Phase Equilibria and Thermodynamic Evaluation Approximating Short-range Ordering Energy in the Fe–Rh Binary System

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Phase equilibria between the α (A2), α′ (B2) and γ (A1) phases in the Fe–Rh binary system were investigated using electron probe micro-analysis (EPMA) and differential scanning calorimetry (DSC) techniques. The A2/B2 order-disorder transformation temperature was also examined by a transmission electron microscope (TEM) observations and high-temperature X-ray diffraction (HTXRD). It was confirmed that while the transition temperature from the α (A2) phase to the γ (A1) phase decreases with increasing Rh content up to about 20 at% Rh, the b.c.c. region is stabilized by further Rh addition in the composition range between about 20 and 50 at% Rh, and then again the stability of b.c.c. phase decreases in the composition region over 50 at% Rh. It was also shown by TEM observation and HTXRD examination that the compositions of the phase boundary of the A2/B2 ordering at 500°C and 600°C were determined to be 16.5 and 19.1 at% Rh, respectively. On the basis of those experimental results, a thermodynamic analysis was carried out. The results of the thermodynamic calculation suggest that the anomalous behavior of the stability of the b.c.c. phase is caused by the A2/B2 ordering.

KEY WORDS: CALPHAD; order-disorder transition; short-range ordering; magnetic ordering; phase stability.

1. Introduction

Since Fallot1,2) reported an anomalous magnetic property, i.e., a sharp increase in the magnetization with increasing temperature, the Fe–Rh system has attracted much interest.3–6) In the vicinity of the stoichiometric composition Fe0.5Rh0.5, there is a CsCl-type B2 superstructure which undergoes a magnetic first-order transition from ferromagnetic to antiferromagnetic at about 60°C. The transition temperature and the hysteresis depend on composition, heat treatment, magnetic field and pressure. The Fe–Rh system is mainly applied in thin film devices, e.g., thermomagnetic motors, thermomagnetic switches and actuators. From the viewpoint of phase stability, the Fe–Rh system also shows unusual and interesting features. Rhodium has a tendency to stabilize the austenite γ (A1) phase, which results in an increase of the temperature range of the γ-Fe phase with increasing rhodium content, as shown in Fig. 1.7) However, at a rhodium content higher than 20 at%, a different tendency, i.e., stabilization of the ferrite α (A2) phase appears. The origin of such inconsistent behavior is not yet understood, however, it seems that the α (A2)/α′ (B2) ordering transition in the vicinity of 20 at% Rh may play a considerable role in this anomalous phenomenon.

Despite such technological importance and metallurgical interest, most of the phase boundaries between α (A2), α′ (B2), γ (A1) and liquid phases are drawn with dotted curves as shown in Fig. 1, which means that the binary phase diagram is still unknown. In this paper, the phase equilibria between the α (A2), α′ (B2) and γ (A1) phases in the Fe–Rh binary system were investigated experimentally, some results of which have been quoted in other papers.8,9) Then, the origin of the anomalous behavior of the phase equilibria was examined using a thermodynamic calculation optimized on the basis of the experimental results.

2. Experimental Procedures

Two-phase alloys of the Fe–Rh system were prepared by arc melting under an argon atmosphere. The starting ma-
Materials were Fe (99.9 mass%) and Rh (99.97 mass%), and the composition range of the prepared alloys was Fe–(10–55) at%Rh as listed in Table 1. Each as-cast specimen was sealed in an evacuated quartz capsule, back-filled with argon, and annealed at temperatures between 650°C and 1350°C for duration of between 24 h and 4380 h. After the heat-treatment for equilibration, the specimens were quenched into ice water. Results of chemical analysis of as-cast specimens are listed in Table 1. After microstructure examination by an optical microscope, equilibrium compositions were determined by electron probe microanalysis (EPMA: JEOL JXA-8100) using a standard calibration method. The transition temperature of some alloys at about 20 at% Rh was also determined by differential scanning calorimetry (DSC: SEIKO DSC-320) at heating rate of 3°C/min.

In order to determine the A2/B2 ordering temperature, DSC measurement, transmission electron microscopic (TEM: JEOL JEM-2000EX II) examination and high temperature X-ray diffraction (HTXRD: Phillips X’pert) were performed. The specimens for the TEM observation were solution-treated at 1300°C for 1 h, cooled down to 500°C or 600°C, and aged at those temperatures for 72 h. The centers of disks cut from the as-aged specimens were processed into thin foils by dimple-grinding and ion-milling. TEM examination at room temperature was carried out on the thin foils. Powdered specimens were annealed at 1300°C and analyzed by HTXRD at 500°C and 600°C.

3. Experimental Results

3.1. Phase Equilibria between the α (A2), α’ (B2), γ (A1) Phases

A typical example of the microstructure of the α’ (B2)+γ (A1) two-phase alloy annealed at 1200°C for 96 h is shown in Fig. 2. It can be seen that the size of the precipitated α’ (B2) phase is sufficiently large to be analyzed by EPMA. The equilibrium compositions of the α’ (B2) and γ (A1) phases were determined by averaging more than seven data for each phase. DSC measurements of Fe–14.6, 20.4 and 25.6 at% Rh alloys were also performed. A typical example of the heating curve is presented in Fig. 3. It is seen that an endothermic signal due to α (A2)/γ (A1) transition is detected at 632°C. The starting temperature of the α (A2)/γ (A1) transformation of the Fe–14.6, –20.4 and –25.6 at% Rh alloys was determined to be 654, 632 and 668°C, respectively. These results are consistent with the phase boundary determined by EPMA measurements. All the results on the phase equilibria between the α (A2), α’ (B2), γ (A1) phases are listed in Table 2 and plotted in Fig. 4, where the previously assessed phase diagram is superimposed with thin broken lines. It is seen that the present result is not so different from the previous diagram, whereas the width of two-phase region and the congruent transition temperature from α’ (B2) to γ (A1) is underestimated in the previous diagram.

3.2. Phase Stability of B2-Ordered Structure

In order to evaluate the stability of the B2 phase in the Fe-rich portion, DSC, HTXRD and TEM examinations...
were carried out. Figures 5(a) and 5(b) show electron diffraction patterns at room temperature taken from (a) Fe–16.5 at% Rh and (b) Fe–19.1 at% Rh specimens aged at 600°C. It is seen that while the diffraction pattern taken from the 16.5 at% Rh alloy has no superlattice spots, that from the 19.1 at% Rh alloy clearly shows {100}B2 superlattice reflections, as shown in Fig. 5(b). The dark-field image taken from the (100)B2 reflection exhibits low density of anti-phase domain boundaries (APB), as shown in Fig. 5(c), which suggests that the 19.1 at% Rh alloy has a B2-ordered structure at 600°C. According to the results of the HTXRD analysis, the B2-ordered structure could not be distinguished from A2 disordered structure in the vicinity of 20 at% Rh because the order line is too small to detect. It was found, however, that the composition dependence of the 2\(\theta\) value of (310)\(_{A2}\) line slightly changes at 16.5 and 19.1 at% Rh at 500°C and 600°C, respectively, as shown in Fig. 6. All these results suggest that the 19.1 at% Rh alloy has a B2-ordered structure at 600°C. According to the results of the HTXRD analysis, the B2-ordered structure could not be distinguished from A2 disordered structure in the vicinity of 20 at% Rh because the order line is too small to detect. It was found, however, that the composition dependence of the 2\(\theta\) value of (310)\(_{A2}\) line slightly changes at 16.5 and 19.1 at% Rh at 500°C and 600°C, respectively, as shown in Fig. 6. All these results suggest that the \(\alpha\) (A2)/\(\alpha\) (B2) boundary at 500°C and 600°C should be located at 16.5 and 19.1 at% Rh, respectively. The composition dependence of the \(\alpha\) (A2)/\(\alpha\) (B2) boundary is quite steep as plotted with X marks in Fig. 4.

### 4. Thermodynamic Calculation

The Gibbs energies of the stable and metastable structures of the pure elements are taken from the SGTE database compiled by Dinsdale.\(^{10}\) In the Fe–Rh system, three disordered solution phases, the liquid, \(\alpha\) (A2) and \(\gamma\) (A1),

<table>
<thead>
<tr>
<th>Composition of alloy / at.% Rh</th>
<th>Temperature / °C</th>
<th>Heat-treatment duration / h</th>
<th>Equilibrium composition / at.% Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 *</td>
<td>1350</td>
<td>6</td>
<td>50.2</td>
</tr>
<tr>
<td>55 *</td>
<td>1300</td>
<td>24</td>
<td>50.3</td>
</tr>
<tr>
<td>55 *</td>
<td>1200</td>
<td>72</td>
<td>50.4</td>
</tr>
<tr>
<td>55 *</td>
<td>1000</td>
<td>336</td>
<td>50.3</td>
</tr>
<tr>
<td>55 *</td>
<td>800</td>
<td>1680</td>
<td>50.1</td>
</tr>
<tr>
<td>45 *</td>
<td>1300</td>
<td>24</td>
<td>45.0</td>
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<td>1200</td>
<td>96</td>
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</tr>
<tr>
<td>34.7</td>
<td>700</td>
<td>1680</td>
<td>35.5</td>
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<tr>
<td>25.6</td>
<td>650</td>
<td>4380</td>
<td>31.6</td>
</tr>
</tbody>
</table>

* Nominal composition.

Table 2. Experimental data of the equilibrium composition between the \(\alpha\) (B2) and \(\gamma\) (A1) phases.

Fig. 5. Electron diffraction patterns taken from (a) Fe–16.5 at% Rh and (b) Fe–19.1 at% Rh heat-treated at 600°C, and (c) dark-field image taken from (100)\(_{B2}\) reflection in Fig. 5(b).

Fig. 6. (a) High temperature X-ray diffraction pattern taken from the b.c.c. phase in Fe–14.6 at% Rh alloy at 500°C, and the relationship between Rh content and the 2\(\theta\) values of the (310) line at (b) 500°C and (c) 600°C.

Fig. 4. (a) A2 : Fe-16.5Rh (b) B2 : Fe-19.1Rh (c) APB : Fe-19.1Rh
and an ordered b.c.c. phase, \( \alpha' \) (B2), are considered to constitute the equilibrium phases. The Gibbs energy descriptions of these four phases are given below and evaluated thermodynamic parameters are listed in Table 3.

### 4.1. Disordered Solution Phases

The liquid, \( \alpha \) (A2) and \( \gamma \) (A1) phases are modeled as substitutional solution, and the Gibbs energy without the magnetic contribution is described by the sub-regular solution approximation

\[
\gamma = \text{Fe} \times \text{Rh} \times \sum x_{\text{Fe}} x_{\text{Rh}} \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \tag{1}
\]

where \( \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \) represents the interaction parameter which has a composition dependence in the form of the Redlich-Kister polynomial described by the following equation:

\[
\Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} = \sum x_{\text{Fe}} x_{\text{Rh}} \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \tag{2}
\]

Coefficients, \( \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \), are evaluated on the basis of the experimental data of phase boundaries and thermochemical properties.

### 4.2. Ordered Phase

The Gibbs energy of the ordered \( \alpha' \) (B2) phase \( G_{\text{m}}^{\alpha'} \) is described by the two-sublattice split compound energy form:

\[
G_{\text{m}}^{\alpha'} = \Phi_{\text{Fe}, \text{Rh}} \times \sum x_{\text{Fe}} x_{\text{Rh}} \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \tag{3}
\]

where \( \Phi_{\text{Fe}, \text{Rh}} \) and \( \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \) are the Gibbs energies of pure Fe and pure Rh, respectively, in the corresponding structure of the disordered solution phase \( \varphi \), relative to their reference states. \( x_{\text{Fe}} \) and \( x_{\text{Rh}} \) are the mole fractions of Fe and Rh, respectively. \( \Phi_{\text{Fe}, \text{Rh}} \) is the interaction parameter which has a composition dependence in the form of the Redlich-Kister polynomial described by the following equation:

\[
\Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} = \sum x_{\text{Fe}} x_{\text{Rh}} \Phi_{\text{Fe}, \text{Rh}, \text{Fe}, \text{Rh}} \tag{4}
\]
The magnetic contribution to the Gibbs energy, $G^\text{mag}_m$, was introduced into the $\alpha$ (A2) and $\gamma$ (A1) disordered solution phases. Its description was originally suggested by Inden[13] and the modified description by Hillert and Jarl[14] is applied to the calculation as follows:

$$G^\text{mag}_m = RT \ln(\beta + 1) \cdot f(\tau) \quad (6)$$

$$f(\tau) = \frac{A}{1} \cdot \left( \frac{79\tau^{-1}}{140p} + \frac{474}{497} \left( \frac{1}{p} - 1 \right) \right) \times \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right), \quad \text{for } \tau = \frac{T}{T_c} \leq 1 \quad (7)$$

$$f(\tau) = \frac{A}{1} \cdot \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-14}}{315} + \frac{\tau^{-25}}{1500} \right), \quad \text{for } \tau = \frac{T}{T_c} \geq 1 \quad (8)$$

where $T_c$ is the Curie temperature and $\beta$ is the mean atomic moment expressed in Bohr magneton units $\mu_B$. Both values are functions of alloy composition as follows:

$$T_c = \frac{5}{5} T_{\text{Fe}} \cdot x_{\text{Fe}} + \frac{5}{5} T_{\text{Rh}} \cdot x_{\text{Rh}} + x_{\text{Fe}} \cdot x_{\text{Rh}} \sum_n^n \frac{\Delta T_{\text{FeRh}}(x_{\text{Fe}} - x_{\text{Rh}})^n}{n} \quad (9)$$

$$\beta = \frac{5}{5} \beta_{\text{Fe}} \cdot x_{\text{Fe}} + \frac{5}{5} \beta_{\text{Rh}} \cdot x_{\text{Rh}} + x_{\text{Fe}} \cdot x_{\text{Rh}} \sum_n^n \frac{\beta_{\text{FeRh}}(x_{\text{Fe}} - x_{\text{Rh}})^n}{n} \quad (10)$$

$p$ represents the ratio of the magnetic enthalpy due to short-range ordering to the total amount of magnetic enthalpy, the values $p = 0.4$ for b.c.c. and $p = 0.28$ for f.c.c. alloys having been suggested by Inden[13].

In the description of Eqs. (9) and (10), effects of the atomic order-disorder on the magnetic properties were not taken into account. It is suggested, however, that both $T_c$ and $\beta$ depend on the degree of ordering. The thermodynamic calculation of this effect has been discussed in detail in our previous papers.[12,15] The effect of the interaction was introduced into the present calculation by considering $\Delta T_{\text{FeRh}} = -0.15^\circ C$ and $\Delta \beta_{\text{FeRh}} = -0.13 \mu_B$ was accepted, which resulted in good agreement between empirical and calculated Curie temperature and magnetic moments of the ordered B2 phase as shown in Fig. 7.[16-23] The evaluated parameters of the magnetic properties are listed in Table 3.

4.4. Approximation of the Gibbs Energy of SRO

The chemical ordering contribution introduced by the split compound energy formalism (s-CEF) contains only the long-range ordering (LRO) energy. Thus, the effect of the short-range ordering (SRO) is compensated for by the ordering contribution of the LRO description, which results in the deviation of the calculated order-disorder boundary.

![Fig. 7](image_url)
from the practical one determined by experiments, as reported for the A2/B2 order-disorder boundary in the Ti–Al binary system.24) Sundman et al.25) proposed that the effect of the SRO due to pair probabilities can be approximated by introducing reciprocal parameters into the CALPHAD method and reported a thermodynamic assessment of the Au–Cu system. This approximation is based on the quasi-chemical formalism for the ionic liquid phase,26,27) and the effect of the SRO for the two-sublattice CEF is described as

\[ \Delta g^{\text{SRO}}_m = -z y_A y_A y_B y_B \times \frac{(\Delta^0 G^{AB}_m)^2}{zRT} \]  

where \( z \) represents the coordination number and \( R \) is the gas constant. The relation of \( \Delta^0 G^{AB}_m \) to the Gibbs energy of formation is represented by the following equation:

\[ \Delta^0 G^{AB}_m = \gamma A_B + \gamma G_{AB} - \gamma G_A + \gamma G_B \]  

The reciprocal component of the Gibbs energy described by the 2-sublattice s-CEF, \( -(\Delta^0 G^{AB}_m)^2/zRT \) (\( = \Delta G^{\text{SRO}}_{\text{FeRh}} \)), should have an effect not only on the ordering contribution, \( \Delta G_m^{\text{B2}}(Y_1) \), but also on the Gibbs energy of the disordered solution, \( G_m^{\text{FeRh}}(x) \). The contribution of \( \Delta G^{\text{SRO}}_{\text{FeRh}} \) which consists of a composition dependent term \( \Delta G^{\text{FeRh}}_{\text{SRO}(1)} \) as well as a composition independent term \( \Delta G^{\text{FeRh}}_{\text{SRO}(0)} \) (= \( s_r/T \)), was involved in the Gibbs energy as listed in Table 3, which represents that its ordering contribution is described in the following formula.

\[ \Delta g^{\text{B2-SRO}}_m = y_A y_A y_B y_B \{ L_{A,AB,B}^{(0)} + (y_A y_B y_B) L_{A,AB,B}^{(1)} \} \\
+ (y_A y_A y_B) L_{A,AB,B}^{(2)} + (y_A y_B y_B) \Delta G^{\text{FeRh}}_{\text{SRO}(0)} + (y_A y_B y_B) \Delta G^{\text{FeRh}}_{\text{SRO}(1)} \]  

Both parameters, \( s_r \) and \( s_1 \), were evaluated arbitrarily on the basis of a practical thermochemical optimization in the CALPHAD approach.

5. Discussion

5.1. Comparison of Calculated and Experimental Data

Figure 8 shows the calculated and experimentally determined thermodynamic properties related to the chemical potential of Fe in f.c.c. alloys at 1200°C.28) The result of the calculation is in good agreement with the experimental data. Figure 9 shows a comparison of the calculated phase equilibria without taking the SRO effect into account; (a) between the liquid, \( \delta (A2) \) and \( \gamma (A1) \) phases and (b) between the \( \gamma (A1) \), \( \alpha (A2) \) and \( \alpha' (B2) \) phases together with the experimental data.29) The stability of the B2 ordered structure is shown in Fig. 10. The \( \alpha (A2)/\alpha' (B2) \) boundary was calculated in the meta-stable region and the maximum temperature was evaluated to be 2858°C at the Rh composition of \( x_{\text{Rh}} = 0.574 \). The deviation of the Curie temperature of the B2-ordered phase (thick chained curve) from that of the A2-disordered phase (thin chained curve), which is caused by the interaction between the chemical and the magnetic ordering, is also shown in Fig. 10. Agreement between the calculation and the experimental results for the phase equilibria is quite satisfactory. However, significant deviation in the A2/B2 transition boundary is observed as shown by X marks (Exp.) and a hatched curve (Cal.) in Fig.
9. This overestimated stability of the B2-ordered structure in this calculation seems to be caused by the insufficient thermodynamic description of s-CEF without the SRO effect as pointed out in Sec. 4.4.

5.2. Effect of B2-ordering Energy on Phase Equilibria

Figure 11 illustrates the effect of B2 ordering on the $\alpha$ (A2)/$\gamma$ (A1) equilibrium calculated without taking the SRO effect into account. Solid and open circles indicate the stable and the metastable phase equilibria, respectively. The ordering energy due to B2 configuration,

$$\Delta G_m^{B2} = G_m^{\alpha(B2)} - G_m^{\alpha(A2)} \quad (14)$$

is shown by shaded areas in Fig. 11(a) and 11(b). Without the contribution of this excess ordering energy, the $\gamma$ (A1) phase is stable over the whole composition range at 1000°C and the disordered b.c.c. phase $\alpha$ (A2) is in equilibrium with $\gamma$ (A1) at 500°C, whose equilibrium compositions are indicated by open circles with characters, I and J, in Figs. 11(b) and 11(c).

5.3. Effect of the Short-range Ordering (SRO)

The SRO contribution to the Gibbs energy is indispensable for calculating the phase equilibria of the order-disorder system. In the present calculation, this effect in the B2 ordering was approximated by introducing reciprocal parameters into the s-CEF model.\textsuperscript{15,25) Figure 12 shows a comparison of (a) A2/B2 boundaries, (b) Gibbs energy of b.c.c. phases and (c) ordering contributions, $\Delta G$, relative to the Gibbs energy of the disordered A2 phase described by the LRO model, $G_{A2}^{LRO}$, calculated with and without taking the approximated SRO contribution into account. These ordering contributions of the SRO and LRO models can be described as follows:

$$\Delta G_{B2}^{SRO} = G_{B2}^{SRO} - G_{A2}^{LRO} \quad (15)$$
$$\Delta G_{B2}^{LRO} = G_{B2}^{LRO} - G_{A2}^{LRO} \quad (16)$$

and the net SRO contribution shown as shaded areas in Fig. 12(c) is calculated by

$$\Delta G_{B2}^{SRO} = \Delta G_{B2}^{SRO} - \Delta G_{B2}^{LRO} \quad (17)$$

The approximated SRO contribution causes the stabilization of the disordered A2 phase around the A2/B2 boundary and results in a decrease of the A2/B2 transition temperature $T_{A2/B2}^{SRO}$ (hatched curve) compared with $T_{A2/B2}^{LRO}$ (dashed curve) as shown in Fig. 12(a). In addition, as both $\Delta G_{FeRh}^{SRO}$ and $\Delta G_{FeRh}^{LRO}$ parameters contain a reciprocal temperature term $1/T$, which results in the over estimation of the SRO effect at low temperatures, the A2/B2 boundary calculated using the SRO approximation model shrinks at low temperature and a A2+B2 two phase separation ap-
pears along the boundary below 445°C. These anomalous equilibria indicate that the present SRO approximation is inappropriate for low temperature calculations, such as the formation enthalpy at 0 K calculated by Eleno et al.\(^\text{18}\) Figure 13 shows the calculated phase diagram including the SRO approximation. The calculated result with the SRO effect is in good agreement with the present experimental data not only on the phase equilibria between the \(\alpha'\) (B2) and \(\gamma\) (A1) phases shown by solid circles, but also on the \(\alpha\) (A2)/\(\alpha'\) (B2) transition boundary shown by X marks in Fig. 13.

### 6. Conclusions

1. Phase equilibria between the \(\alpha\) (A2), \(\alpha'\) (B2) and \(\gamma\) (A1) phases in the Fe–Rh binary system were precisely determined at temperatures between 650°C and 1 350°C. It was confirmed that the \(\alpha\) (A2) to \(\gamma\) (A1) transition temperature rises with the addition of more than 20 at% Rh, where the \(\alpha\) (A2)/\(\alpha'\) (B2) transition boundary meets the \(\alpha\) (A2) + \(\gamma\) (A1) equilibria. Thermodynamic analysis quantitatively proves that the anomalous equilibrium is caused by the B2 ordering energy.

2. The \(\alpha\) (A2)/\(\alpha'\) (B2) order-disorder transition boundary at 500°C and 600°C was determined to be 16.5 and 19.1 at% Rh, respectively, by HTXRD analysis and TEM examination.

3. Thermodynamic assessment of the Fe–Rh binary system was carried out on the basis of previous and present experimental data. The ordering contribution to the Gibbs energy of the \(\alpha'\) (B2) configuration and its interaction with the magnetic ordering were described by the split compound energy formalism (s-CEF). The short-range ordering (SRO) contribution to the Gibbs energy due to the pair probability was approximated by introducing reciprocal parameters into the s-CEF description. The calculated phase diagram was found to be in good agreement with experimental data.

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