EVALUATION METHOD OF CHROMIUM ORE FOR SOLID STATE REDUCTION PROCESS (SRC)

HIROSHI SAITO

Chief Manager, Chichibu Research Laboratory
Showa Denko K.K.

YOSHIHIRO MACHIDA

Chichibu Research Laboratory
Showa Denko K.K.

YOSHIJI SEKITA

Chichibu Research Laboratory
Showa Denko K.K.

(Speaker)

TAKASHI SHOJI

Assistant Staff Manager, Chichibu Research Laboratory
Showa Denko K.K.

ABSTRACT

Showa Denko developed technology for solid-state reduction of chromium ore and, with that as the base, went on to establish an integrated system for high carbon ferrochrome manufacture that extends to the hot-charging of reduced pellets into electric furnaces. Called the SRC Process, it is being operated with success.

Showa Denko has also established an integrated system for evaluation of the chromium ore, carbonaceous reduction material and bentonite binder used in the SRC Process.

This paper introduces the method thereunder for evaluation of chromium ore, the most important material in the SRC Process.

The evaluation method comprises two stages. The first stage consists mainly of tests on small quantities of chromium ore, and the second stage consists mainly of physical property tests on pellets, in which the focus is on physical properties that are considered from the results obtained in the first stage as likely to cause problems.

The results of the evaluation performed in the manner mentioned above are reflected in the process design and the operating conditions.

INTRODUCTION

The stainless steel industry, which is the largest user of ferrochrome, has made marked progress in modernizing production and technology. The result has been broad reductions in stainless steel manufacturing cost.

Directly influenced by the technical progress of the stainless steel industry, the ferrochrome industry has undergone a phenomenal transformation in production and technology in a short time.

However, for the Japanese ferrochrome industry, which must rely on imports for its entire requirements for chromium ore, the main material for ferrochrome, the problem of chromium ore resources is more important and more serious than the problem of energy and environmental pollution.

Moreover, chromium ore is present in limited parts of the world, and it comes in a wide variety of properties, qualities and prices.

Also, imports of low-priced ferrochrome are compelling the Japanese ferrochrome industry to use low-priced chromium ore to achieve drastic reductions in manufacturing cost.

In view of such circumstances, we developed a Solid State Reduction Process for Chromium Ore (SRC Process) that enables use of low cost chromium ore fines. We have additionally developed sophisicated technologies such as those for hot-charging of reduced pellets into electric furnaces and kilns, and conversion to low cost energy.

The SRC Process is being operated with success at Toyama Showa Denko K.K. (formerly our Toyama Works), Shunan Denko K.K. (our joint venture with Nisshin Steel Co., Ltd.) and the South African company Consolidated Metallurgical Industries, Limited.

An integrated system established by the authors and their associates for evaluation of the chromium ore, carbonaceous reduction material and bentonite binder used in the SRC Process is reflected in the design and operating conditions of the process.

This paper introduces the above-mentioned evaluation system as it applies to chromium ore, the main material for ferrochrome, and reports on the effect of the properties of chromium ore on the thermal properties of pellet obtained from it.

OUTLINE OF INTEGRATED EVALUATION SYSTEM

The flow of the SRC Process is given in outline in Fig.1. Since the different materials go through a sequence of processes, as can be seen from the figure, their evaluation requires that the conditions of the respective processes be adequately grasped and simulated.

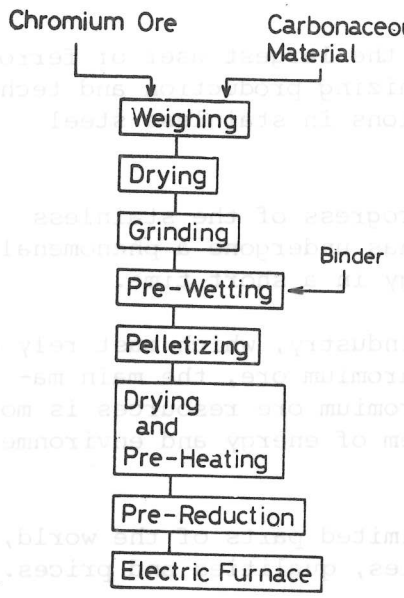

Fig.1 SRC Process Flow Sheet

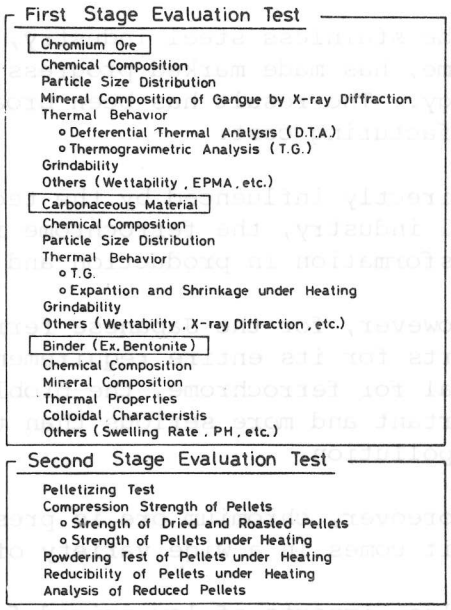

Fig. 2 Integrated System for Evaluation of SRC Process Row Materials

Testing under the evaluation system, which is graphically presented in Fig.2, is conducted in two stages.

In the first stage, each raw material is thoroughly examined to determine its basic physical properties for the purpose of anticipating what will happen in the respective processes. For this step, samples of about one kilogram each will suffice except in the case of materials where grindability is a factor.

In the second stage, attention is directed primarily to such physical properties of the raw materials as are considered from the results obtained in the first step as likely to cause problems.

Hence, the second stage is performed mainly with pellets prepared by our laboratory at the actual blending ratios.

Thus, the system is for integrated evaluation on the basis of the first and second steps described above.

When we started conducting raw material evaluation tests, we also used tests by pelletization with a small pan-pelletizer, pre-roasting of pellets with a pot-grate kiln, and roasting and reduction with a batch-type kiln.

Today, however, owing to reflection on field operating conditions of the results of the evaluation test and feedback of the operating results thereby obtained and close exchange of data between the laboratory and operating personnel in the field, we are able to anticipate from the second step evaluation the suitability of the raw materials and their behavior in the different processes.

It must be mentioned that we tested about 50 brands of chromium ore, 20 brands of carbonaceous reduction materials and about 35 brands of bentonite.

Also, most of the measuring methods used in the above-mentioned tests have been standardized.

CHROMIUM ORE EVALUATION METHOD

Our method for evaluating chromium ore is detailed below.

1. lst stage test

1) Chemical composition of chromium ore

The chromium ore is first checked for its Cr/Fe ratio and its phosphorus and sulfer contents. Furthermore, mineral components other than Cr and Fe after reduction of the ore are estimated from the SiO_2, Al_2O_3 and MgO contents.

2) Grinding test

The Japanese Industrial Standard, specifically, JIS-M-4002, specifies the method of measuring the work index by, as proposed by F.C. Bond, a ball mill.

Since, however, calculation of the work index by that method takes a considerably long time, we devised a method where the work index can be simply calculated in a short time by comparing the test ore with ore of a predetermined standard, in respect of grain size, both before and after grinding and of number of revoultions of the test mill.

3) Identification of mineral components of gangue in chromium ore and estimation of its effect on thermal behavior of pellet.

Since the gangue contained in chromium ore amounts to several percent at most, it is difficult to identify its components, even by X-ray diffraction, if the test ore is used as is.

We, therefore, prepared 35-100 mesh test samples and removed the gangue from them with tetrabromothane heavy fluid or a small magnetic separator for X-ray diffraction.

Differential thermal analysis (D.T.A.) and thermogravimetric analysis (G.T.) also are conducted to detect the thermal behavior of the mineral components of gangue. In such cases, however, it is especially important that the analysis be conducted in the atmosphere and then in an argon or nitrogen stream.

Since chromite spinel, the main component of chromium ore, increases in weight in the atmosphere owing to oxidation, the analysis is also conducted in an argon or nitrogen gas stream,

where oxidation does not occur.

4) Other

In addition to measurement of particle size distribution and true specific gravity, analysis by SEM and EPMA are conducted when necessary.

2. Second stage test

1) Pelletizing test

Fig.3 shows a pelletization apparatus.
Green pellet is obtained with a drum-type pelletizer (inner dia., 250mm; length, 480mm) by operating it at 50rpm, inclined at three degrees.

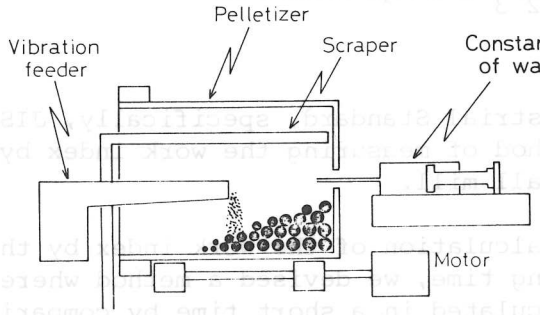

Fig. 3 Apparatus for Pelletization Test

In pulverizing chromium ore and carbonaceous reduction material the same ball mill as that for measurement of the work index is used. Pulverization is effected to cause practically all the materials to pass a 150 mesh (105 μ) sieve. In that case the specific surface area (by the air permeability method) of the pulverized material is 3,000-4,000cm^2/g.

The quantity of carbonaceous material to be mixed with the chromium ore is indicated by a ratio to the total theoretical reduction quantity of iron and chromium.

In advance of pelletization, the material (ore plus carbonaceous material) has the necessary quantity of bentonite and is pre-wet six percent with water. The material is then continuously fed, at 100g/minute, into a pelletizer, where the diameter of pellet grows to 18-20mm. The quantity of material fed per pelletization run is 1,200 grams.

The pelletizability of the material is evaluated from the optimum range of moisture for the material, as determined by using different quantities of water. Pellets that have been given a moisture level within the optimum range are used in the test.

2) Measurement of physical properties of green pellet and dry pellet

Green pellet is measured for water content, for compression strength, and for apparent density (by the mercury buoyance method). Dry pellet is measured for practically the same items.

3) Measurement of physical properties of roasted pellet

After dry pellets are roasted in an electric furnace, like the one shown in Fig.4, they are divided into three groups and kept in a nitrogen atmosphere or in coke for one hour at 500°C, 600°C and 1,200°C, respectively, after which they are measured for strength with a Universal Tester at a room temperature. We call this compression strength "roasted pellet strength".

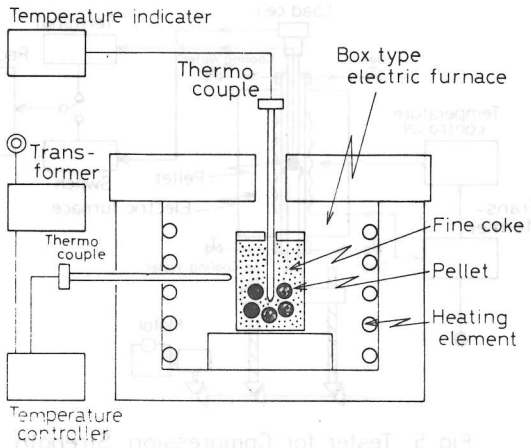

Fig.4 Pellet Heating Apparatus

However, in the SRC Process, where the pellets are sintered in the high temperature zone, not only sintering but also reduction occurs. This makes it necessary to measure the strength of pellets having a strength close to that of those actually used.

We, therefore, devised the tester shown in Fig.5 for measurement of thermal strength. The tester is a gas tight electric furnace equipped to record the temperature rise and strength of pellets. The strength of the pellets is measured after they have been successively kept for 30 minutes at the temperatures mentioned, by heating in a nitrogen stream. We call such strength "pellet thermal strength".

4) Observation of pellet under heating

The pellets are observed while they are under heating, to determine whether the pellets in the reaction vessel (rotary kiln in the actual process) easily develop softening in the reduction process and, if so, the temperature at which softening occurs.

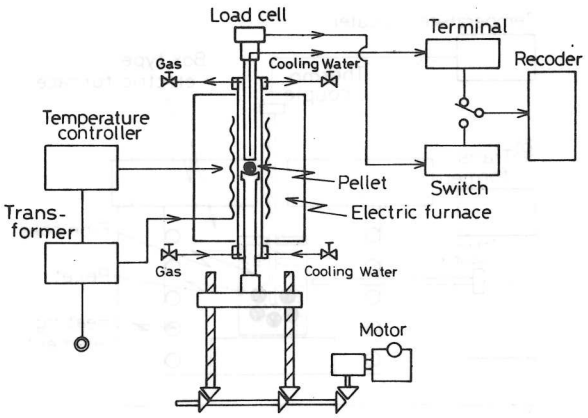

Fig. 5 Tester for Compression Strength Under Heating

In observing pellets that are undergoing heating, either the apparatus shown in Fig.6 or the Heating Microscope of Ernst Leitz of West Germany shown in Fig.7 is used. In the former case photos are continuously taken of the pellets in the reaction vessel to determine the extent of their expansion/shrinkage, while, in the latter case, a small quantity of sample test piece is placed in the equipment and observed.

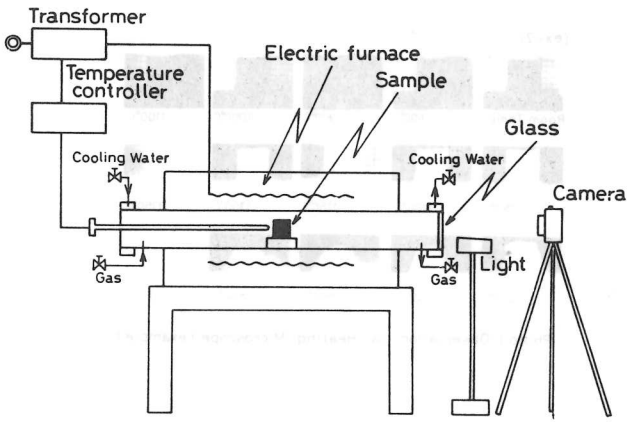

Fig 6 Observation Method for Shape of Pellet Under Heating

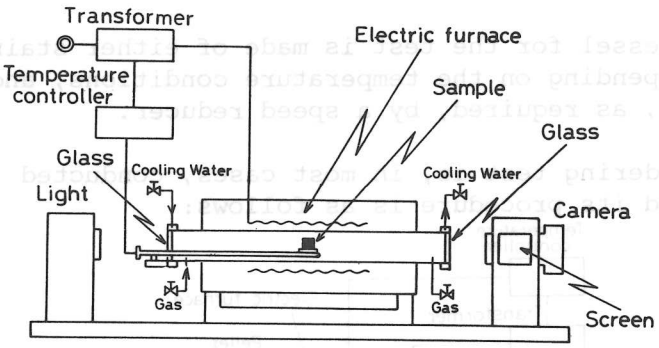

Fig. 7 Heating Microscope

In the event the composition of the ore does not present problems, the latter method is often applied

Photo 1 shows an example of the results of measurement by the Heating Microscope of pellets of chromium ores of different brands. In this case the quantity of the carbonaceous material added was 100% of the theroretical reduction volume of the chromium ore.

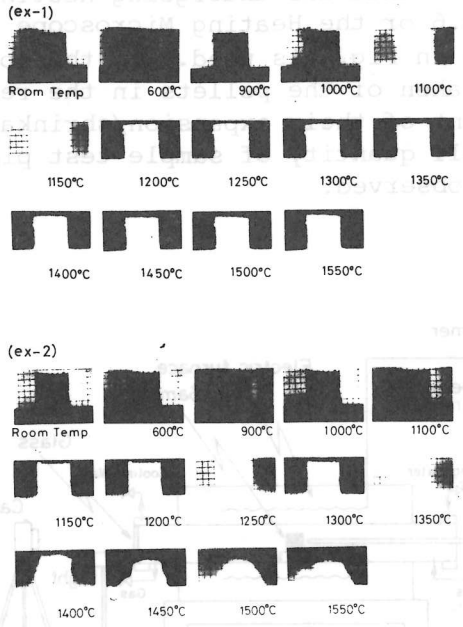

Photo.1 Observation by Heating Microscope (example)

5) Pellet powdering under heating test

Since development of dam-rings poses a great operational problem when a rotary kiln is used as the reaction vessel in the actual process, we sometimes put hot pellets to a powdering test to anticipate bursting and/or powdering of pellets owing to abrasion of their surfaces.

The reaction vessel for the test is made of either stainless steel or alumina, depending on the temperature conditions, and its speed can be changed, as required, by a speed reducer.

The pellet powdering test is, in most cases, conducted in an N_2 atmosphere, and its procedure is as follows:

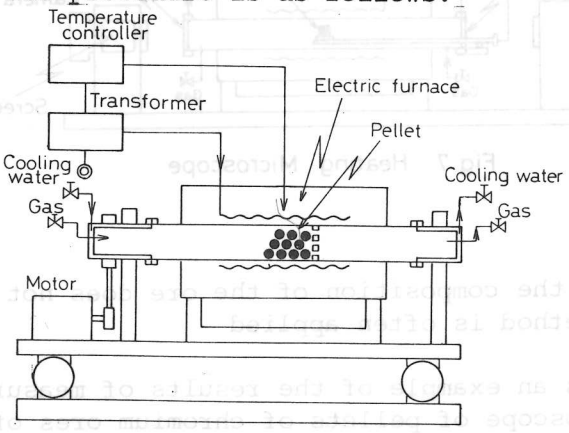

Fig. 8 Apparatus for Test Powdering of Pellet

1. Feed dry pellets into the reaction vessel.
2. Raise the temperature of the pellets in accordance with the prescribed temperature raising conditions in an N_2 gas stream.
3. Keep the pellets at the prescribed temperature for a prescribed length of time.
4. Discharge the pellets from the reaction vessel and sieve them.
5. Take the percentage of pellets that passes a 3mm sieve as the powdering rate.

6) Reducibility test

The reducibility of pellets is judged by their reaction rate.

The method of the measuring of the reaction rate is given in Fig.9.

Junder's quation is used for that purpose.

Junder's equation

$$[1-(1-X)\frac{1}{3}]^2=K.t$$

where K = reaction rate constant
t = reduction time
X = reduction ratio

Fig.9 shows examples of reaction rate measurements, while Fig.10 shows examples of measurements for comparison of the reducibility of two kinds of pellets for which coke and artificial graphite, respectively, were used as the carbonaceous material.

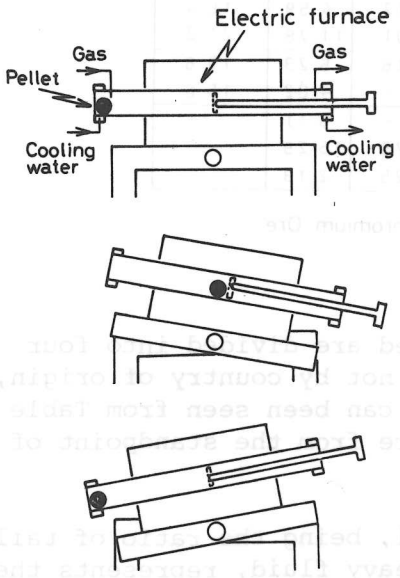

Fig. 9 Reducibility Test Procedure

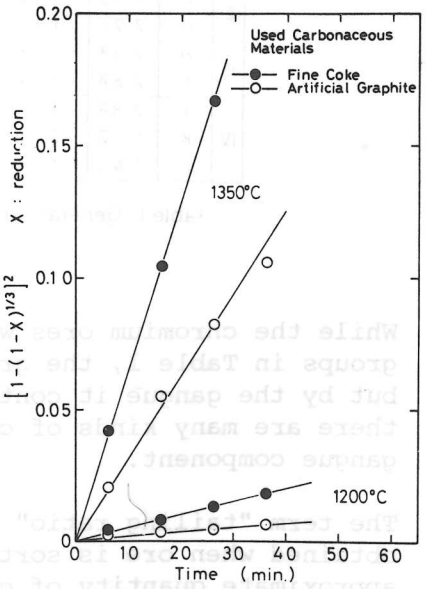

Fig 10 Reducibility Test Results (example)

As can been seen from Fig.10, excellent linearity was obtained for both kinds of pellet. As calculated by Junder's equation, however, artificial graphite-containing pellets are inferior in reducibility.

7) Other

We conduct, when necessary, X-ray diffraction of reduced pellet, observation of the microstructure of broken surfaces thereof, and analysis of reduced pellet by X-ray micro analyzer.

EFFECT OF MINERAL COMPONENTS OF GANGUE ON PELLET STRENGTH

Explanations of methods of measuring pellet strength are given above, together with examples of measurements obtained by them. Introduced below are some results of studies we made on the influence on pellet strength of mineral components of gangue in chromium ore that are present to the extent of a few percent. We evaluated about 50 brands of chromium ore for the above-mentioned purpose.

1. General properties of chromium ore

Table 1 shows the general properties of the chromium ores used in our experiments.

		Cr/Fe	MgO/Al_2O_3	SiO_2 (%)	True specific gravity	Tail ratio (%)	Work index (KwH/s.ton)
I	A,B,C	1.55 1.59	0.74 0.79	2.1 2.6	4.35 4.41	0.23 1.28	14.4 17.4
	D	1.52	0.75	5.6	4.24	1.19	—
	E	1.32	0.56	2.4	4.78	—	49.9
II	F	1.53	1.02	8.2	4.12	4.59	16.4
	G	2.21	1.50	7.1	4.01	11.78	21.2
III	H	2.38	1.25	3.4	4.16	5.23	15.6
	I	2.88	1.56	9.2	—	4.02	15.6
IV	J	2.86	1.09	9.3	—	8.11	—
	K	1.42	0.79	12.9	3.78	15.29	—
	L	1.41	1.71	5.1	4.25	2.13	—

Table 1 General Properties of Chromium Ore

While the chromium ores we evaluated are divided into four groups in Table 1, the grouping is not by country of origin, but by the gangue it contains. As can been seen from Table 1, there are many kinds of chromium ore from the standpoint of gangue component.

The term "tailing ratio" in Table 1, being the ratio of tail obtained when ore is sorted with heavy fluid, represents the approximate quantity of gangue. Also, the work index measurements of some of the chromium ores we evaluated indicate that they are comparatively hard.

2. Mineral components of gangue

1) Results of X-ray diffraction

		Enstatite $MgO \cdot SiO_2$	Serpentine $3MgO \cdot 2SiO_2 \cdot 2H_2O$	Anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$	α-Quartz $\alpha\text{-}SiO_2$	Kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	Goethite $Fe_2O_3 \cdot H_2O$
I	A	◎	○	○	◎	–	–
	B	◎	○	○	○	–	–
	C	◎	○	○	○	–	–
	D	◎	○	○	○	–	–
	F	◎	○	○	◯	–	–
II	F	◯	◎	○	○	–	–
	G	◯	◎	–	○	–	–
III	H	–	◎	–	–	–	–
	I	–	◎	–	–	–	–
IV	J	–	◯	–	◎	○	○
	K	–	◯	–	◎	○	◯
	L	–	○	–	◎	○	◯

Table 2 Results of X-ray Diffraction Analysis

The results of X-ray diffraction of the tail of the chromium ores are shown in Table 2. It can been seen from them that the ores can be divided into four groups according to the mineral components of the gangue they contain.

2) Results of differential thermal analysis and thermogravimetric analysis Figs.11 and 12 show the results of differential thermal analysis and thermogravimetric analysis of the chromium ore.

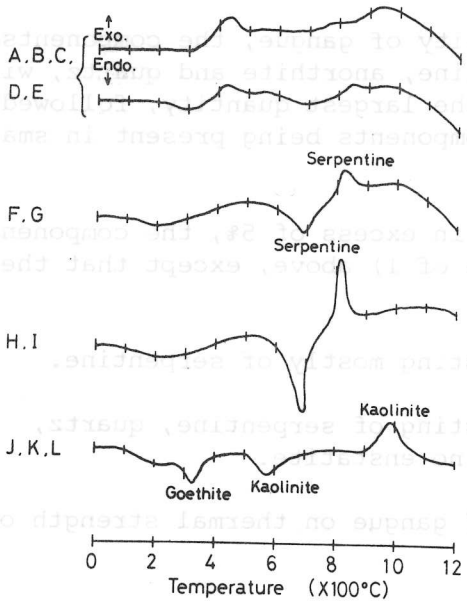

Fig. 11 Differential Thermal Analysis Curves

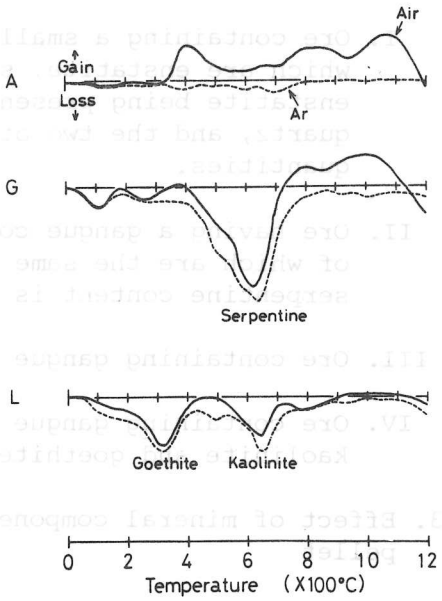

Fig.12 Thermogravimetric Analysis Curves

The heat generation that starts in the vicinity of about 350°C in Fig.11 is attributable to oxidation of iron contained in chromite spinel. The transfer of the curve to the endothermic side at temperatures above 1,000°C is considered attributable to dissociation of oxygen from oxidized iron and sintering of the samples.

Fig.12 shows differential curves obtained by thermogravimetric analysis of ores as measured at every 50°C.

It is clear from Figs.11 and 12 that serpentine, kaolinite, goethite, etc. are present in the chromium ore.

If the effect of the increase in weight of chromium ore attributable to oxidation is excluded and the temperature range is limited, the quantity of the mineral components of the gangue contained in chromium ore can be calculated from the volume of dehydrated water.

We, therefore, tried to calculate the serpentine content of the chromium ores on the following conditions:

1. On the basis of thermogravimetric analysis of the ore we conducted in an argon atmosphere, the decrease in weight of the serpentine in the 450°C to 650°C temperature range is attributable to dehydration of the serpentine.

2. The structural formula of the serpentine is $3MgO \cdot 2SiO_2 \cdot 2H_2O$.

In calculating the serpentine content of the chromium ores in Table 1, the ores are generally divided as follows:

I. Ore containing a small quantity of gangue, the components of which are enstatite, serpentine, anorthite and quartz, with enstatite being present in the largest quantity, followed by quartz, and the two other components being present in small quantities.

II. Ore having a gangue content in excess of 5%, the components of which are the same as ore of I) above, except that the serpentine content is 2-5%.

III. Ore containing gangue consisting mostly of serpentine.

IV. Ore containing gangue consisting of serpentine, quartz, kaolinite and goethite, but no enstatite.

3. Effect of mineral components of gangue on thermal strength of pellet

We studied the effect on thermal strength of pellet of "G"-chromium ore, which contains much serpentine, and of "L"-chromium ore, which has many kinds of mineral components in its gangue, such as goethite and kaolinite, in addition to serpen-

tine, each of which contains structural water. The results of the study are given in Figs.13 and 14.

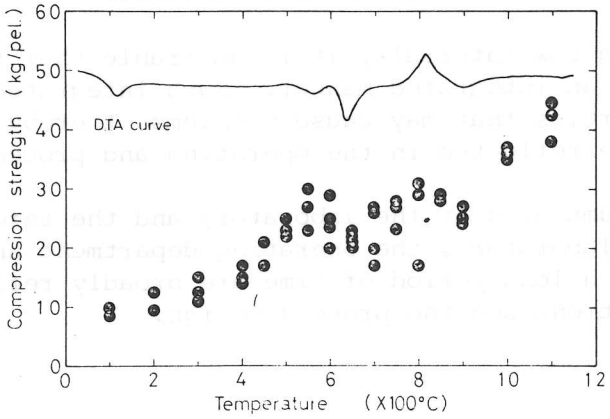

Fig. 13 Compression Strength of G-Ore Pellet Under Heating

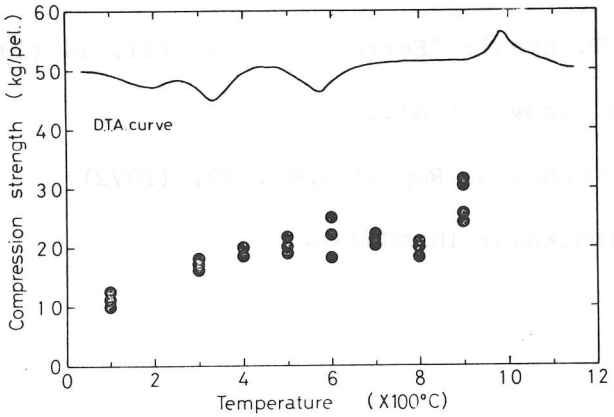

Fig. 14 Compression Strength of L-Ore Pellet Under Heating

As can been seen from Figs.13 and 14, it was recognized that the thermal strength of pellets of both G-ore and L-ore went down in the vicinity of dehydration reaction temperature and in the temperature zone of decomposition reaction of serpentine and kaolinite.

Since the above-mentioned study was made to determine the effect of the mineral components of gangue, the pellets used were made of chromium ore only, to avoid complicated factors.

Although the pellets were, therefore, different from those actually used in the SRC Process, it was observed, as can been above, that a small quantity of gangue in chromium ore effects pellet strength.

CONCLUSION

This paper reports the chromium ore evaluation method of our system for evaluating SRC Process raw materials.

In evaluating raw materials, it is desirable that their properties be evaluated in an integrated manner. Such integrated evaluation clarifies properties that may cause problems, thereby enabling such properties to be reflected in the operating and process conditions.

The data accumulated at the laboratory and the information exchanged by the laboratory, the operating department and the design department over a long period of time are broadly reflected in the operating conditions and the process design.

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