

Study on the Mechanism of Heterogeneous Catalysis (3)

—The Catalysis of W, Mo, S and SiO₂ on Carbon Dissolving and Mechanism of Carbon Dissolving in the Iron-Graphite Compact

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Abstract

This is an article that validates Electron Cyclic Donate-Accept Catalysis Mechanism-ECDAM or Electron Orbital Deformation-Recovery Cycle Catalysis Mechanism-EODRM. In this paper, the influence of compact density, sintering temperature and time, vacuum degree, atmosphere and alloying element on the carbon dissolving rate into γ -Fe were studied. The experiment results have been reported. The way that the carbon is dissolved into γ -Fe was discussed. Gas phase composition and temperature play an important role on the carbon dissolving rate. The carbon gasification reaction is the determining step of dissolving carbon process. K₂CO₃, W and Mo are a catalysts, and their active size are K₂CO₃ > W > Mo. S and SiO₂ are a poison, and their poison size are SiO₂ > S. The experiment results are completely consistent with the original judgment of ECDAM.

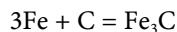
Keywords

Heterogeneous Catalysis, Powder Metallurgy, Sintering

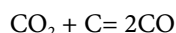
1. Introduction

Fe-C alloy sintered steel is the most essential and important material of iron based P/M. This conventional production process of P/M sintered steel part consists of admixture, pressure forming and sintering. In order to improve the mechanical strength of the sintered steel, the alloy elements of Cu, Ni, W, Mo etc. which is not easy oxidizing are often added to admixture powder. In order to improve the processing performance and to reduce the mold wear, the sulfur is usually added to admixture powder.

During sintering, the particle graphite dissolves in iron, and then sintered steel has formed. So, in what mechanism does graphite dissolve into iron? With respect to this problem of carbon transfer, there are only two possibilities. One is that the carbon directly dissolves into iron, and other is that the carbon indirectly dissolves into iron. The directly or contact dissolution should be



The indirectly dissolution should be



- The transfer of carbon relies on the carbon gasification reaction. In the compact, the iron is in close contact with carbon, the contacting reaction of iron with carbon is entirely possible to take place. So the direct dissolve and indirect dissolve, which one is the dominant one? If indirect dissolution is the main one, then what is about the role of alloying elements or catalysts? This is the purpose of this study. In fact, the main purpose of this subject is to validate the ECDAM or EODRM.

2. Experiments

Iron powder used in this study is electrolytic iron powder. Its chemical composition and sieve analysis were listed in **Table 1** and **Table 2**.

Synthetic graphite powder was chosen, its chemical and physical properties were listed in **Table 3**.

Some alloy elements and compound additives such as tungsten powder (average particle size around 1 μm), molybdenum powder (average particle size around 2.6 μm), potassium carbonate (around 7.8 μm , chemical purity), silica powder (around 0.1 μm) and sulfur powder (around 9.3 μm) were added respectively into the iron-graphite compacts. The amount of graphite added to the iron powder was 0.8%, and the amount of additive added to graphite powder was 15% - 18% of graphite.

In process, first, the additives such as W, Mo etc. is mixed with graphite, and then mixed with iron powder. In order to eliminate the interference of lubricants, it will not be used.

Table 1. Chemical analysis of iron powder, %.

Total iron	Carbon	Oxygen	Sulfur	Phosphorus	Insolubles
99.8	0.02	0.092	0.01	0.005	0.02

Table 2. Sieve analysis of iron powder particle (Mesh)%.

-60 + 100	-100 + 150	-150 + 200	-200 + 250	-250 + 360	-360
9.7	26.6	15.2	17.3	21.8	9.4

Table 3. Chemical composition and physical properties of graphite.

Chemical analysis			Particulate size (μm), average			Specific surface
Carbon	Ash	Water	Volates	F.S.S.S	B.E.T	B.E.T (M^2/g)
99.0	0.37	0.03	0.41	2.7	1.03	2.6

The mixed iron powder is pressed in steel die to densities 5.8 and 7.0 g/cm^3 . The size of cylindrical compact is 10 mm dia. and 10 mm height.

The sintering process is carried out in a high temperature quartz tube furnace. There are four kinds of sintering atmosphere;

- a) Vacuum, the vacuum degree is 4×10^{-5} torr.
 - b) Vacuum, the vacuum degree is 1.2×10^{-2} torr.
 - c) Protective atmosphere. Nitrogen 25% + Hydrogen 75%. And its dew point was about -15°C , the gas flow rate was 2 l/min. The sample was exposed to the protective atmosphere.
 - d) In the package or cover boat. The sample was closed in package. It is cut off from protective atmosphere. The atmosphere in the package would be self-generated by chemical reaction of remnant oxygen with graphite within the compact pores as well as air gap in package.
- Metallographic microscope was applied to estimate the amount% of pearlite on the friction mirror face which is corroded by 5% nitric acid alcohol. Based on national standard, the amounts of Pearlite are measured by professional technicians. The black field of vision, empty except, shows Pearlite (contained carbon 0.8%), and the white field of vision shows Ferrite (contained carbon 0.08%). The more pearlite content, the more dissolved carbon.

3. Results and Discussion

1) Direct and indirect dissolving of carbon in the sintering process?

From **Figure 1** and **Figure 2**, it can be seen that the dissolving rate of carbon of high density compacts (7.0 g/cm^3 , porosity 11%) is slower than that of low density, 5.8 g/cm^3 (porosity 26%). The differences are more remarkable for the samples sintered in the covered boat. If the carbon absorbing by iron took place by solid-solid reaction, hence it would be favour for the high density compacts, due to the contact points between particle graphite and iron are more than that of low density. But the experimental results are just the opposite. This clearly shows that the dissolution of carbon mainly relies on indirect dissolution, which relies on carbon gasification reactions. The carbon gasification reaction becomes the process control step.

From **Figure 3**, although the vacuum degree and compact density are higher, however, the rate of dissolution of carbon in a with tungsten compact is still higher than that of unadded tungsten compact, and the tungsten still has appeared the catalytic active, the result show that the gas phase in porosity still plays an important role in carbon dissolving process.

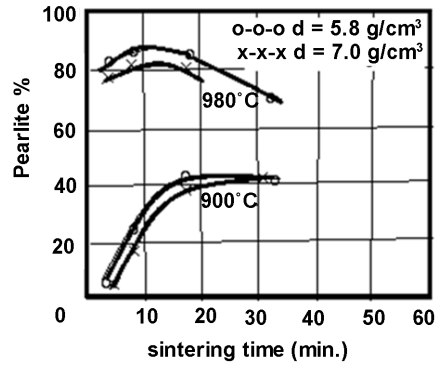


Figure 1. Variation of pearlite%-sintering time for two densities sintered in N_2 -H.

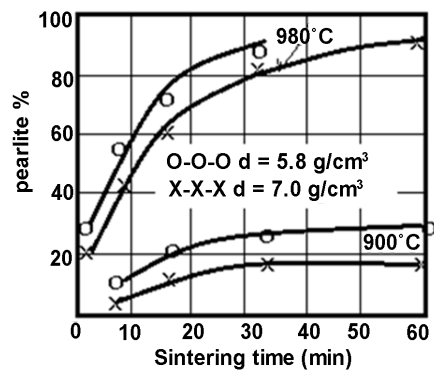


Figure 2. Variation of pearlite%-sintering time (min.) for two densities sintered in the covered boat.

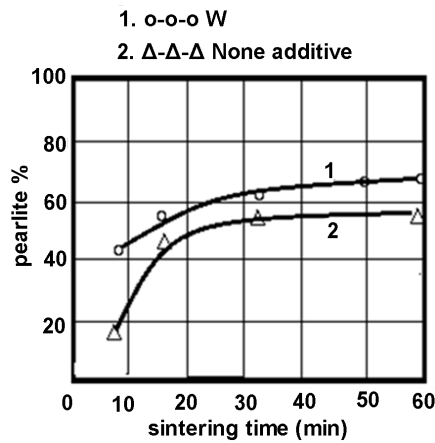


Figure 3. Variation of pearlite%-sintering time for W additive and no additive sintered in vacuum $980^\circ C$, $d = 7.0 \text{ g/cm}^3$, $P = 10^{-5} \text{ torr}$.

From **Figure 4**, it is surprising to compare the metallograph of (a) (b), (c), (d), (e). It can be found that the photos (b), (c) of putting some W and K_2CO_3 are full of pearlite, and the photos (d), (e) of putting some S and SiO_2 are almost a white field, especially SiO_2 . These results are clear to tell that the dissolution of carbon

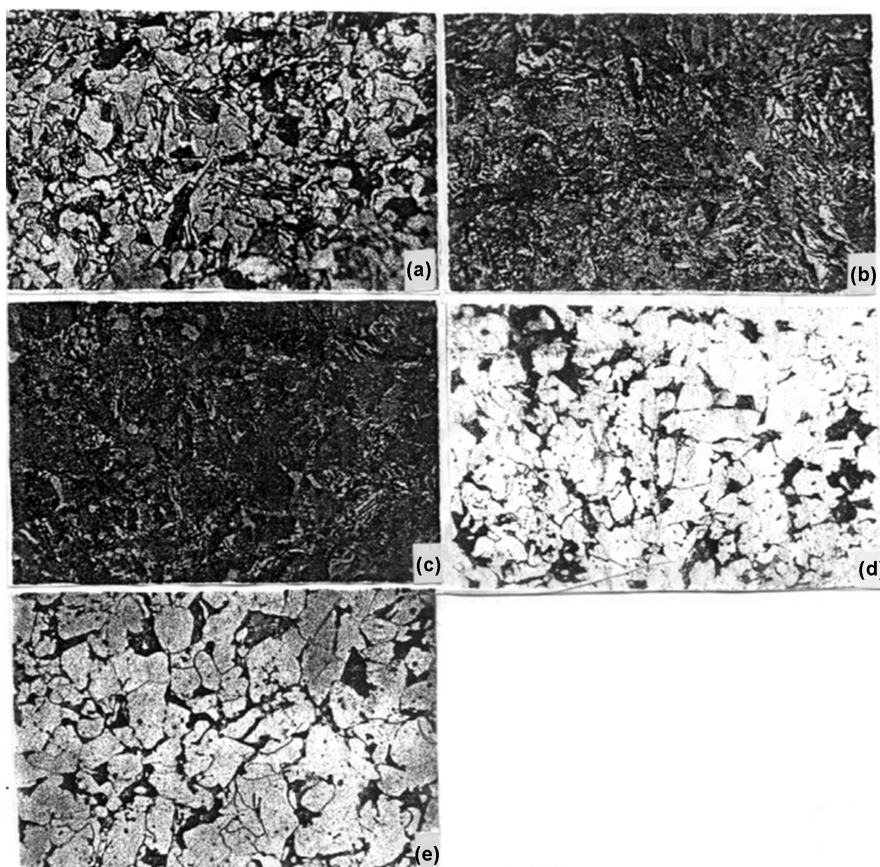


Figure 4. The effect of additives in Fe-C mixture compact on pearlite amount formed after sintering specimen is coated iron box 980°C. 8 min. N₂ + H₂ atmosphere. (a) Fe + 0.8%C; (b) Fe + 0.8%C + 0.12%K₂CO₃; (c) Fe + 0.8%C + 0.14%W; (d) Fe + 0.8%C + 0.12%SiO₂; (e) Fe + 0.8%C + 0.12%S.

is almost entirely indirect dissolving, and that there is almost no direct solution, and the solid-solid reaction almost completely absent.

It is worth noting that, from **Figure 4**, photo (d) and (e), on the one hand it is obvious that S and SiO₂ appear clearly poison effects, and on the other hand it is obvious that there is no direct dissolving, because of it can't see the pearlite in the field of vision. But the author believes that direct dissolution is completely excluded, this judgment needs to be further research.

2) Effects of sintering atmosphere and time on the dissolving carbon rat.

Figure 5 shows the effects of different sintering atmospheres on the dissolving rate of carbon. In N₂-H₂ atmosphere, it can be seen that the dissolving rate is the fastest during the initial period. In high vacuum, $p = 4 \times 10^{-5}$ torr, the dissolving rate of carbon is lowest than that the low vacuum, $p = 2 \times 10^{-2}$ torr. These results shown clearly that indirect dissolving was the main way of carbon dissolving, and the carbon gasification reaction still played an important role. Because the point of contact between iron and graphite, after all, not much.

From **Figure 1**, **Figure 5**, **Figure 6**, it can be seen that the dissolving rate of carbon is higher fast in the N₂ + H₂ atmosphere during sintering process, and the

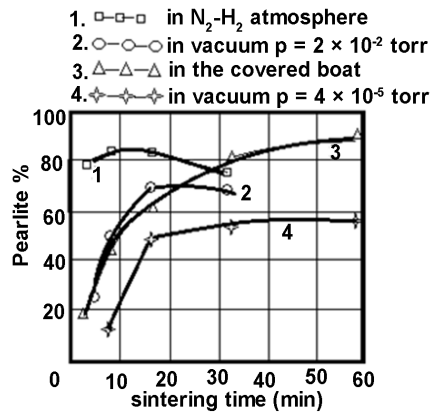


Figure 5. Variation of pearlite%-sintering for several atmospheres, 980°C, $d = 7.0 \text{ g/cm}^3$.

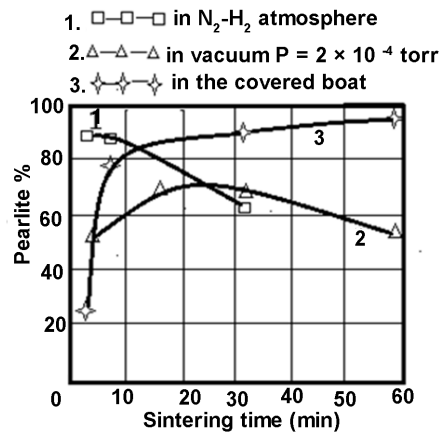


Figure 6. Variation of pearlite%-sintering time for several atmospheres, 1060°C, $d = 7.0 \text{ g/cm}^3$.

curve appears downward tendency. Author considers that the first rise then descend phenomenon is caused by hydrogen. ECDAM or EODRM has an important argument, namely, there is a demarcation between the catalyst and poison, any elements or compounds that are less electronegative value than carbon are a catalyst, on the contrary, any elements and compounds that is more electronegative value than carbon are a poison. Electron Negative Value (ENV) of hydrogen is $X_{\text{H}_2} = 2.2$, it is less than carbon $X_{\text{C}} = 2.55$, $\Delta\chi_{\text{C-H}_2} = 2.55 - 2.2 = +0.33$, so hydrogen is a catalyst to carbon Gasification, it can increase the rate of carbon gasification. The other one is that the hydrogen has the ability to decarburize. It is to say that hydrogen has double effects. Hydrogen has two roles of catalysis and decarburization. The author considers that is the reason that causes the curve to go up and down.

From Figure 2, Figures 5-9, it appears that repeated experiments did not appear decarburization phenomenon in the package sintering. This may be very valuable to avoid hydrogen decarburization for P/M factory which is to use the dissociated ammonia as a protective gas.

From **Figure 9**, when the sintering time exceeds 60 minutes, there was no significant difference between adding and not adding catalyst to pearlite content formed. From **Figure 4**, sintering temperature 980°C, sintering time 8 minutes, sintering in package, on the K_2CO_3 catalyst, the photograph shows clearly that the whole field of vision seen in metallographic microscope are almost pearlite (empty except). It shows clearly that 0.8% K_2CO_3 has good catalytic active. The catalytic active size is arranged: $K_2CO_3 > W > Mo$.

Dautzenberg etc [1] have studied the catalysis of carbonates in Fe-C alloy compact sintering, it has found that the additions of 2% K_2CO_3 was not catalytic active, and think that the carbon is dissolved in the iron in a direct dissolving. Tanaka etc. [2] have also studied the catalytic effect of carbonates in iron-graphite compacts sintering, they have obtained similar results. But it's completely different from that Hong [3] get. Author considers that the different experimental results are caused by inappropriate sintering temperature (1100°C high temperature), time (long time), and atmosphere. The wrong experimental method will be to get unreliable experimental results

3) Catalysis of alloy elements on the carbon dissolving

From **Figure 7**, **Figure 8**, **Figure 9** and photograph **Figure 4**, it can be seen that the K_2CO_3 , W, Mo. have a significant catalytic effect on carbon dissolving during sintering process. On the contrary, the S and SiO_2 had showed a retarding effect on it, and SiO_2 is more poison than that the S. Although the sulfur has been completely gasified at 980°C, the contact with carbon is far better than that of the solid SiO_2 . However, due to the ENV (estimate: $X_{SiO_2} = 2.86$) of SiO_2 is more than that the S ($X_S = 2.58$), so poison of silica is naturally greater than that the S.

In iron based P/M parts production, in order to reduce mold wear, the sulfur is always added to the admixture; However, sulfur is a poison that will slow down the dissolution rate of carbon and the formation of pearlite.

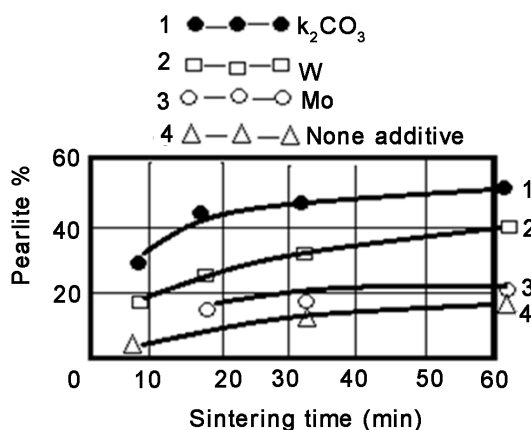


Figure 7. Variation of pearlite%-sintering time for W, Mo, K_2CO_3 additives, sintered in covered boat. 900°C, $d = 7.0 \text{ g/cm}^3$.

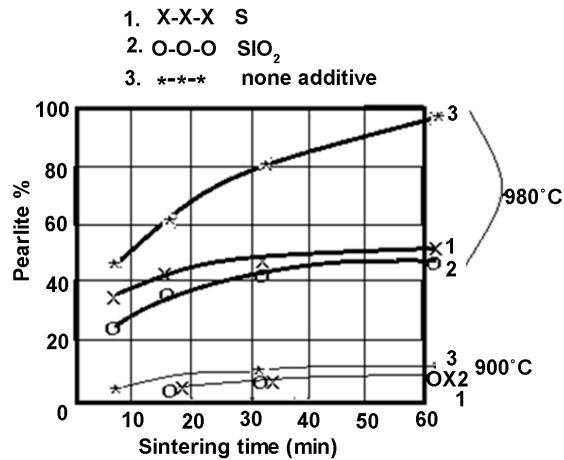


Figure 8. Variation of pearlite%-sintering time for S and SiO₂ additives sintered in covered boat. 900°C, 980°C, d = 7.0 g/cm³

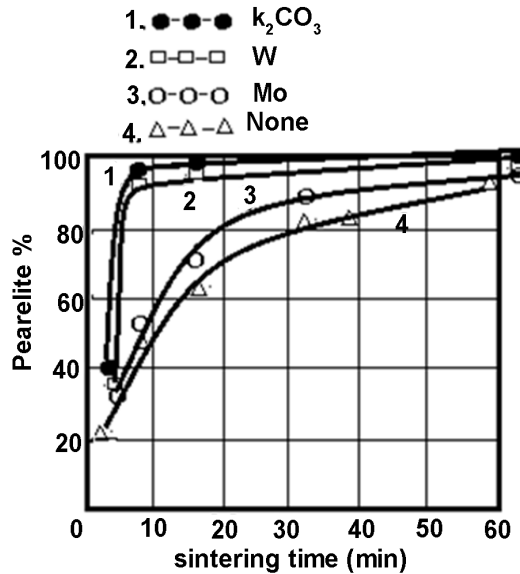


Figure 9. Variation of pearlite%-sintering time for W, Mo, K₂CO₃ additives, sintered in covered boat. 980°C, d = 7.0 g/cm³.

The Copper is commonly used as an alloying element in the production of oil bearing. According to ECDAM, copper has a catalytic effect and its catalytic activity is greater than that of W and Mo. It is conducive to the rapid dissolution of carbon and pearlite formation.

The author considers that ECDAM or EODRM is generally applicable for heterogeneous catalysis. Such as automotive catalyst, iron based ammonia synthesis catalyst, Ru based ammonia synthesis catalyst etc.

As for automotive catalysts, noble metal catalysts Pt, Pd, Rh are supported by a cordierite (2MgO-Al₂O₃-5SiO₂) honeycomb monolith coated with high surface area γ -Al₂O₃. At present, the automotive exhaust catalytic converter TWC is

widely used, the annual consumption is 60×10^6 units, noble metals consumption is about 150 tons. According to ECDAM, the ENV of cordierite (estimate value; $X_{2\text{MgO-Al}_2\text{O}_3-5\text{SiO}_2} = 2.62$) and alumina (estimate value, $X_{\text{Al}_2\text{O}_3} = 2.54$) is all greater than the electronegative of Pt, Pd, Rh ($X_{\text{Pt}} = 2.2$), $\Delta X_{\text{Pt-Al}_2\text{O}_3} = 2.2 - 2.54 = -0.34$, $\Delta X_{\text{Pt-2MgO-Al}_2\text{O}_3-5\text{SiO}_2} = 2.2 - 2.62 = -0.40$, both are all poison to noble metal catalysts. To achieve emission standards, more catalysts must be used. Thus, TWC costs are increased. Author [4] considered that it is not appropriate to use cordierite ceramic honeycomb as support and $\gamma\text{-Al}_2\text{O}_3$ as wash-coat layer. Compared with the experimental data of Fe-Cr-Al metal roll film honeycomb support, almost 1/2 noble metals are wasted [5]. Fortunately, metal roll film honeycomb support and rare earth oxides instead of alumina have been developed at present. Unfortunately, metal roll film honeycomb support has a small specific surface area, and the coating is easy to beat.

Aika [6] experiment has proved that Al_2O_3 was poison to Ru catalyst. At the same time, Du [7] experiment has also proved that the Al_2O_3 was poison to carbon gasification, for this reason, the ENV of Al_2O_3 should be greater than 2.55. Estimate value by author is: $X_{\text{Al}_2\text{O}_3} = 2.54$ (arithmetic mean value) and $X_{\text{Al}_2\text{O}_3} = 2.71$ (geometric mean value), therefore this paper has adopted $X_{\text{Al}_2\text{O}_3} = 2.71$.

As for Fe based ammonia synthesis catalyst, the catalyst produced in the whole world contains always 2.5% - 3.0% Al_2O_3 as a structural promoter. Author [8] [9] has repeatedly pointed out that Al_2O_3 is a poison to iron catalyst, because the molecular ENV of Al_2O_3 is much greater than that of iron. Let's see $\Delta\chi_{\text{C-Al}_2\text{O}_3} = 2.55 - 2.71 = -0.16$, $\Delta\chi_{\text{Ru(Pt)-Al}_2\text{O}_3} = 2.2 - 2.71 = -0.51$, $\Delta\chi_{\text{Fe-Al}_2\text{O}_3} = 1.8 - 2.71 = -0.91$, $\Delta\chi_{\text{Fe-Al}_2\text{O}_3} \gg \Delta\chi_{\text{C-Al}_2\text{O}_3}$. ECDAM has an argument that the larger the $-\Delta\chi$ value, the greater the poisoning. In terms of $-\Delta\chi$ value, Al_2O_3 is much more poison to iron catalysts than carbon.

Author considers that the three high (high temperature, high pressure and high energy consumption) situation appeared of ammonia production are likely to be caused by improper application of Al_2O_3 as promoter [8].

4. Conclusions

1) The experiment results have demonstrated that the carbon dissolving into $\gamma\text{-Fe}$ takes place mainly by indirect dissolving during the sintering process of iron-graphite compacts, *i.e.*, the carbon gasification reaction plays an important role. And it is a determining step of dissolving process, even in high vacuum sintering.

2) Hydrogen in the protective gas $\text{N}_2 + 3\text{H}_2$, which is both a catalyst and a decarburizing agent, can significantly increase the rate of carbon dissolving and significantly accelerate decarburization or reduce Pearlite content.

3) Sintering temperature plays an important role on the process. The rate increases considerably by raising sintering temperature.

Sintering under high vacuum conditions, the dissolution rate is significantly reduced.

4) The experiment results have demonstrated that the K_2CO_3 , W, Mo are catalysts, and the S, SiO_2 are poison, and carbon gasification reaction is a determining step. This result is consistent with ECDAM's judgment or Original imagine.

References

- [1] Dautzenberg, N. (1971) *Powder Metallurgy International*, **3**, 5; (1977) Dautzenberg, N. and Hewing, J. *Powder Metallurgy International*, **9**, 16.
- [2] Tanaka, Y. and Lund, T.A. (1988) Catalytic Effect of Carbonates in Iron-Graphite Compacts. *Powder Metallurgy*, **1**, 45-51. <https://doi.org/10.1179/pom.1988.31.1.45>
- [3] Hong, T. (1986) Study on the Mechanism of Sintering and Dissolution of Iron Carbon Alloy. Master's Thesis, Shanghai Research Institute of Materials, Shanghai.
- [4] JIN, J.M. (2005) Study on the Insufficiency of Ceramic Honeycomb Support for Automobile Exhaust Gas Purification Catalyst. *Shanghai Advance Materials*, **6**, 5.
- [5] Zheng Y., Li, H.Y. and Liu, J.B. (1997) The Comparison of Performance between Finland KEMIRA Metal Support Catalytic Converter and Commercial Ceramic Support Catalytic Converter. *World Automotive*, **11**, 19.
- [6] Aika, K., Ohya, A., Ozaki, A., Inoue, Y. and Yasumoli, I. (1985) Support and Promoter Effects of Rhenium Catalyst. *Journal of Catalysis*, **93**, 305-311. [https://doi.org/10.1016/0021-9517\(85\)90265-9](https://doi.org/10.1016/0021-9517(85)90265-9)
- [7] Du, G.H. and Yan, J.H. (2002) Catalysis of Metallurgical Coke Solution Loss Reaction by Minerals. *Ironmaking*, **21**, 22.
- [8] Jin, J.M. and Bao, W.F. (2012) Re-Exploration on the Relation between Support and Noble Metal Catalyst. *Materials Review*, **26**, 52.
- [9] Jin, J.M. (2015) Several Problems Existed in the Production and Study of Heterogeneous Catalysis. *Guangzhou Chemical Industry*, **43**, 47.