the $RRR_{H,0K}$ range of 1000 to 10000.

The induction melting under hydrogen atmosphere at a reduced pressure is quite effective to remove oxygen, and no oxygen contamination is detected by vacuum melting following floating zone refining in hydrogen. Oxygen content of these samples are less than the detection limit of the conventional inert gas fusion method used in this study, and the high efficiency of oxygen removal of the floating zone refining method is also supported by activation analysis. Conventional oxygen analysis methods are not suitable for oxygen contents smaller than 1 mass ppm, and further study by activation analysis is needed to examine the effect of hydrogen pressure and flow rate on elimination of oxygen from iron.

To prepare purer iron by this process, the concentration of Co, Ni, Al and Mo in the starting material is a key point, which is proposed by the sound basis of purity evaluation, *i.e.* RRR and GDMS analysis. Combination of solvent extraction¹²⁾ and anion exchange methods in hydrochloric acid media is a possible way to prepare purer starting material.⁹⁾

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