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KINETICS OF ALUMINUM EXTRACTION WITH DI–2–ETHYLHEXYL PHOSPHORIC ACID①

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ABSTRACT

The kinetics of solvent extraction of aluminum with di–2–ethylhexyl phosphoric acid (DEHPA) in n-heptane have been studied in a constant interfacial area cell. A HCl-KHC$_8$H$_4$O$_4$ (potassium biphthalate, KHL) buffer solution was used to maintain a constant pH during extraction. The effects of the concentration of aluminum, pH, the concentration of the extractant, the interfacial area and the temperature on the extraction rate were investigated. A method has been invented to determine amont of the extracted aluminum in the organic phase with 8–hydroxyquinoline. Based on calculation of the coordination states of the aluminum ions and their contribution to the reaction rate, a raaction mechanism which includes two main reaction paths, has been proposed to describe the process. One path starts from $Al(H_2O)_6^{3+}$, and the other starts from $Al(H_2O)_4L^+$. The reaction could take place both in the aqueous phase and at the interface. The main reaction region could be changed as the conditions of extraction were changed. When $[HA] < 0.03$ mol / L the process was controlled by the interfacial reaction, and when $[HA] > 0.03$ mol / L it was shifted to a homogeneous aqueous solution reaction.

Key words: aluminum solvent extraction kinetics constant interfacial area cell di–2–ethylhexyl phosphoric acid.

1 INTRODUCTION

The kinetics of aluminum extraction with di–2–ethylhexyl phosphoric acid (DEHPA) have been studied by some authors[1–6]. In Matsui's view[1], key steps in the process was

$$Al(H_2O)_4A_2^+ + A^- \longrightarrow Al(H_2O)_3A_3 + H_2O$$

$$Al(H_2O)_3A_3 + HA \longrightarrow Al(H_2O)_2A_3(HA) + H_2O$$

or, when $Al(OH)^{2+}$ was extracted

$$Al(H_2O)_5(OH)^{2+} \longrightarrow Al(H_2O)_4(OH)^{2+} + H_2O$$

But other authors have obtained different results, for example, according to Sato and his coworkers[3,4], the mechanism is SN1, so the key steps should be

$$Al(H_2O)_{6(a)}^{3+} \xleftrightarrow[\text{fast}]{\text{slow}} Al(H_2O)_{5(a)}^{3+} + H_2O_{(a)}$$

$$Al(H_2O)_{5(a)}^{3+} + HA_{2(l)}^- \xleftrightarrow{\text{fast}} Al(H_2O)_5HA_{2(l)}^{2+}$$

$$\xrightarrow{\text{fast}} Al(A_2H)_{3(o)}$$

In the present study, a constant interfacial area cell was used to investigate the kinetics of solvent extraction of aluminum from HCl potassium biphthalate solution with DEHPA. A model taking account of all the aluminum species in a reaction zone extending from the interface to the bulk aqueous phase was applied to fit the experimental results.

2 EXPERIMENTAL

2. 1 *Analytical Methods*

A mehod has been invented in this work to determine the extracted amount of aluminum by directly developing colour in the organic phase with an 8–hydroxyquinoline alcohol solution, which produced a strong adsorption peak at 385 nm. This procedure is much

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①The project was supported by China National Natural Science Foundation; manuscript received March 3, 1992 simpler than stripping and analysis of Al in the stripping solution and much more precise than determination of the Al extracted by the difference between the aluminum in the aqueous phase and the aluminum at the imterface. DEHPA also reacted with oxine, but a good experimental line could be obtained using the same organic phase as blanks if the concentration of DEHPA wasn't too high.

2. 2 *Experimental Methods*

DEHPA was purified by recrystallization with its copper salt, yielding a purity greater than 99 %. The improved constant interfacial area cell used in the present work has already been reported[7]. The same cell has also been used to study the kinetics of HEHEPA–$Co(ClO_4)_2$, and it was found that when the agitation speed was higher than 3 s^{-1} the system was under kinetic control[8]. Since the extraction of aluminum by DEHPA is much slower than the above system, all the experiments have been carried out at a stirring speed of 3 s^{-1} in both phases.

3 RESULTS AND DISCUSSION

3. 1 *Effect of Aluminum Concentration*

In order to maintain a constant pH during extraction, $HCl-KHC_8H_4O_4$ solutions were employed as buffer systems. Although the pH was almost unchanged, the $C_8H_4O_4^{2-}$ which formed coordination compounds with Al^{3+} made the system complicated. To maintain the ionic strength, KCl was added in feed solution.

The relationship between extraction rates and aluminum concentrations in feed solution at different concentrations of the DEHPA is shown in Fig. 1. Because the coordination between $H_2C_8H_4O_4$ and Al^{3+} caused the change in the pH value, the extraction rates weren't simply proportional to the initial feed aluminum concentrations.

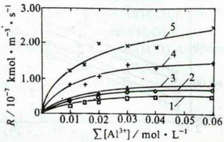

Fig. 1 Effect of aluminum concentration ($\Sigma[Al^{3+}]$) on the extraction rates (R)

[HA]: 1—0.0075 mol / L; 2—0.015 mol / L; 3—0.030 mol / L, 4—0.045 mol / L; 5—0.060 mol / L; T = 298 K

3. 2 *Effect of Acidity on Extraction*

The aqueous acidity not only affected the coordination state between Al^{3+} and H_2L and the acidic dissociation, but the surface activity equilibrium with its ions. Fig. 2 shows the effects of acidity on the logarithm extraction rates with different concentration of DEHPA and a constant concentration of aluminum.

3. 3 *Effect of Extractant Concentration on the Extraction Rate*

The extraction rates at several DEHPA concentrations have been determined with different feed solutions. The results are shown in Fig. 3 and 4. They show that when $[HA] > 0.03$ mol / L, extraction rates were directly proportional to the 1.5 power of the DEHPA concentration. When $[HA] < 0.03$ mol / L, extraction rates were directly proportional to the square root of the DEHPA concentration. These results are in concordance with those reported by Shingo Matsui[1].

3. 4 *The Apparent Activè Energy in the Extraction Process*

The difference in the effect of the concentration of the extractant on the extraction rate could be caused by the different mechanism.

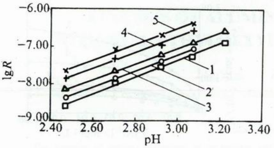

Fig. 2 Effect of pH on extraction rates (R)

[HA]: 1—0.007,5 mol / L; 2—0.015 mol / L; 3—0.030 mol / L; 4—0.045 mol / L; 5—0.060 mol / L; $T = 298$ K; $\sum[Al^{3+}] = 0.02$ mol / L

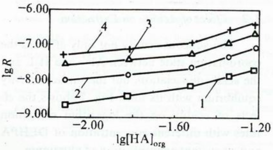

Fig. 3 Effect of [HA] on the extraction rates (R) at different pH

1—pH = 3.07; 2—pH = 2.92; 3—pH = 2.70; 4—pH = 2.47; $T = 298$ K; $\sum[A^{3+}] = 0.02$ mol / L

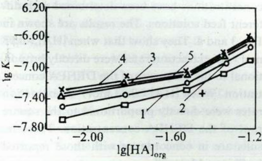

Fig. 4 Effect of [HA] on extraction rates (R) at different $[Al^{3+}]$

$\sum[Al^{3+}]$: 1 = 0.01 mol / L; 2 = 0.02 mol / L; 3 = 0.03 mol / L; 4 = 0.04 mol / L; 5 = 0.06 mol / L; $T = 298$ K

To unveil the exact reason, the extraction rates with chosen extractant concentrations were determined at several temperatures. Straight lines between lg R and $1 / T$ were obtained, when DEHPA = 0.03 mol / L, an apparent acitive energy of 57.8 kJ / mol has been calculated according to Arrenhus' Equation E_{α}; when DEHPA = 0.007,5 mol / L, $E_{\alpha} = 58.3$ kJ / mol. Since the two E_{α} above are reasonabl close, then it is possible that the mechanism is remained unchanged at different concentrations of DEHPA.

3.5 *The Effects of Interfacial Area on Extraction Rate*

In order to study the effect of the interfacial area the extraction rate, the extraction rates at diffrent interfacial areas have been determined with chosen DEHPA concentrations. The results are listed in table 1.

Table 1 The extraction rate at different interfacial area

DEHPA / kmol · m^{-3}	$\sum[Al^{3+}]$ / kmol · m^{-3}	pH	S / 10^{-3}m^2	R / 10^{-8} kmol · m^{-3} · s^{-1}
0.0075	0.02	3.07	4.206	3.592
			6.267	5.519
0.045	0.02	3.07	4.206	22.88
			6.267	25.42

General speeking, if the extraction was controlled by chemical reactions in the bulk aqueous phase, the area of the interface wouldn't affect the extraction rate. If the extraction was controlled by chemical reactions at the interface, the extraction rate would be directly proportional to the inter facial area. As shown in Table 1, the extracation rates are directly proportional to the interfacial area at the lower extractant concentration, so the extraction reaction could take place at the interface; at the higher extractant concentration, the interfacial area has only a slight effect on the extraction rate, so the process might be controlled by a chemical reaction in the aqueous phase.

It was reported that the minimum saturated adsorption concentration of DEHPA at the n-heptane-H_2O interface C_{min} was 6.0 ×

10^{-3} mol / L[9]. It is reasonable that the main path of the reaction would change from the interface to the aqueous bulk phase as the interface becomes saturated.

4 MECHANISM OF THE REACTIONS

4.1 *Coordination of Aluminum Ions in the Aqueous Phase*

With the addition of $HCl-KHC_8H_4O_4$, the following reactions could simultaneously happen[10, 11]:

$$L^{2-}+H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HL^- \qquad \lg K_1 = 4.74 \quad (1)$$

$$HL^-+H^+ \overset{K_2}{\rightleftharpoons} H_2L \qquad \mathrm{Ig}K_2 = 2.66 \quad (2)$$

$$Al^{3+}+L^{2-} \overset{\beta_1}{\rightleftharpoons} AlL^+ \qquad \lg\beta_1 = 3.18 \quad (3)$$

$$Al^{3+}+2L^{2-} \overset{\beta_2}{\rightleftharpoons} AlL_2^- \qquad \lg\beta_2 = 6.32 \quad (4)$$

$$Al^{3+}+OH^- \overset{\beta_{OH}}{\rightleftharpoons} Al(OH)^{2+} \qquad \lg\beta_{OH} = 9.27 \quad (5)$$

H_2L stands for $H_2C_8H_4O_4$ in the above equations.

Taking all of these equilibria into account, the following equations can be obtained:

$$[L]=[L^{2-}](1+10^{4.74-pH}+10^{4.74+2.66-2pH}+[Al^{3+}] \cdot (10^{3.18}+2\times 10^{6.32}[L^{2-}])) \quad (6)$$

$$[Al]=[Al^{3+}](1+10^{9.27+pH-14}+[L^{2-}] \cdot (10^{3.18}+10^{6.32}[L^{2-}])) \quad (7)$$

The above two equations couldn't be solved directly because they are related to each other. Therefore a sequential calculation method was adopted to calculate the distribution of H_2L, HL^-, L^{-2}, AlL^+, AlL^{-2}, $Al(OH)^{2+}$ and Al^{3+} with the change of Al^{3+} and pH. Fig. 5 is a typical result.

It was found that the main forms of aluminum were $Al(H_2O)_2L_2^-$, $Al(H_2O)_4L^+$ and $Al(H_2O)_6^{3+}$, and that the concentration of $Al(H_2O)_5(OH)^{2+}$ was very low under the experimental conditions.

4.2 *Reaction Mechanisms*

The following mechanism is suggested based on the calculation of the coordination states of aluminum.

(1) $Al(H_2O)_6^{3+}+A^- \longleftrightarrow Al(H_2O)_5A^{2+}+H_2O$
(2) $Al(H_2O)_5A^{2+}+A^- \longleftrightarrow Al(H_2O)_4A_2^+ +H_2O$
(3) $Al(H_2O)_4A_2^+ +A^- \longleftrightarrow Al(H_2O)_3A_3+H_2O$
(4) $Al(H_2O)_3A_3+HA \longleftrightarrow Al(H_2O)_2A_3(HA)+H_2O$
(5) $Al(H_2O)_2A_3(HA)+HA \longleftrightarrow Al(H_2O)A_3(HA)_2+H_2O$
(6) $Al(H_2O)A_3(HA)_2 \longleftrightarrow AlA_3(HA)_2+H_2O$
(7) $AlA_3(HA)_2+HA \longleftrightarrow AlA_3(HA)_3$

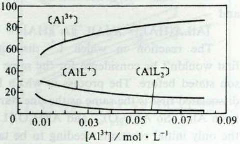

Fig. 5 Distribution of coordinated Al

$\sum[C_8H_4O_4^{2-}]=0.05$ mol / L

Each equation above includes a dissociation and a complex formation reaction, and the dissociation process was fast. Equation (7) was the rate-determining step which controlled the extraction rate because this reaction has the greatest steric hindrance. The rate equation was

$$R_{Al^{3+}} = K_5[AlA_3(HA)_2][HA] \quad (8)$$

The reactions (1 ~ 6) are fast, so they may be expressed by a single equation.

$$Al(H_2O)_6^{3+}+3A^-+2HA \overset{K_1}{\longleftrightarrow} AlA_3(HA)_2+6H_2O$$

Therefore

$$[AlA_3(HA)_2]=K_1[Al^{3+}][A^-]^3[HA]^2 \quad (9)$$

There are two reactions starting from $Al(H_2O)_4L^+$:

(1) The probability that L^2 would dissociate from the complex first is very low, because of the higher stability of the chelate bond than the single bond.

(2) H_2O dissociated first, and it was followed by sequential exchanges between H_2O and HA and A^-, so the fast-equilibrium

reactions can be expressed as

$$\mathrm{Al(H_2O)_4L^+ + A^- + 3HA \xleftrightarrow{k_1} AlLA(HA)_3 + 4H_2O}$$

and the reaction which contains the dissociation of the chelate bond is supposed to be the ratedetermining reaction because of the stability of the chelate bond.

$$\mathrm{AlLA(HA)_3 \longleftrightarrow AL(HL)A_2(HA)_2}$$

The rate of the above reactions can be expressed as

$$R_{\mathrm{AlL^+}} = K_{1,4}[\mathrm{AlLA(HA)_3}] \qquad (10)$$

and

$$[\mathrm{AlLA(HA)_3}] = K_2[\mathrm{AlL^+}][\mathrm{A^-}][\mathrm{HA}]^3 \qquad (11)$$

The reaction in which L^{2-} dissociated first wouldn't be considered for the same reason stated before. The process in which H_2O dissociated first is the same as the one starting from AlL^+. So $Al(H_2O)_6^{3+}$, and $Al(H_2O)_4^+L$ are the only initial reactants needing to be taken into account.

4. 3 *Location of the Reaction Zone*

So far in most of the kinetics model of solvent extraction, the reactions were considered to take place in a single zone such as at the interface, in the aqueous film adjacent to the interface or in the bulk aqueous phase. In fact, the reactions could take place at the interface and in the bulk phase simultaneously. The over-all reaction rate should include the contributions from all of the reaction no matter where they are taking place.

If the extraction is slow, the extractant can be considered to be in equilibrium at the interface and in the two phases and $[HA]_{aq}$ and considered to be proportional to $[HA]_{org}$

In dilute solution, employing Gibbs's adsorption equation and Schishkovsky's empirical formula one obtainned

$$[\mathrm{HA}]_{\mathrm{int}} \propto \frac{\beta\sqrt{[\mathrm{HA}]_{\mathrm{org}}}}{1+\beta\sqrt{[\mathrm{HA}]_{\mathrm{org}}}}$$

If the reactions take place in aqueous phase, therefore

$$\begin{aligned} R_{\mathrm{aq}} &= \sum_{j=1}^{2} R_{\mathrm{aq(j)}} \\ &= K_{\mathrm{aq(Al^{8+})}}[\mathrm{Al^{3+}}]_{\mathrm{aq}}[\mathrm{HA}]_{\mathrm{aq}}^{6}[\mathrm{H^+}]_{\mathrm{aq}}^{-3} + \\ &\quad K_{\mathrm{aq(AlL^+)}}[\mathrm{AlL^+}]_{\mathrm{aq}}[\mathrm{HA}]_{\mathrm{aq}}^{4}[\mathrm{H^+}]_{\mathrm{aq}}^{-1} \\ &= K'_{\mathrm{aq(Al^{3+})}}[\mathrm{Al^{3+}}][\mathrm{HA}]_{\mathrm{org}}^{3}[\mathrm{H^+}]^{-3} + \\ &\quad K'_{\mathrm{aq(AlL^+)}}[\mathrm{AlL^+}][\mathrm{HA}]_{\mathrm{org}}^{2}[\mathrm{H^+}]^{-1} \qquad (12) \end{aligned}$$

If the reactions take place at interface, then

$$\begin{aligned} R_{\mathrm{Int}} &= \sum_{J=1}^{2} R_{\mathrm{int(j)}} \\ &= K_{\mathrm{int(Al^{3+})}}[\mathrm{Al^{3+}}]_{\mathrm{int}}[\mathrm{HA}]_{\mathrm{int}}^{6}[\mathrm{H^+}]_{\mathrm{int}}^{-3} + \\ &\quad K_{\mathrm{int(AlL^+)}}[\mathrm{AlL^+}]_{\mathrm{int}}[\mathrm{HA}]_{\mathrm{int}}^{4}[\mathrm{H^+}]_{\mathrm{int}}^{-1} \\ &= K'_{\mathrm{int(Al^{3+})}}[\mathrm{Al^{3+}}]\left(\frac{\beta\sqrt{[\mathrm{HA}]_{\mathrm{org}}}}{1+\beta\sqrt{[\mathrm{HA}]_{\mathrm{org}}}}\right)^{6} \cdot \\ &\quad [\mathrm{H^+}]^{-3} + \mathrm{K}'_{\mathrm{int(AlL^+)}}[\mathrm{AlL^+}] \cdot \\ &\quad \left(\frac{\beta\sqrt{[\mathrm{HA}]_{\mathrm{org}}}}{1+\beta\sqrt{[\mathrm{HA}]_{\mathrm{org}}}}\right)^{4}[\mathrm{H^+}]^{-1} \qquad (13) \end{aligned}$$

R equals the sum of R_{aq} and R_{int}. The total reaction rate

$$R = R_{\mathrm{int}} + R_{\mathrm{aq}} \qquad (14)$$

The proposed mechanism was concordant with the experimental results in the following respects:

(1) For a single extraction reaction, it is first order with respect to $[Al^3]$ and $[AlL^+]$. The reason why the realationship between the determined extraction rates was not linear with aluminum concentrations, as shown in Fig. 1, is that the pH of the aqueous phase decreased with the increase of the aluminum concentration as the same concentration of buffer solution was used.

(2) In equation (12), R_{aq} is directly proportional to the second or third power of extractant concentration. Although R_{int} is related to the high power of $[HA]_{int}$, $[HA]_{org}$ has no effect on $[HA]_{int}$ as the adsorption is saturated. As $[HA] = 0.03$ mol / L, $R \propto [HA]^{1.5}$ and

R_{int} approximates R_{ag}.

(3) The experimental results showed $R \propto [H+]^{-2}$, but in equation (12) and (13) $R_{Al3+} \propto [H^+]^{-3}$ and $R_{AiL+} \propto [H^+]^{-1}$, respectively. This could be due to the dependence of $[Al^{3+}]$ and $[AIL^+]$ on $[H^+]$, although it is not a linear relation, the overall effect R is approximately proportional to $[H^+]^{-2}$.

4.4 *Comparison of the Calculation and the Experimental Data*

A least square regression method was applied to all of the experimental data simultaneously. With $\beta = 197$, the following parameters are worked out as

$$K'_{\text{aq}(Al^{3+})} = 3.77 \times 10^{-11} \ \text{s}^{-1}$$

$$K'_{\text{int}(Al^{3+})} = 2.35 \times 10^{-15} \ \text{kmol}^{-1} \cdot \text{m}^{-9} \cdot \text{s}^{-1}$$

$$K'_{\text{aq}(AlL^+)} = 5.56 \times 10^{-6} \ \text{kmol}^{-1} \cdot \text{m}^{3} \cdot \text{s}^{-1}$$

$$K'_{\text{int}(AlL^+)} = 6.46 \times 10^{-9} \ \text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$$

$$\sum_{i=1}^{n} (R_e - R_c)^2 = 7.41 \times 10^{-15} \ \text{kmol}^2 \text{m}^{-6} \text{s}^{-2}$$

As shown in Fig. 6, the calculated values agree with the experimental data fairly well.

5 CONCLUSIONS

The dominate forms of aluminum in the aqueous phase were $Al(H_2O)_6^{3+}$, $Al(H_2O)_4L^+$ and $Al(H_2O)_2L^{-2}$, While the concentration of $Al(H_2O)_5(OH)^{2+}$ was very low.

Based on the calculation of the coordination states of the aluminum ions, a reaction mechanism which included two paths has been proposed to describe the process:

(1) The control reaction controlling the path starting from $Al(H_2O)_6^{3+}$ was

$$AlA_3(HA)_2 + HA \longrightarrow AlA_3(HA)_3$$

(2) The reaction controlling the path starting from $Al(H_2O)_4L^+$ was

$$AlLA(HA)_3 \longrightarrow Al(HL)A_3(HA)_2$$

The extraction reactions could take place not only at the interface but also in the bulk aqueous phase: As $[DEHPA] < 0.03$ mol / L, the interfacial reactions were the primary contributors to the extration. As $[DEHPA] > 0.03$ mol / L, the reactions in the bulk aqueous played the main role.

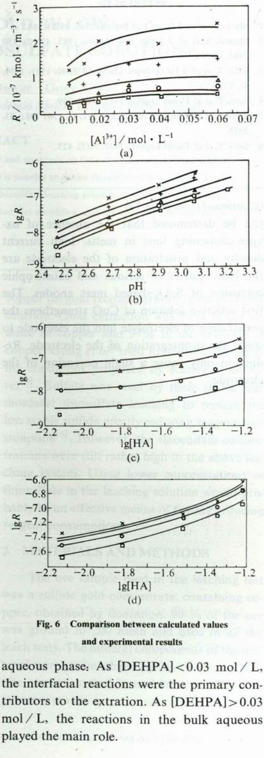

Fig. 6 Comparison between calculated values and experimental results

REFERENCES

1 Mastui,S. *et al.* J Japan Inst Metals, 1985, 49(5): 364.

2 Mastui, S. *et al.* J Japan Inst Metals, 1983, 47(10): 850 1983, 47(12): 1055.

3 Sato, T. *et al.* J Inorg. Nucl. Chem, 1978, 40: 1571: 1979, 41: 731.

4 Sato, T. *et al.* Denki kagaku, 1983, 50(9): 759.

5 Sato, T. *et al.* J Inorg Nucl Chem, 1981, 43: 1361 1981, 43: 2955.

6 Sato, T. *et al.* Denki kagaku, 1982, 51(5): 423.

7 Zhu Tun, *et al.* Chemistry (China), 1988, (2): 32–34.

8 Chen, Changqing, *et al.* in: Proc Int Sol Ext Conf '86 Vol 2, Munich, FRG: 1986. 339–343.

9 Cox, M. *et al.* in: Osseo–Asare, K. eds, Hydrometallurgy-Research, Development and Plant Practice. Atlanta, Georgia: 1983. 357–373.

10 Sillen, L. G. *et al.* Stability Contants of Metal–Ion Complexes. 2nd Edn, London: Burlington House, 1964. 65.

11 Perrin, D. D. Stability Constants of Matel-Ion Complexes, Part B–Organic Ligands. Pergamon Press, 1979. 552.

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can be determined that the absence of oxygen-containing ions in melts, high current density and penetration of the electrode are the basic causes of serious and catastrophic corrosion of SnO_2–based inert anodes. The first selective solution of CuO strengthens the penetration of electrolyte into the electrode to speed the disintegration of the electrode. Reduction only cause a slight corrosion of the electrode.

REFERENCES

1 Alder, H.. US Patent, No. 3,960,678, 1976.

2 Alder, H.. Swiss Patent, (14) 609, 1973.

3 Clark, I. M. *et al.* US Patent, No. 4, 430, 189, 1984.

4 Ray, S. P.. Light Metals, 1986, 287–298.

5 Ray, S. P.. Light Metals, 1987 367–380.

6 Wang, H. *et al.* Light Metals, 1989. 283–290.

7 Cai, Qifeng *et al.* Light Metals, 1986, (9): 28–33.

8 Xue, Jilai *et al.* Transactions of Northeast Univ of Technology, 1984, (2): 107.

9 Xiao, Haiming *et al.* Light Metals, 1992.