Wetting Behavior of Al₂O₃ Substrate by Calcium Ferrite Series Melts

Bin YU, Xuewei LV,* Shenglin Xiang, Chenguang Bai and Jiaqing Yin

School of Materials Science and Engineering, Chongqing University, No. 174 Shazhengjie, Shapingba, Chongqing, 400044 China.

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Calcium ferrite (CF) is the adhesive phase formed in high-basicity sinter. The wettability of CF with other solid phases plays an important role in assimilation process. In this study, an improved sessile drop technique was used to explore the wettability of a CF series slag, in which constant contents of Al₂O₃, MgO, SiO₂, and TiO₂ were added, with solid Al₂O₃ substrate at 1 250°C. The interfacial structure and spreading mechanisms were also discussed. The dissolution of Al₂O₃ into the slag was found to be the driving force of the wetting process. The CF series slag could rapidly spread after melting until a low apparent contact angle of approximately 10°–20° was attained. The spreading time positively correlated with the dissolution amount. The addition of MgO, SiO₂, and TiO₂ improved the wettability of CF on Al₂O₃ and decreased the surface tension of CF melt. After cooling, a three-layer structure was formed in the slag phase.

KEY WORDS: calcium ferrite; wettability; contact angle; dissolution.

1. Introduction

Currently, many iron and steel enterprises are using low-grade ores with harmful elements and gangue, as well as various kinds of industrial waste materials with iron to cut down the cost of raw materials for the blast furnace process. The use of such ores results in the frequent fluctuation of chemical composition and size distribution of the raw material mixture before the sintering strand process. These ores also influence liquid phase formation, assimilation, and solidification in the sintering process.

Sintering is a high-temperature physicochemical process that depends on the formation and crystallization of a liquid phase to bond ore particles. Wettability, which can be characterized by the contact angle, is important for assimilation. The liquid phase of calcium ferrite (CF) is first formed and continually spread along solid interfaces, such as Al₂O₃. Therefore, analyzing the wettability of Al₂O₃ by the CF series melt is important to understand the assimilation step and optimize the chemical composition of the mixture before sintering.

Nakashima et al.⁹ has studied the wetting behavior of CF slag with sintered hematite. They concluded that the wettability of a CF-based slag on a sintered hematite substrate can be improved by adding Al₂O₃, and that the spreading rate increases with increasing η/γ (viscosity/surface tension). Beyond that, there are limited report on the wettability of calcium ferrite series melts. It is reported that increasing Al₂O₃ content in the iron ore can reduce the strength and the sintering yield.²⁻⁴ The present study investigated the wetting and spreading mechanisms of CF series with Al₂O₃.

2. Experimental

2.1. Materials

For the analysis, pure-grade reagents were used to prepare the slag samples in the wetting experiments. The chemical compositions of the samples that represent the various initial liquid phases during the sintering are listed in Table 1. CaO was replaced by equal moles of CaCO₃ because of the good moisture absorbent ability of CaO.

Reagents (10 g) were weighed, mixed homogeneously, and then pressed into a cylindrical pellet (φ20 mm) using a uniaxial hydraulic presser with 10 Mpa pressure. The pellets were loaded into an electric resistance furnace for roasting. The samples were heated in air atmosphere to 900°C for 1 h, continuously heated up to 1 200°C for 8 h, and then naturally cooled to room temperature in the furnace. The roasted samples were analyzed using XRD on a Rigaku Ultima X-ray diffractometer and Cu Kα radiation. The XRD patterns are shown in Fig. 1.

The XRD results showed that CaFe₂O₄ (CF) was formed in all samples (Table 1) after roasting. Aside from CF, no Table 1. Chemical composition of the samples (mass%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>MgO</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>74.01</td>
<td>25.99</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CF-2A</td>
<td>72.53</td>
<td>25.47</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CF-2S</td>
<td>72.53</td>
<td>25.47</td>
<td>–</td>
<td>2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CF-2M</td>
<td>72.53</td>
<td>25.47</td>
<td>–</td>
<td>–</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>CF-2T</td>
<td>72.53</td>
<td>25.47</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2</td>
</tr>
</tbody>
</table>

* Corresponding author: E-mail: lvxuewei@163.com
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other phases were formed in CF and CF-2A. A small amount of C2F was detected in CF-2M. Ca2SiO4 and CaTiO3 were generated in CF-2S and CF-2T after roasting, respectively.

Cubic bulk samples 3 mm × 3 mm × 3 mm in dimension and approximately 60 mg in weight were used for the wetting experiment.

The Al2O3 substrate used in this experiment was 20 mm × 20 mm × 5 mm in dimensions, 2.47% in porosity, and 99(wt.)% in purity. The major impurity was yttria. A smooth surface is important to achieve an accurate measurement of wettability behavior. To obtain a smooth surface, the Al2O3 substrate was ground with an abrasive paper four times (400, 600, 800, and 1200 CW, successively) and polished with diamond paste four times (DNW3.5, DNW2.5, DNW1.5, and DNW0.5 successively). The average surface roughness of the polished substrate was approximately 300–500 nm as measured by an IFM microscope (Boyue Instruments Co. Ltd., Dektak 150).

2.2. Wetting Equipment

High temperature and vacuum furnace were used in the wettability measurement through an improved sessile drop technique. The schematic of this experiment is shown in Fig. 2.

The experimental setup mainly includes a furnace, a heating-control system, a vacuum-made system, a gas circulation system, a promotion and a demotion of the sample stage, a sample-dropped system, and an image-forming and data-processing system. In summary, the operation involves heating the furnace by resistance (pure Ta) to the experiment temperature, dripping the sample into the high-temperature zone, and then capturing photos with a camera. Laser was used to irradiate the sample and reduce the strong background influence on the image. Surftens43 software with an accuracy of ±1° was used to facilitate the calculation of the appearance contact angle.

2.3. Wetting Experiment

The samples and Al2O3 substrate were cleaned with acetone (≥99.5%) using an ultrasonic wave cleaner for 10 min. The mass of the dry sample was weighed with an electronic balance (Huazhi, HZK-FA110).

When the temperature of the chamber reached 1250°C, it should be kept for 20 min at first. The slag sample that was initially placed in a tube outside the chamber was dropped into an open alumina tube in the chamber and rested on the substrate surface. As soon as the drop was observed, the drop profile was recorded by a high-resolution optical camera. The time at which the sample completely melted was defined as the starting point of wetting. Pure Ar (99.9999%) was blown into the furnace, and the pressure was controlled at approximately 1.05 atm under the experimental conditions.

The samples with the substrate after the wetting experiment were embedded with resin and then vertically cut along the center of the drop. The cross-section of the drop and the substrate were polished for SEM and EDS observations.

3. Results and Discussion

3.1. Wetting Behavior

The wetting processes of the Al2O3 substrate by various samples at 1250°C are shown in Fig. 3. The apparent contact angle (θ) of the slag droplets was measured from these images.

Figure 4 presents the three runs of θ as a function of time for the Al2O3 substrate by CF. The reproducibility of the
measurements was poor because the contact angle was influenced by the sample size, shape, and defined initial wetting time, among others. At least two runs of the experimental were carried out, and the results were regarded accurate if the relative error was less than 5%. Experiments were repeated until satisfactory results were obtained. The average of two reproducible runs was regarded as the final result.

The wetting process for each melt is shown in Fig. 5. All the CF series melts rapidly spread along the substrate after melting. Most of the melts, except for CF-2S, approached the equilibrium contact angle after 200 s. The apparent contact angle gradually decreased until a constant value was reached. This constant value is referred as the equilibration apparent contact angle, which mostly varies between 11° and 16°. The equilibration apparent contact angles of the samples on the Al2O3 substrate are listed in Table 2. The underlined data indicate a large relative error (>5%), and thus, were not adopted. The average contact angle of two creditable runs was considered as the final equilibration apparent contact angle.

3.2. Interface Microstructure and Spreading Mechanisms

Figure 6 shows the interface microstructure of the CF-Al2O3 substrate after the wetting experiment. As shown in Figs. 6(a) and 6(a'), the dissolution track of the Al2O3 substrate was developed with the movement of the triple line of the system. This result indicates that the wetting process was driven by the dissolution of Al2O3 into the melt. In addition, the corrosion depth became deeper from the triple line to the center of the droplet. Figures 6(b) and 6(c) show that the slag phase can be divided into three layers (I, II, III). The formation process is shown in Fig. 7. Layer (I) consisted of large lump crystals. Spectrogram 1 shows that this layer was a solid solution phase that contained Fe2O3 and Al2O3, and that the solvent was Fe2O3. The total molar concentrations of Fe2O3 and Al2O3 were higher than that of CaO because Al2O3 dissolved in the melt and served as the Fe2O3 for the same crystal structure. During the cooling process, the Fe2O3 solid solution with a high melting point (1318°C) initially crystallized at the interface, which worked as the
nucleation particle, and continually developed along the vertical direction of the interface. In addition, calcium aluminate bearing some Fe₂O₃ was generated, as shown in spectrogram 2. Layer III, which was not continuous, was composed of lath-shaped crystals. Spectrogram 3 shows that this layer represented the CaO·Al₂O₃ phase with a melting point of 1362°C. During the cooling process, a high-melting point CaO·Al₂O₃ was generated at the surface and grew along the interior of the melt because the surface melt cooled faster than the center melt. Layer II was composed of columnar crystals. Spectrogram 4 shows that this layer represented a columnar CF solid solution phase that contained Al₂O₃ and was generated during the cooling process when the total molar contents of Fe₂O₃ and Al₂O₃ were almost equal to 0.5 molar CaO.

These phenomena indicate that the wetting process was driven by dissolution.

Figure 8 shows the interface microstructure of the other four slag systems. After the wetting experiment, the slag systems CF-2A, CF-2S, and CF-2T were very similar to
each other in interface structure and products. A three-layer structure was initially formed. Layer I was the lump solid solution phase containing Fe₂O₃ and Al₂O₃, and the solvent was Fe₂O₃. In addition, some nubby calcium aluminates dispersed in this layer. Layer II was the columnar CF solid solution containing Al₂O₃. Layer III principally consisted of lath-shaped crystal CaO·Al₂O₃. The difference was that some special compounds and crystals were generated in different slag systems. Acicular SFCA ((b)-spectrogram 4) was generated at the CF-2S slag system and was randomly distributed in layer II. It was the only distribution form of SiO₂. CaTiO₃ was generated at the CF-2T slag system and was relatively uniformly distributed in layer II.

The interface structure and products of the CF-2M slag differed from those of the other slag systems in the experiment. The main body of the whole slag was almost a uniform solid solute phase that contained Fe₂O₃, CaO, Al₂O₃, and MgO ((d)-spectrogram 1), and the molar ratio of Ca and (Fe, Al) was approximately 1:2. The lump CaAl₂O₄ ((d)-spectrogram 2) and Fe₂O₃ solid solute that contained Al₂O₃ ((d)-spectrogram 3) were uniformly distributed in the slag. Some bubbles were also formed in the melt, and the spectrogram results in (d)-spectrogram 4 indicate that the composition of the bubbles’ surface was principally Fe. The reason remains to be further discussed.

Figure 9 shows the SEM of the CF-Al₂O₃ substrate and the schematic of the wetting process. To the wetting driven by dissolution, the real contact angle (α) cannot be directly measured because the melt is opaque. To reflect the actual wettability of the wetting system, θ' was measured, and the total contact angle α can be obtained by adding θ and θ'. The results are listed in Table 3.

As shown in Table 3, all the total contact angles were smaller than 30°, indicating that all the slag systems were wetting well with Al₂O₃. Adding a certain amount of MgO, SiO₂, and TiO₂ can improve the wettability of CF to Al₂O₃. The addition of 2(wt)% Al₂O₃ only exerted minimal effects on the wettability of CF to Al₂O₃.

On the basis of Young’s equation, the equilibrate contact...
angle is related to the interfacial tension of the solid/liquid/gas phase. In this study, we assume that the interfacial tension of the solid/liquid (γ_s) phase would not change in the wetting process, thus the equilibrium contact angle positively correlates with the interfacial tension of the liquid/gas phase (γ_l). In other words, decreasing the surface tension of the melt improves its wettability.

A model based on Butler’s equation was derived by Masahito et al. to estimate the surface tension of ionic mixtures to the molten slag system. The surface tension γ of the two- or three-component molten slag is calculated from the following equation:

\[
γ = γ_i^{\text{pure}} + \frac{RT}{A_i} \ln \frac{M_i^{\text{Surf}}}{M_i^{\text{Bulk}}} \tag{1}
\]

where

\[
M_i^\gamma = \left( \frac{R_A}{R_X} N_i^\gamma \right) \left( \sum R_{\text{cation},i} N_i^P + R_{\text{anion},i} N_i^O \right)
\]

\[
A_i = N_i^{1/3} \sqrt{V_i^{2/3}}
\]

\[
R_A = R_{\text{cation},i} R_{\text{cation},i} R_{\text{cation},i}, R_{\text{anion},i} R_{\text{cation},i} R_{\text{anion},i}. \tag{2}
\]

The data on ionic radii are obtained from Shannon, and the data on the molar volumes of the pure oxides are recommended by Mills and Keene. Regarding the temperature dependence of the surface tensions for pure CaO, SiO_2, and Al_2O_3 are collected from NIST. The surface tensions of pure MgO, TiO_2, and Fe_2O_3 were obtained by extrapolating the temperature dependence of the surface tension measured in previous works. The surface tensions of each slag system calculated based on the model are listed in Table 4.

As shown in Table 4, the surface tension gradually decreases upon the addition of MgO, SiO_2, and TiO_2, which serve as surfactants to the CF melt. This result indicates that the equation contact angle decreases with decreasing surface tension of the melt. In other words, decreasing the surface tension of melt improves its wettability.

The viscosity and spreading time of the slag system are listed in Table 4. The viscosity is calculated by thermodynamics software FactSage 6.2. The spreading time is defined as the time in which the apparent contact angle can attain the value φ:

\[
\phi = (1 + 3\%) \cdot \theta \tag{2}
\]

because the measured apparent equilibrium contact angle is fluctuant. θ is the final apparent contact angle measured from the experiment.

The relationship between the spreading time and the value of η/γ is shown in Fig. 10. This result indicates that the spreading time is inversely proportional to η/γ. In other words, the spreading rate positively correlates with η/γ and increases with decreasing η/γ upon the addition of Al_2O_3, MgO, SiO_2, and TiO_2.

This result agrees with the result obtained by Nakashima et al., who studied the wetting behavior of the CF slag with the sintered hematite and concludes that the wettability of the CF-based slag on the sintered hematite substrate is improved by adding SiO_2 or Al_2O_3. The spreading rate increases with increasing η/γ (viscosity/surface tension).

However, the relationship between the spreading rate and viscosity/surface tension from this study is opposite to that of Schonhorn et al. and T. P. Yin. The former measured the spreading rates of spherical droplets onto rigid, horizontal substrates while the latter showed the theoretically calculation results. They concluded that the spreading rate correlates with the surface tension γ of the melt and inversely correlates with the viscosity η. Note that they measured or calculated the spreading rate without considering the substrate dissolution. The case may be different when substrate dissolution is considered.

Figure 11 is the schematic illustration of the dissolution process. We assume that Al_2O_3 dissolution only occurs at

| Table 3. Real contact angle in different experiments (unit: °). |
|----------------|----------------|----------------|----------------|----------------|----------------|
| Samples       | CF             | CF-2A          | CF-2M          | CF-2S          | CF-2T          |
| θ             | 15.3           | 13.7           | 14.6           | 11.5           | 11.7           |
| θ'            | 10.6           | 11.9           | 8.2            | 6.8            | 6.3            |
| α=θ+θ'        | 25.9           | 25.6           | 22.8           | 18.3           | 18.0           |

| Table 4. Calculated surface tension, viscosity, and spreading time of each melt. |
|----------------|----------------|----------------|----------------|----------------|----------------|
| Sample         | CF             | CF-2A          | CF-2M          | CF-2S          | CF-2T          |
| Surface tension (γ, N/m) | 0.675 | 0.678 | 0.669 | 0.63 | 0.642 |
| Viscosity (η, Pa·s)    | 0.043 | 0.046 | 0.045 | 0.044 | 0.044 |
| Spreading time (t, s)  | 292 | 208 | 220 | 194 | 223 |
| w/h                 | 25.885 | 44.208 | 36.973 | 49.353 | 29.36 |
| η/γ×10^-2 Pa·s/N·m^-3 | 6.37 | 6.78 | 6.73 | 6.98 | 6.66 |
a boundary layer approaching the substrate with width $\delta$ and that $\text{Al}_2\text{O}_3$ is homogeneous in the slag bulk. Then, the mass transfer equation in the slag can be expressed as

$$D_L \frac{\partial^2 C}{\partial x^2} + f \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad \text{............... (3)}$$

where $D_L$ is the diffusion coefficient of $\text{Al}_2\text{O}_3$ and $f$ is the dissolution rate.

When the process attains equilibrium state, $\partial C / \partial t = 0$, $D_L$ and $\delta$ are constants. The boundary conditions are $x=0$, $C = C_L$; $x=\delta$, $C = C_b$. The integral result of Eq. (3) can be expressed as

$$C - C_L = \frac{1}{1 - \exp(-f \delta / D_L)} \quad \text{............... (4)}$$

where $C$ is the $\text{Al}_2\text{O}_3$ concentration in the boundary layer; $C_L$ is the $\text{Al}_2\text{O}_3$ concentration at the interfacial and equal to the saturation solubility; $C_S$ is a constant representing the $\text{Al}_2\text{O}_3$ concentration of the substrate; and $C_b$ is the $\text{Al}_2\text{O}_3$ concentration in the slag bulk. The dissolution flux of $\text{Al}_2\text{O}_3$ is

$$N = D_L \frac{dC}{dx} \bigg|_{x=0} = f(C_S - C_L) \quad \text{............... (5)}$$

Then, $f$ will be solved using Eqs. (4) and (5)

$$f = \frac{D_L}{\delta} \ln \left( 1 + \frac{C_L - C_b}{C_S - C_L} \right) \quad \text{............... (6)}$$

Therefore, the $\text{Al}_2\text{O}_3$ dissolution rate negatively correlates with the concentration in slag bulk. In other words, the solute concentration increases and the dissolution rate decreases with the progress of dissolution. Moreover, the dissolution rate has a significant decrease in the final stage. To different dissolution systems, the solid’s maximum solute amount which is the real solute amount in the experiment would be different. Some of it is low, and the other is high, but the dissolution and spreading for all the systems stop when attaining the maximum. For the former system with low-solute amount, the dissolution and spreading would stop when its maximum attain, but the latter system with high-solute amount would continue to dissolve and spread because its maximum dose not attain. Hence, for the pure dissolution driving wetting system, the spreading time of the higher solute amount system is longer than that of the lower solute amount system.

In this study, the wetting process is driven by dissolution. The relationship between spreading time and $w/h$ is shown in Fig. 10. Due to the limited added amount of oxide, the systems are similar in solubility. However, the systems differ in dissolution amount and will not saturate for the limited time. Larger $w/h$ state means shallower corrosion pit and less dissolution amount (homologous shorter spreading time based on the above analysis). Figure 10 shows that the spreading time negatively correlates with $w/h$, which is consistent with the analysis list on the above paper. This result indicates that the spreading time for the pure dissolution driving wetting system is decided by the dissolution amount of the substrate dissolves into the melt. Higher dissolution amount means longer dissolution time, and thus, longer spreading time. Notably, this case is only suitable for the pure dissolution driving wetting system with similar $D_L/\delta$, $C_L$.

In these systems, $w$ represents the ability of horizontal direction spread and $h$ represents the dissolution ability of solid substrate. Therefore, $w/h$ represents the relative magnitude between the spreading and the dissolution. Liang Yin et al. analyzed in detail for a dissolution wetting system and asserted that spreading at the early stage mainly occurs at the horizontal direction and is dominated by convective transport. Meanwhile, spreading at the late stage is dominated by vertical diffusion transport, which directly leads to the spread of the dissolution wetting system dominated by dissolution. Viscosity is the resistance of the convective process and principally affects the horizontal direction spread. The rise–fall of liquid surface in a capillary tube ($f(\text{Fig. } 12)$ indirectly reflects the vertical dissolution ability of liquid to solid. Higher liquid surface rise (with larger $H$) means higher solid dissolution amount from the vertical into the liquid, namely, deeper dissolution at the vertical direction. However, $H$ is proportional to the surface tension of the liquid. Therefore, the surface tension affects the vertical dissolution of the substrate. In other words, $\eta/\gamma$ itself might reflect the relative intensity relationship between spreading and dissolution. Thus, $w/h$ and $\eta/\gamma$ change in the same way.

In fact, viscosity and surface tension are related to the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the CF-based melts phase, and the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ might be affected by the oxygen partial pressure in the furnace.

In this study, the furnace was first vacuumed to $5 \times 10^{-5}$ Pa.
and then filled with Ar gas until 0.8 atm was attained. Therefore, the residual oxygen partial pressure was 1.05 × 10^-8 Pa. At the experimental temperature of 1250°C, the residual oxygen partial pressure was 1.25 × 10^-9 Pa because the total pressure in the furnace reached 1.0–1.1 atm. Conversely, the Ar gas with initial purity of 99.99% was purified by pure Mg at 450°C before being poured into the furnace. The reaction of the purification process can be described as

\[
\text{Mg(s)} + 0.5\text{O}_2(g) = \text{MgO(s)}
\]

\[
\Delta G^0 = -601 \cdot 230 + 107.59T \quad J/\text{mol}
\]

Thus, the oxygen partial pressure in Ar gas phase decreased to 2.4 × 10^-76 Pa if the reaction reached the equilibrium state.

Moreover, the disintegration of FeO\(_3\) into O\(_2\) and FeO\(_4\) at a high temperature may be considerable. If this process is considered, then the reaction can be expressed as

\[
6\text{Fe}_2\text{O}_3(s) = 4\text{Fe}_4\text{O}_4(s) + \text{O}_2(g)
\]

\[
\Delta G^0 = 477658 - 277.2T \quad J/\text{mol}
\]

The equilibrium oxygen partial pressure can be calculated as 1.26 × 10^-7 on the basis of the reaction. This value is greater than that of the residual oxygen partial pressure and the oxygen partial pressure in Ar gas phase, which leads to the inevitable disintegration of FeO\(_3\). Thus, FactSage 6.2 can be used to calculate the ratio of Fe\(^{2+}\)/Fe\(^{3+}\) and the viscosity of each melt. The results are listed in Table 5. The surface tension of each melt, calculated by Eq. (1), is also listed in Table 5. The surface tension for pure FeO was collected from NIST.\(^{15}\)

Compared with the above calculated surface tension and viscosity, surface tension and viscosity decreased by approximately 2% and 13%, respectively. However, the general variation regularity of surface tension or viscosity/surface tension did not change.

4. Conclusion

An improved sessile drop technique was used to measure the apparent contact angle of CF series melts, with Al\(_2\)O\(_3\), MgO, SiO\(_2\), and TiO\(_2\) as additives and Al\(_2\)O\(_3\) as the substrate. The interfacial structures and spreading mechanisms of the systems were also discussed. The following results were obtained:

1. The slag samples melt at 1250°C and then slowly spread on the substrate but wet well with the Al\(_2\)O\(_3\) substrate.

2. Dissolution of the Al\(_2\)O\(_3\) substrate is the driving force of the wetting process. No distinct reaction product layer is generated near the interface.

3. Addition of certain amounts of MgO or SiO\(_2\) or TiO\(_2\) can improve the wettability of CF to the Al\(_2\)O\(_3\) substrate.

4. The spreading time for the pure dissolution driving wetting system increases with increasing relative dissolution amount.

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REFERENCES

3) Y. Wu: Rev. Iron Steel, 6 (2005), 5.
18) A. Dietzel: Sprechsaal, 75 (1942), 82.