# SOLID SOLUBILITIES OF Ce, Nd AND Y IN α—Fe AT ROOM TEMPERATURE①

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## ABSTRACT

Using the thermodynamic formula of solid solubility in dilute solution, the solid solubilities of Ce, Nd and Y in α-Fe at room temperature have been calculated The results are 48, 32 and 1 ($\times 10^{-4}$wt.-%) respectively and the mechanism influencing the values of solid solubilities are also discussed.

**Key words**: solubility thermodynamics dilute solution

## 1 INTRODUCTION

Since the rare earths(RE) were applied in steel productions, the metallurgical properties of the steels have been improved by their additions. However, the functions of rare earth in steels were not clear up till now, the main reason is that people have not made precise measurements to their solubilities. Although the atomic radii of rare earth elements are much larger than that of iron, they can still be partially dissolved in iron. In regard to this problem, some studies have been reported[1-4]. Unfortunately, these studies were almost focused on the high temperature range. However the solubility at room temperature is a very important property for metallurgists to make high quality materials.

Recently, the solubility of lanthanum at room temperature was reported to be 0.11 wt.-%[5], cerium 0.047 wt.-%, neodymium 0.055 wt.-%[6] and 0.082 wt.-%[2]. But these results are almost equal to the high temperature values obtained by Refs. [1], [3] and [4]. By an elaborate analysis of their practical experimental processes, we found that the researchers kept the samples at high temperature for only 10 h, and then cooled them down to room temperature at a rate of 10 C/h. Since the solute atoms are almost diffusionless or diffuse very slowly below 500 C, the solubilities measured by those techniques can not be considered as real solubilities at room temperature. Actually, they are much higher than the correspondingly real solubilities.

In addition to the influence of the treating program, the measuring methods and the purity of the original materials also greatly affect the final results. Generally, the solubilities of rare earth in iron are very small. Therefore, only highly sensitive and advanced experimental apparatus are available to obtain accurate results.

Based on the solubilities of Ce, Nd and Y at 880, 800, 700 and 600 C, which were determined by four different methods, we have calculated their room temperature solubilities by a thermodynamic solubility formula and obtained some theoretical results.

① Manuscript received Oct. 21, 1992

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## 2 EXPERIMENTAL

An extremely high purity iron containing other elements less than 0.02 wt.-% was used in our experiment. Among those other elements, the most deleterious is oxygen, because it can react actively with the rare earth to form a compound and thus affect the measurement accuracy. In order to solve this problem, dry hydrogen which was filtered through a molecular sieve was used in the deoxidation of the iron at 850 C for 80 h[7]. After this process, the oxygen content decreased to 0.004 wt.-%. The purities of Ce, Nd and Y are 99.9 wt.-%. The iron and Ce, Nd and Y are melted in a tungsten vacuum arc furnace with magnetic control to prepare a series of specimens with different compositions which are listed in Table 1. It should be emphasized that we adopted premelting parent alloy technique as the first procedure to cut down the errors coming from the weighing process. After heat treatment in a high vacuum furnace at 880, 800, 700, 600 C for 240, 480, 720, 1 440 h respectively, we quenched the specimens to room temperature to ensure that they have reached phase equilibria at different temperatures.

**Table 1 Compositions of the specimens**

| NO | Ce/wt.-% | Nd/wt.-% | Y/wt.-% |
|---|---|---|---|
| 1 | 0.000 0 | 0.000 0 | 0.000 0 |
| 2 | 0.004 8 | 0.004 4 | 0.004 4 |
| 3 | 0.009 5 | 0.008 9 | 0.008 9 |
| 4 | 0.019 1 | 0.017 7 | 0.013 3 |
| 5 | 0.029 0 | 0.026 6 | 0.017 7 |
| 6 | 0.038 0 | 0.035 5 | 0.026 6 |
| 7 | 0.057 0 | 0.053 2 | 0.035 5 |
| 8 | 0.076 0 | 0.070 9 | 0.043 3 |
| 9 | 0.095 0 | 0.088 7 | 0.053 2 |
| 10 | 0.114 0 | 0.106 0 | 0.071 0 |
| 11 | 0.143 0 | 0.133 0 | 0.088 7 |
| 12 | 0.286 0 | 0.266 0 | 0.266 0 |
| 13 | 0.477 0 | 0.443 0 | 0.443 0 |
| 14 | 0.953 0 | 0.887 0 | 0.887 0 |

**Table 2 Solubilities obtained with different techniques/at.-%**

| T/K | RE | EMQA | XLPA | MCFA | PAA | Avg. |
|---|---|---|---|---|---|---|
| 1 153 | Ce | 0.040 | 0.039 | 0.042 | 0.043 | 0.041 |
| | Nd | 0.034 | 0.036 | 0.033 | 0.037 | 0.035 |
| | Y | 0.035 | 0.035 | 0.044 | 0.034 | 0.037 |
| 1 073 | Ce | 0.038 | 0.034 | 0.040 | 0.033 | 0.036 |
| | Nd | 0.033 | 0.032 | 0.033 | 0.035 | 0.033 |
| | Y | 0.028 | 0.028 | 0.029 | 0.031 | 0.029 |
| 973 | Ce | 0.032 | 0.033 | 0.031 | 0.033 | 0.033 |
| | Nd | 0.028 | 0.028 | 0.026 | 0.028 | 0.028 |
| | Y | 0.023 | 0.026 | 0.027 | 0.024 | 0.025 |
| 873 | Ce | 0.029 | 0.029 | 0.030 | 0.029 | 0.029 |
| | Nd | 0.023 | 0.024 | 0.026 | 0.023 | 0.024 |
| | Y | 0.017 | 0.017 | 0.020 | 0.018 | 0.018 |

## 3 RESULTS AND DISCUSSION

Table 2 shows the solubilities of Ce, Nd and Y at different temperatures which were determined by four methods: electron microprobe quantitative analysis (EMQA), X-ray lattice parameter analysis (XLPA), positron annihilation analysis (PAA) and magnetic coercive force analysis (MCFA). A detailed description of these four measurement techniques was given in our previous papers[1,8].

Based on a careful analysis of thermodynamic normal solution theory of the binary system, we derived the solid solubility equation as follows.

$$X^{\alpha}_{RE} = \exp\left[-\frac{1}{RT}(\Delta^{\circ}H^{\beta-\alpha}_{RE} - T\Delta^{\circ}S^{\beta-\alpha}_{RE} + (1 - X^{\alpha}_{RE})^{2} \cdot I^{\alpha}_{Fe-RE})\right] \quad (1)$$

Noting that the rare earth contents in alloys are extremely low, the alloys can be considered as dilute solutions. Then equation (1) becomes

$$\ln X^{\alpha}_{RE} = \frac{\Delta^{\circ}S^{\beta-\alpha}_{RE}}{R} - \frac{1}{RT} \times (\Delta^{\circ}H^{\beta-\alpha}_{RE} + I^{\alpha}_{Fe-RE}) \quad (2)$$

where $X^{\alpha}_{RE}$ refers to the solubility of the rare earth in $\alpha$-Fe (atomic percentage); $\Delta^{\circ} H^{\beta-\alpha}_{RE}$ to the difference in enthalpy per unit volume of pure rare earth element between $\beta$ and $\alpha$ phases; $\Delta^{\circ} S^{\beta-\alpha}_{RE}$ to the difference in entropy; $R$ to the universal gas constant and $I^{\alpha}_{Fe\text{-}RE}$ to the interactive coefficient. They are all constants. Therefore, equation (2) becomes

$$\ln X^{\alpha}_{RE} = A + B/T \qquad (3)$$

where $A$, $B$ are constants

We find $\ln X^{\alpha}_{RE} \propto 1/T$ in equation (3), $A$ and $B$ can be calculated easily using the solubility data determined at high temperatures. $\ln X^{\alpha}_{RE}$ against $1/T$ is plotted in Fig. 1, for Ce-Fe system: $A = -6.765$, $B = -1220.3$; for Nd-Fe system $A = -6.774$, $B = -1357.8$; Y-Fe system $A = -5.892$, $B = -2363.7$.

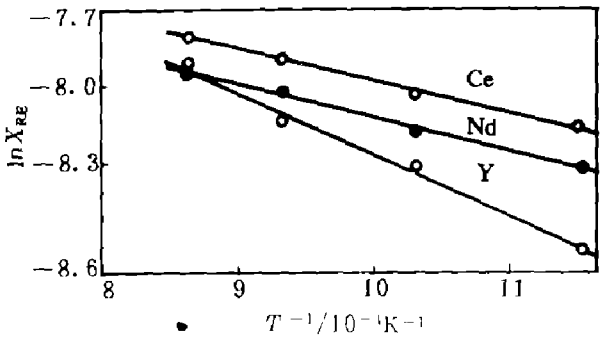


**Fig. 1 Temperature dependences of solubilities of Ce, Nd and Y in $\alpha$-Fe**

Supposing the room temperature is 293 K, we have calculated the solubilities at this temperature and got the following data: Ce—0.0048wt.-%; Nd—0.0032wt.-%; Y—0.0001 wt.-%.

We noted that the accuracy of low temperature solubilities is related closely to the high temperature data. Because of the pure materials used in our experiments and the adoption of parent alloy technique during the manufacture of the final specimens, we are confident that the effects of inclusions on accuracy can be minimized. Moreover, the solid solubilizing time is 10 times longer than that used in other studies. Such long time treatment can ensure the alloys to reach equilibrium states. The solubility data at each temperature, determined by means of the above four methods, agree well with each other. Thus the average value is more credible than that achieved by only one method. Therefore, the solubilities at room temperature calculated by thermodynamic formula can be considered more accurate and reasonable.

It is found that the solubilities of rare earth in $\alpha$-Fe are very small, probably owing to the big difference of atomic radii between rare earth and iron. The results indicate the relationship between solubilities of Ce, Nd and Y are

$$X^{\alpha}_{Ce} > X^{\alpha}_{Nd} > X^{\alpha}_{Y}$$

which highly corresponds with the theory associating the formation of binary solution, and an appropriate explanation can be given by analyzing the melting points of their stable compounds as follows:

For Fe17Ce2, $T_m$ = 1068 C; for Fe17Nd2, $T_m$ = 1185 C; Fe17Y2, $T_m$ = 1400 C. Where $T_m$ is melting point and the highest $T_m$ is of the Fe17Y2. It means that yttrium in the Y-Fe alloy has a strong tendence to form a stable compound but not a solution, so the solubility of yttrium in $\alpha$-Fe is the smallest.

## 4 CONLUSIONS

(1) The solubilities of Ce, Nd and Y in $\alpha$—Fe at room temperature, calculated with the aid of the data obtained at 600~880 C, are 0.0048, 0.0032 and 0.0001 wt.-% respectively.

(2) Referring to the room temperature solubilities, we discussed the reasons causing large difference between calculation and ex-

perimental determination by cooling down to low temperature at a certain rate. We conclude that the sluggish diffusion of rare earth solutes at low temperature and the relatively low purities of original materials are the key factors bringing about errors in final measurement results.

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$e_{Ce}^{Sn}=0.85$, $e_{Ce}^{Sn}=-1.56$, $\varepsilon_{Ce}^{Pb}=\varepsilon_{Pb}^{Ce}=(230M_P/M_{Al})$

$e_{Ce}^{Pb}=-5\ 027$, $\varepsilon_{Ce}^{Sn}=\varepsilon_{Sn}^{Ce}=(230M_{Sn}/M_{Al})$,

$e_{Ce}^{Sn}=-1\ 861$.

## 4 CONCLUSIONS

(1) The equilibrium products are identified as $Ce_3Al_{11}$ for both of the two systems. Besides, there exists $Ce_mPb_n$ or $Ce_iSn_j$ for them, respectively;

(2) The equilibrium constant is $7.48\times10^{-5}$ at 800 C for reaction $Ce_3Al_{11(s)}=11Al_{(l)}+3[Ce]$ in liquid aluminum;

(3) The standard Gibbs energy of formation of the equilibrium product, $Ce_3Al_{11}$, is −84.8 kJ/mol at 800 C in liquid aluminum;

(4) At 800 C, the activity interaction coefficients between Ce and Pb are: $e_{Ce}^{Pb}=-2.85$, $e_{Pb}^{Ce}=-4.21$, $\varepsilon_{Ce}^{Pb}=\varepsilon_{Pb}^{Ce}=-5\ 027$, and these between Ce and Sn are: $e_{Ce}^{Sn}=-1.84$, $e_{Sn}^{Ce}=-1.56$, $\varepsilon_{Ce}^{Sn}=\varepsilon_{Sn}^{Ce}=-1\ 861$.

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