ON A NEW SMELTING PROCESS OF METALS (THE 1ST REPORT)

— THE FUNDAMENTAL PRINCIPLES —

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Synopsis

We have studied a new smelting process of metals. We apply the method of alloying to this process. We call that "Metal Exchange Process".

We explain the gist of this process as follows:

At first we make a mother alloy of the reqired metal(M) from its bearing ores by alloying the second metal(A), which is liable to make an alloy of the needed metal(M), by means of the suitable methods.

We use this mother alloy(M-A) as raw material of this process. The first metal(M) is separated in a free state from the mother alloy(M-A) by alloying the third metal(B) further under certain condition. Therefore we must select the third metal(B) which combines strongly and selectively with the second metal(A) as an auxiliary metal.

We have thought about the mechanism of reactions in this method from a view point of chemical bond. By giving the outline of this influence in the next place, we recognize the existence of π electron in the mother alloy(M-A). π electron bond in the mother alloy(M-A) is weakened by the intervention of the third metal(B) and buried by B electron.

We think this fact brings about a result of making $(M \cdots A \cdots B)$ alloy, the so called "activated complex". In addition of energy, (M-A) bond is cut off, but, on the other hand, (A-B) bond grows strong. Then the required metal(M) is isolated in a free state. We formularize the above facts as following chemical formula:

$$(M\text{-}A) + B \pm \text{energy} = (M \cdots A \cdots B)$$
$$(M \cdots A \cdots B) \pm \text{energy} = M + (A\text{-}B)$$

We call this process "Metal Exchange Process", from applying the method of alloying to a smelting process of metal.

I explain the gist of the process as follows; At first we make a mother alloy of the required metal (M) from its bearing ores by alloying the second metal(A) which is liable to make an alloy of the required metal, by means of the suitable methods. We use this mother alloy as raw material of this proess. The required metal is separated in a free state from the mother alloy by alloying the third metal (B) further under certain conditions.

I explain the concrete process of operation as follows (using 3 atoms system as a simple case).

At first we make a mother alloy of the required metal(M) from its bearing ores by alloying the second metal(A), being liable to make an alloy of the needed metal(M); by means of the suitable methods. Using this alloy as raw materials for metal smelting, we make it separate in a free state from the mother alloy (M-A) by alloying the third metal(B) further under certain conditions. It is desirable that the third metal (B) which combines strongly and selectively with the second metal(A) as an auxiliary metal should be selected as carefully as possible.

If the by-product, alloy (A-B), is worthy to be utilized as an important material in industry in this case, it is purposefull in economy we think. We use the mather alloy as raw materials for smelting in this process but we must consider how it has influences upon the smelting by using the mother alloy as raw material. Generally, alloy in the metallurgical conception means alloy-system, *i.e.* phase relation. That is, alloy forms the so called alloy system in which solid solution, inter-mediate phases, intermetallic compounds or these mixtures are disposed metallographically. As for the mother alloy for raw material that we produce, there is not the limit that it is not an object for smelting unless its system is composed by each of them. We need not to be patricular about phase relation from what phase it is consisted. In short, alloy (we called here) means an atomic theoretical combined substance consisted of atoms of metal. Then it seems to be proper for us to consider as stated before. I will subsequently consider the reaction mechanism of this process in a view point of force between atom and atom, *i.e.* bond energy and bond form among atoms.

We make a mother alloy containing the required metal(M) from its bearing ores, (now we make 2 component system(M-A) alloy as a simple example) and let (M-A) alloy react with metal(B). Here (-)sign means to be formed(combined) atomictheoretically without relation to phase. It is desirable that general amount of bond energy of (M-A) is lower than that of (A-B). But if the difference between them is altered by a certain condition, the metals with the quality like that, while they do not hold good ordinalily, become to be good because the general result is upset by how to decide the specified condition. This point is the key of this process.

For example, suppose that a beautifull girl(M) and a boy(A) have been combined, but now another pretty girl (B) appearsd. Two girls can not be combined because they repulse each other.

So if A would entertain good will toward B under general condition and others, A and B should be combined, and consequently A must be separated from M. On the contrary case to this, even though A entertains good will toward M, if the other conditions of B are better for A it may happen that A and B are combined. In this process both conditions are throughly used. Though we say that M was separated in a free state, it is under a certain condition that A is combined with B through intrusion of B into combination of M and A. We cannot help considering temporary triangular relation of them on the way that M is separated.

We think that the triangular relation of M, A and B, is liable to be most controlled. In the intrusion of B, B influenced the relation between A and M, and the bond force between M and A is weakend by B and the force between A and B is weakend by M. This fact is formularized as follows;

$$(M\text{-}A)+B\pm\text{energy}=(M\cdots A\cdots B)$$
$$(M\cdots A\cdots B)\pm\text{energy}=M+(A\text{-}B)$$

There is an intermediate substance (triangular relation), $(M\cdots A\cdots B)$ in the process of reaction as stated above. So we consider what qualities this intermediate substance has and how this is formed in the view of chemical bond, *i.e.* combination methood of atoms.

$$(M\text{-}A)+B\pm\text{energy}=(M\cdots A\cdots B)$$

π electron is probably contained in $(M\text{-}A)$, we suppose. If so, π bonds in $(M\text{-}A)$ are influenced and altered by the intrusion of B and consequently the intermediate substance $(M\cdots A\cdots B)$ is formed.

Bond energies of $(M\cdots A\cdots B)$ intermediate substance under that conditions are measured by other energy, although conbination of $(M\text{-}A)$ is cut off by the subcondition, then conbination of A and B is strengthened and M is removed.

$$(M\cdots A\cdots B)\pm\text{energy}=M+(A\text{-}B)$$

Also we consider the mechanism of reaction in view of the bond energy of atoms. This intermediate substance $(M\cdots A\cdots B)$ corresponds to the so called "activated complex", we think.

It is to say that the state, or a mountain pass into product system from reaction system, indicating as a sign, is a semistable, middle state, that is, a complex in a transition state, (which is unclear and doubtfull itself *I* think).

Now we consider under what conditions L and M react each other in the reaction $(L+M=P+Q)$. Of caurse, valency force acts upon between L and M, and if there are proper conditions, bond force acts. L must be in contact with M to react each other, but it is not to say that a reaction occurrs owing to only a contact. This is a valley of minimum in potential energy in view of the energy, also $(P+Q)$ state is the other valley. The chemical reaction is that molecules move from $(L+M)$ state to $(P+Q)$ state, and for this purpose the movement have to pass a mountain pass. The height of the pass corresponds to the activation energy. If the molecules lay themselves in the valley at room temperature, reaction does not occur. If the system is given a large energy to pass through a mountain pass by our activating the molecules, reaction occurs and the molecules move from $(L+M)$ valley to $(P+Q)$ valley, that is, reaction $L+M=P+Q$ occurs and the top of a mountain pass corresponds to the activated complex. Most of the reactions indicating $L+MN=M+LN$ generally in three atoms reaction take a $(L\cdots M\cdots N)$ state on the way.

Suppose that in this case L, M and N have unpaired electrons, and MN or LN molecules have a covalent bond. If in the reaction of $(L+MN)$ L approaches MN, potential energy is maximized producing a activated complex in the reaction $L+MN=(L\cdots M\cdots N)$ for potential energy is increased by decreasing the attractive force between M and N. And as L combines N and produces a molecule and M is separated in free state, the reaction ends to decrease the potential energy. Namely, we think that the reaction finishes with the decomposition of the activated complex in $(M\cdots L\cdots N)=M+LN$. "Metal exchange process" is throughly identical with this reaction, we think.

Although, above, we explain the brief process and idea of "metal exchange process", this theory is only assumption and should be established by study in ground of the structural data. But how does this idea occurr. This is not produced by only consideration. We tried to explain all the phenomena in series of research with theories established already, but we found phenomena which can not be simply explained. It is attributed to the want of taken conditions, defect of using methods of the theorem or fault of the theory (till now).

At our laboratory we have studied on the metallurgy of metallic calcium by the process of reaction between calcium carbide and calcium silicide. When we used an iron crucible as a vessel, after reaction we found a large hole produced by the errosion. And so we investigated the reason in every way, but we coud not understand why at about 1100°C this phenomenon happened. So we examined on the each pair. As we maintained the iron crucible with calcium siliside for 1hour at 1100°C, we found metallic glancing calcium at cold place and the iron crucible to have been very eroded.

In order to know what reaction occurs in this case, we did a X-ray diffraction test on the reaction residue, showing in Fig. 1 and Fig. 2. From this we knew that iron existed as iron silicide ($FeSi_2$, FeSi etc), and that there was silicon in the residue. According to the above, we have to consider the following reaction formula;

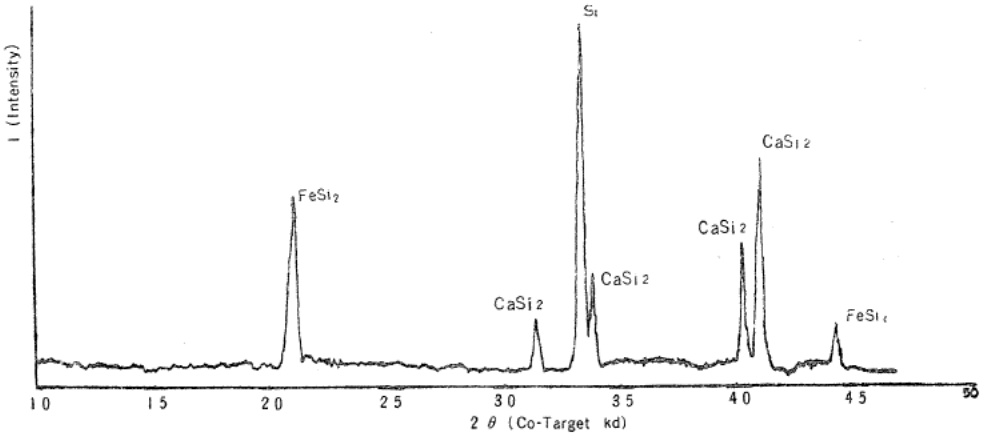

FIG. 1. X-ray diffraction analysis chart of carbide process residues.

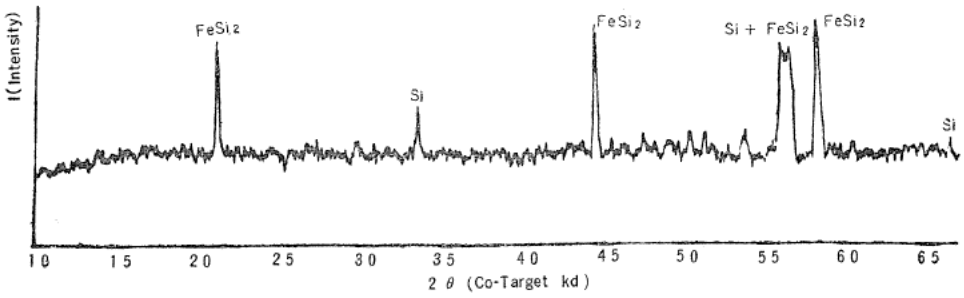

FIG. 2. X-ray diffraction analysis chart at the calcium smelting period.

$$(Ca\text{-}Si)+Fe=Ca+(Fe\text{-}Si)$$

in the region existing as $CaSi_2$, $FeSi_2$, and FeSi phases,

$$CaSi_2+Fe=Ca+FeSi_2$$
$$CaSi_2+2\,Fe=Ca+2\,FeSi \qquad \text{etc.}$$

Although we tried to inspect the possibility of this reaction using the traditional calculation methods of thermodynamic chemistry, we obtained the results that these reactions did not proceed toward right. Though in calculation such results are obtained the reaction really proceed toward right in this experiment. Why does this reaction occur? Here we became to use the new idea and to inspect more and to consider the influence of the pressure as a wanted element till now on the bond energy of the Ca-Si system and Fe-Si system. We could not know how did the pressure influence the bond energy of them. And also we found the phase theory for alloy not enough for explaining this reaction. So we proceeded to "metal exchange process" and obtained the proof in regards to calcium metallurgy and we became to postulate the new theory here.

Now we state about the application of this "metal exchange process" metallurgy. All the application can not be showed throughly and it is difficult to show them, as this theory requires high order conception as above.

Though we can know fully the application after discovery of the new thermodynamic chemical data, we show here all the application that we can understand at the present. We think this process can apply directly at least to the following; alkali metal, alkali earth metal, other volatile metals, in short Na, K, Mg, Ba, Ca, Be, etc. Na, Mg, Ca etc, especially, are important in atomic power branch and metallurgy as a reductant, and also it is applicble directly to Cd and Be metallurgy, in which we succeeded at our laboratory. At the present we are studing on the application of this process to the metallurgy of Be, Zn, Ti, Al, Sb, Ni, Cr, Mn etc. except Na, Ca and Mg. We shall report the results from them as the 2nd report (application section of this series of papers).