Measurement of the Size Distribution of Nonmetallic Inclusions in Steel*

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Synopsis

Although several methods are available for determining the particle size distribution of nonmetallic inclusions in steel, they are not so satisfactory for precise measurements. A particle size analyzer named Coulter Counter is applied with a hope that it may measure not only the precise size but the absolute number of nonmetallic inclusions in steel. After a series of experimental works, it has been found that the Coulter Counter was suitable for this purpose. The Coulter Counter has the following remarkable advantages in measuring the particle size distribution of nonmetallic inclusions in steel.

- (1) Measurement is carried out automatically.
- (2) Not only the size of inclusions but their number in a unit volume of specimen can be measured simultaneously, and therefore the concentration of inclusions can be determined.
- (3) Only very small amount of inclusions, i.e., 0.1 to 1 mg, is enough for precise measurements.

I. Introduction

It is well known that nonmetallic inclusions significantly degrade the mechanical properties of steel. Present knowledge, although still limited, suggests that the decrease in the mechanical properties of steel depends not only on the amount, the composition, and the shape of inclusions but also on the size and number distribution of inclusion particles. However, information about the latter is even more limited, which requires to develop more reliable technique for the measurement of size distribution.

The accurate measurement of the size and number distribution of nonmetallic inclusions is essential in studying mechanical properties of steel, and is also important in the more fundamental field of steelmaking, i.e., in the study of the nucleation, growth, and flotation of inclusions in steel melt during deoxidation. Recently, several papers¹⁾⁻³⁾ appeared in which the rate of removal of nonmetallic inclusions in the melt was calculated from the particle size distribution of inclusions based on an assumption that the floating velocity of an inclusion depended on its size.

Many methods are available for the measurement of the size and number distribution of fine particles, e.g., the microscopic method, the sedimentation method, and the light scattering method, of which the microscopic method is most commonly used for nonmetallic inclusions in steel.⁴⁾⁻⁶⁾

The microscopic method consists of the direct observation of shape, size, and number of inclusions. While this method has some advantages that it requires only small amount of sample and that data are recorded as photographs, it is rather laborious and the result depends much on observer's skill. In the sedimentation method, the size distribution is measured by means of

the difference in sedimentation times corresponding to the different particle sizes. This method is simple, accurate, and reproducible for a wide range of size, but not suitable for nonmetallic inclusions, because of the difficulty in dispersing powder particles and the large amount of sample required. The light scattering method is based on the principle that the intensity of passing light is a function of particle concentration in a dispersion system. This method is relatively suitable for the measurement of nonmetallic inclusions, because it can be applied to smaller volume of dispersing solution in lower concentration of dispersed particles.

Although each method has its unique features and the size distribution of fine particles can be measured accurately under favorable conditions, the absolute number of particles contained in a unit volume of specimen can not be determined.

The present investigation was started with a hope that the Coulter Counter might be applicable in measuring not only the size but the absolute number of nonmetallic inclusions contained in a unit volume of steel. After a series of experimental works, it was found that the Coulter Counter was suitable for this purpose.

II. Principle and Operation of the Coulter Counter

A particle size analyzer named Coulter Counter was first devised by Coulter⁷⁾ in 1956 as a high-speed and high-accuracy instrument for blood counting. The application of this instrument for industrial purposes was later described by Berg.⁸⁾ The most remarkable advantage of this instrument is that not only a particle size distribution but the number of dispersed particles in a unit volume of liquid can be measured simultaneously.

The schematic diagram of the Coulter Counter is shown in Fig. 1. Particles to be measured are dispersed in a slightly conducting liquid in a beaker equipped with an electrode. A sealed glass tube having a small hole (aperture) aside and containing another electrode inside is immersed in the beaker, and external current is applied between two electrodes. By balancing the mercury column, the electrolyte containing fine particles is forced to flow from the beaker to the tube through the aperture. Since the electric resistance between two electrodes is practically controlled by the actual cross-sectional area of the aperture, whenever a particle travels through the aperture, the cross-sectional area decreases and the corresponding increase in resistance gives a momentary drop in the current flow, which is converted to a pulse of cor-

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Fig. 1. Schematic diagram of the Coulter Counter

responding height. Accordingly, the number of particles per unit volume of the electrolyte can be obtained from the number of pulses and the volume of the electrolyte which passed through the aperture during the period of measurement. The size distribution can also be obtained by analyzing the height of pulses. The increase in resistance, ΔR , can be expressed as,

$$\Delta R = \frac{\rho_0 v}{A^2} \cdot \frac{1}{\frac{1}{1 - \frac{\rho_0}{\rho}} - \frac{a}{xA}} \quad \dots\dots\dots (1)$$

where,

- ρ_0 : resistivity of the electrolyte
- ρ : effective resistivity of the particle
- v : volume of the particle
- A : cross-sectional area of the aperture
- a : cross-sectional area of the particle, normal to the aperture axis
- x : ratio of length of particle normal to the aperture axis to the diameter of sphere equivalent in volume.

Since it is possible to assume that $a \ll xA$ and $\rho_0 \ll \rho$ for ordinary nonmetallic inclusions, Eq. (1) can be simplified to,

$$\Delta R = \rho_0 v / A^2 \quad \dots\dots\dots (2)$$

Eq. (2) indicates that ΔR is proportional to the volume of the particle, v , and is independent of its chemical composition.

Volume of the electrolyte which passed through the aperture is determined by the length of calibrated capillary between two probes, i.e., start and stop, and the circuit is arranged so as to start pulse counting automatically when the head of the mercury column in the capillary reaches the start probe and to stop counting when it reaches the stop probe. The movement of mercury is caused by an opening and closing of a stopcock installed at the top of the aperture tube. In this way, total number of particles in the migrated electrolyte, which is 0.5 cm^3 in volume for usual measurements, can be determined by counting pulses.

By calibrating with standard particles of a known radius and by the determination of number and size distribution through a threshold circuit, a complete size analysis can be made for an unknown particle.

Apertures of different sizes are used for the measurements of different size ranges. Particle sizes ranging from 0.5 to 60μ can be measured by the use of apertures ranging in radius from 25 to 200μ . For a particle of irregular shape, the instrument has been found to give a spherical equivalent volume of the particle.

The sample should completely be dispersed, but should not dissolve, agglomerate, or settle down in the liquid.

III. Measurement of the Size Distribution of Powder Particles

1. Size Distributions of SiO_2 and Al_2O_3 Powders

SiO_2 and Al_2O_3 powders for the manufacturing of refractory brick were screened with sieves of 250 and 325 mesh, and the resulting particles ranging in radius from 20 to 30μ were used as the sample for preliminary measurements. The electrically conductive liquid was prepared by adding NaCl into distilled water, in which the sample was suspended. The particle size distribution of the sample was measured with a tube having an aperture of 100μ in radius. The results obtained are shown in Fig. 2. In this figure, $n'(r)$ is plotted against the radius of particles where $n'(r)dr$ expresses the number of particles in a unit volume of liquid ranging in radius from r to $r+dr$.

Fig. 2. Size distributions of SiO_2 and Al_2O_3 powders obtained by the Coulter Counter method

As shown in Fig. 2, there are many particles having a radius smaller than 20μ for both SiO_2 and Al_2O_3 powders. However, considering difficulties to remove completely small particles by screening, it seems reasonable to conclude that the size distribution obtained by the Coulter Counter is fairly satisfactory.

2. Comparison of the Result with that by the Microscopic Method

Size distributions of SiO_2 and Al_2O_3 powders measured by the Coulter Counter are shown in Fig. 3 comparing with the results obtained by the microscopic method. In this figure, the size frequency of powder is plotted against the radius of particle.

As shown in Fig. 3, the size distribution obtained by

Fig. 3. Number frequency distributions of powder obtained by the Coulter Counter and the microscopic method

Fig. 4. Weight frequency distributions of powder obtained by the Coulter Counter and the light scattering method

the Coulter Counter is in satisfactory agreement with that obtained by the microscopic method.

3. Comparison of the Results with those by the Light Scattering Method

The size distribution of SiO₂ powder ranging in radius from 20 to 30 μ was measured by the Coulter Counter and the light scattering methods. Since the latter method gives the weight frequency distribution, the distribution obtained by the Coulter Counter was converted to the weight frequency distribution and is shown in Fig. 4.

As shown in Fig. 4, these two methods gave some difference in results. However, the size distribution determined by the former method seems to be more reasonable if it is considered that the sample powder has been prepared so as to range from 20 to 30 μ in radius, to which the result obtained by the former method corresponds fairly well.

4. Use of a Dispersing Agent

During the measurement of size distribution by the

Fig. 5. Size distribution of SiO₂ powder obtained by the Coulter Counter with and without a dispersing agent, Emulgen 920

Table 1. Amount of powder added to the electrolyte and that calculated from the result obtained by the Coulter Counter

	Amount added to the electrolyte (%)	Amount calculated by the Coulter Counter (%)
SiO ₂ powder	0.082	0.078
Al ₂ O ₃ powder	0.176	0.194

Coulter Counter, the electrolyte was continuously agitated to keep the suspension uniform without any coagulation or settlement of particles. Addition of some dispersing agent was thought to be effective for this purpose. Therefore, the effect of a dispersing agent, Emulgen 920, was examined by comparing the size distributions of SiO₂ powder which were obtained by the Coulter Counter with and without the addition of the dispersing agent (Fig. 5). Practically no effect was observed, however, which indicated that particles were well dispersed even in the liquid without any addition of dispersing agents.

5. Determination of the Concentration of Particles

From the size and number of particles per unit volume of liquid, the concentration of the particles can be calculated if the density of the particle is known. Using the literature value of the density, the concentration of the particles was calculated and was compared with the concentration based on the total amount of sample weighed before suspending in the liquid. The good agreement between these values, as shown in Table 1, confirms the reliability of the result obtained by the Coulter Counter.

IV. Measurement of the Size Distribution of Non-metallic Inclusions in Steel

1. Method of Measurement

About 1 kg of electrolytic iron was melted in a cruci-

ble with an induction furnace. After melting, it was deoxidized by the addition of either 0.5% silicon or 0.5% aluminum. Iron samples were sucked up with silica tubes at scheduled times. About 1 g of each sample was dissolved in nitric acid and the resulting solution was diluted with water to adjust the conductivity. A tube having an aperture of $50\ \mu$ was used.

The number of particles measured by the Coulter Counter ranged from 3 000 to 10 000 for each sample, which was greater than the number usually counted by the microscopic method. This fact gives one of the reasons to conclude that the Coulter Counter is superior to the microscope. The electric noise of the instrument limited the measurable minimum size to $1.5\ \mu$ in radius.

2. Size Distribution of Nonmetallic Inclusions Measured by the Coulter Counter

If the number of nonmetallic inclusions in 1 g of iron ranging in radius from r to $r+dr$ is designated as $n(r)dr$, the amount of those inclusions, $f(r)dr$, can be expressed as,

$$f(r) dr = (4/3) \pi r^3 \rho n(r) dr \dots\dots\dots(3)$$

where ρ is the density of inclusions.

Since the weight of iron samples dissolved in nitric acid and the volume of the liquid used are known, $n(r)dr$ can easily be obtained from the size distribution of nonmetallic inclusions measured by the Coulter Counter. If the density of nonmetallic inclusions, ρ , is known, $f(r)$ can be calculated from Eq. (3).

In Figs. 6 and 7, $n(r)$ and $f(r)$ measured for samples taken in various times after the addition of deoxidizer are shown. The density of nonmetallic inclusion was taken as 2.3 and 3.9 g/cm³ for SiO₂ and Al₂O₃ inclusions, respectively. These figures indicate that the number of inclusions increases with the decrease of radius, whereas the weight distribution curve has a maximum at 2 to 3 μ in radius. The total number of particles greater than detectable minimum limit, N , is given by the following equation.

$$N = \int_{1.5}^{\infty} n(r) dr \dots\dots\dots(4)$$

According to Eq. (4), the values of N were 5.9×10^6 and 4.0×10^6 for samples taken out at 1.5 and 2.5 min after the silicon addition, and 2.1×10^7 and 6.2×10^6 at 0.5 and 1.5 min after the aluminum addition, respectively.

Precise determination of the number of nonmetallic inclusions in a unit volume of iron is important in studying the mechanism of nucleation and growth of non-metallic inclusions. Size distribution expressed as a function of time after the addition of deoxidizer may contribute to the quantitative treatment of coagulation and flotation of inclusions.

3. Reliability of the Measurement

Reliability of the Coulter Counter method and the subsequent data treatment can be examined by com-

Fig. 6. Number and weight size distributions of SiO₂ non-metallic inclusions in steel

Fig. 7. Number and weight size distributions of Al₂O₃ non-metallic inclusions in steel

paring the oxygen content equivalent to the obtained amount of inclusions with that directly determined by vacuum fusion analysis. The equivalent oxygen content was obtained for samples shown in Figs. 6 and 7

Table 2. Oxygen content obtained by vacuum fusion analysis and the oxygen content equivalent to the amount of inclusions obtained by the Coulter Counter

	Time after addition of deoxidizer (min)	Oxygen content by vacuum fusion analysis (%)	Oxygen content by the Coulter Counter (%)
Deoxidation with silicon	1.5	0.052	0.051
	2.5	0.035	0.037
Deoxidation with aluminum	0.5	0.116	0.127
	1.5	0.026	0.040

Fig. 8. Comparison between the oxygen content obtained by vacuum fusion analysis and the oxygen content equivalent to the amount of inclusions obtained by the Coulter Counter

by calculating the total amount of inclusions in 1 g iron, C , and then by converting it to oxygen content. The following relationship was used in these analyses:

$$C = \int_0^{\infty} f(r) dr \quad \dots\dots\dots(5)$$

The result is shown in Table 2, which clearly shows the

consistency of the oxygen contents. Similar comparison was made for several samples containing SiO_2 inclusions and was plotted in Fig. 8.

Considering that the oxygen contents obtained from the two different sources were in fair agreement, and that the particles were well dispersed in the liquid as shown in Fig. 5, it can safely be concluded that the Coulter Counter is a reliable instrument for the measurement of the size and number distribution of non-metallic inclusions.

V. Conclusions

The Coulter Counter was used to measure the size and number of nonmetallic inclusions in steel. The size distribution of nonmetallic inclusions measured by the Coulter Counter was proved satisfactorily reliable.

This method has been found to have the following remarkable advantages for the measurement of the particle size distribution of nonmetallic inclusions in steel:

- (1) Measurement is carried out automatically.
- (2) Not only the size of inclusions but their number in a unit volume of specimen can be measured, and therefore the concentration of inclusions can be determined.
- (3) Only very small amount of inclusions, i.e., 0.1 to 1 mg is enough for precise measurements.

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