

SPECIFICATION

Title of Invention

FLY ASH, CEMENT COMPOSITION, AND PRODUCTION METHOD FOR
FLY ASH

Technical Field

[0001]

The present invention relates to fly ash, a cement composition containing the fly ash, and a method of preparing fly ash, the fly ash being capable of suppressing deterioration in fluidity to improve workability and suppressing color unevenness for use in mortar or concrete.

Background Art

[0002]

The amount of coal ash produced increases as the power generation amount increases in a coal-fired power plant. Most of coal ash produced from a coal-fired power plant or the like is landfilled as industrial waste. Recently, it is difficult to secure a landfill space for industrial waste, and environmental regulations are strengthened. Therefore, the efficient use of coal ash is required.

[0003]

In order to realize the efficient use of a large amount of coal ash while maintaining fluidity, focusing on the fact that a specific surface area value of coal ash measured by a BET method relates to fluidity of mortar or concrete containing the coal ash, coal ash that is prepared by adjusting a 45 μm sieve residue value to be relatively high in a case where a BET specific surface area of coal ash is low and by adjusting a 45 μm sieve residue value to be relatively low in a case where a BET specific surface area of coal ash is high is disclosed (Patent Literature No. 1).

[0004]

Coal ash contains spherical fly ash or the like that is collected from combustion gas of a combustion boiler by a dust collector. Fly ash that is fine powder in coal ash is used as an admixture of concrete or mortar. The quality of fly ash used for concrete or mortar is defined in JIS A6201:2015 "Fly Ash for Use in Concrete". Fly ash used for concrete or mortar contains a large amount of fine and spherical particles. By using fly ash as an admixture, an effect of improving workability of concrete or mortar and an effect of reducing unit water content are expected. Fly ash contains: spherical completely molten particles that are melted in the floating state and spheroidized by burned ash being heated in a melting furnace; and incompletely

molten particles having a larger particle diameter than that of the completely molten particles. The incompletely molten particles include coarse and deformed particles and coarse and hollow particles.

[0005]

In fly ash, unburned carbon particles that do not react in a gasification reaction in a coal-fired power plant or the like remain. Unburned carbon particles are brittle and thus are converted into fine unburned carbon particles by impact or grinding. Fly ash contains: coarse unburned carbon particles; and fine unburned carbon particles obtained by grinding the coarse unburned carbon particles. Therefore, for example, in a case where fly ash is used for concrete or mortar, unburned carbon in the fly ash adsorbs water and/or various admixtures in cement such as a water reducing agent. As a result, fluidity or the like deteriorates, and it is difficult to improve workability. In addition, in a case where fly ash is used for concrete or mortar, unburned carbon contained in the fly ash floats to the surface along with bleeding water during casting of concrete or the like to generate black color unevenness.

[0006]

In order to suppress black color unevenness, a method of reforming fly ash is disclosed, the method including:

incinerating fly ash until the amount of unburned carbon is 1 wt% or lower; and pulverizing the fly ash until a 50% passage diameter is 5 μm or more and 15 μm or less (Patent Literature No. 2).

[0007]

In order to remove unburned carbon from coal ash, a method of reducing unburned carbon is disclosed, the method including: crushing and pulverizing unburned carbon particles, which aggregate and adhere to fly ash in coal ash, using a dry crusher; and putting the fly ash to a dry classifier to separate the pulverized unburned carbon particles from the fly ash (Patent Literature No. 3).

Prior art Literature

Patent Literature

[0008]

[Patent Literature No. 1] Japanese Laid-open Patent Publication No. H09-002848A

[Patent Literature No. 2] Japanese Laid-open Patent Publication No. H11-011999A

[Patent Literature No. 3] Japanese Laid-open Patent Publication No. 2010-030885A

Summary of Invention

Problems to be solved

[0009]

However, in the description of the coal ash disclosed in Patent Literature No. 1, coal ash having a particle diameter corresponding to or smaller than that of fine aggregate is replaced with some of fine aggregates. The use of coal ash as a fine aggregate is different from the use of coal ash as an admixture.

[0010]

In addition, in the method of incinerating fly ash to reduce unburned carbon as described in Patent Literature No. 2, energy is required in the incineration step, time and effort is required to reduce unburned carbon, and the manufacturing process is complicated. In addition, in a case where coal ash is crushed and fine unburned carbon particles are separated by classification as described in Patent Literature No. 3, in order to reduce the amount of unburned carbon in coal ash, energy is required in the crushing step, time and effort is required, and the manufacturing process is complicated.

[0011]

An object of the present invention is to provide fly ash, a cement composition containing the fly ash, and a method of preparing fly ash, the fly ash being capable of improving fluidity to improve workability and suppressing color unevenness on the surface for use in concrete or

mortar.

Solution to Problems

[0012]

The present inventors performed a thorough investigation in order to achieve the object and found that unburned carbon and deformed and coarse particles in fly ash have effects on fluidity of concrete or the like and color unevenness on concrete surface when the fly ash is contained, thereby completing the present invention. That is, the present invention is as follows.

[1] Fly ash

in which a content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is lower than 38 vol%, and

a content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12 vol% or lower.

[2] The fly ash according to [1],

in which an ignition loss is 6.0 mass% or lower.

[3] The fly ash according to [1] or [2],

in which a content of Fe_2O_3 as a chemical composition is 7.1 mass% or lower.

[4] The fly ash according to any one of [1] to [3],

in which a content of hematite is 0.75 mass% or

lower,

a content of magnetite is 1.25 mass% or lower, and
a content of iron (Fe) in crystal phases is 1.45
mass% or lower.

[5] The fly ash according to any one of [1] to [4],
in which an average particle diameter (D50)
corresponding to a cumulative frequency of 50% in a volume
particle diameter distribution measured by a Laser
diffraction particle size analysis method is 15.0 μm or
more and 30.0 μm or less,

a ratio (D30/D50) of a particle diameter (D30)
corresponding to a cumulative frequency of 30% in the
volume particle diameter distribution measured by the
analysis method to the average particle diameter (D50) is
0.50 or higher, and

a ratio (D70/D50) of a particle diameter (D70)
corresponding to a cumulative frequency of 70% in the
volume particle diameter distribution measured by the
analysis method to the average particle diameter (D50) is
1.85 or lower.

[6] A cement composition comprising:
the fly ash according to any one of [1] to [5]; and
cement.

[7] The cement composition according to [6],
in which a content of the fly ash is higher than 1

mass% and 35 mass% or lower with respect to a total amount of the cement composition.

[8] A method of preparing fly ash comprising:

a step of removing at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method from raw material fly ash such that a content of the particles having a particle diameter of 45 μm or more is lower than 38 vol% with respect to 100 vol% of a total amount of the fly ash; and

a step of removing at least a part of particles having a particle diameter of less than 5 μm measured by the analysis method from the raw material fly ash such that a content of the particles having a particle diameter of less than 5 μm is 12 vol% or lower with respect to 100 vol% of the total amount of the fly ash.

Effects of Invention

[0013]

According to the present invention, fly ash, a cement composition containing the fly ash, and a method of preparing fly ash can be provided, the fly ash being capable of suppressing deterioration in fluidity to improve workability and suppressing color unevenness for use in

mortar or concrete.

Brief Description of Drawings

[0014]

Fig. 1 is a SEM picture showing fly ash containing unburned carbon particles.

Mode for carrying out the Invention

[0015]

Hereinafter, the present invention will be described.

[Fly Ash]

In fly ash according to an embodiment of the present invention, the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is lower than 38 vol%, and the content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12 vol% or lower.

[0016]

Among the particles having a relatively large particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method in the fly ash, a large amount of deformed particles are present instead of spherical completely molten particles, and large amounts of coarse and deformed incompletely molten particles, coarse

and hollow incompletely molten particles, and coarse unburned carbon particles are mixed.

Fig. 1 is an SEM picture showing fly ash obtained from a coal-fired power plant. As shown in Fig. 1, the fly ash contains spherical carbon completely molten particles 1, fine unburned carbon particles 2, coarse and deformed incompletely molten particles 3 having a particle diameter of 45 μm or more, coarse and hollow incompletely molten particles 4, and coarse unburned carbon particles 5.

In this specification, "spherical" represents spherical or substantially spherical.

[0017]

In a case where the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is 38 vol% or higher, the fly ash contains large amounts of the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5. For the incompletely molten particles 3 and 4 or the unburned carbon particles 5, a ball bearing effect obtained by a configuration of the spherical completely molten particles 1 cannot be obtained, fluidity of concrete or the like deteriorates, and deterioration in workability cannot be suppressed. In addition, the particles having a particle diameter of 45 μm

or more measured by the analysis method has a low bulk specific gravity. Therefore, for a cement composition—containing fly ash in which the content of particles having a particle diameter of 45 μm or more measured by the analysis method is higher than 38 vol%, the fly ash floats to the concrete surface along with bleeding water during casting, which may cause color unevenness.

[0018]

The relatively fine particles having a particle diameter of less than 5 μm measured by a Laser diffraction particle size analysis method in the fly ash are likely to be the fine unburned carbon particles 2. The coarse unburned carbon particles 5 that incompletely react in a gasification reaction in a coal-fired power plant are brittle and thus are converted into the fine unburned carbon particles 2 by impact or grinding.

[0019]

In a case where the content of particles having a particle diameter of less than 5 μm measured by the analysis method in the fly ash is higher than 12 vol%, the amount of the fine unburned carbon particles 2 in the fly ash increases. In a cement composition containing the fly ash, the fine unburned carbon particles 2 adsorb an admixture or the like. Therefore, fluidity deteriorates, and workability cannot be improved. In addition, in a case

where fly ash containing a large amount of the fine unburned carbon particles 2 are used for concrete or the like, the fine unburned carbon particles 2 float to the concrete surface along with bleeding water during casting, which may cause color unevenness.

[0020]

For fly ash having a specific particle diameter distribution in which the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is lower than 38 vol% and in which the content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12.0 vol% or lower, deterioration in fluidity can be suppressed, workability can be improved, and color unevenness can be suppressed. Therefore, this fly ash is suitable for admixing cement.

[0021]

In the fly ash, the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is preferably 37.0 vol% or lower, more preferably 36.0 vol% or lower, and still more preferably 35.0 vol% or lower. In the fly ash, the content of the coarse particles having a particle diameter of 45 μm or more including large amounts of the

coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5 is low. Therefore, for a cement composition containing the fly ash, fluidity can be improved, and workability can be improved. In addition, in the fly ash, the content of hollow and coarse particles having a low bulk specific gravity and a large particle diameter is low. Therefore, the bulk specific gravity relatively is relatively high. For a mixed cement containing the fly ash in which the content of particles having a particle diameter of 45 μm or more measured by the analysis method is 37.0 vol% or lower, the fly ash is not likely to float to the concrete surface along with bleeding water during casting, and color unevenness caused by a change in the color tone of the fly ash can be suppressed.

[0022]

In the fly ash, the content of particles having a particle diameter of less than 5 μm measured by a Laser diffraction particle size analysis method is preferably 11.0 vol% or lower, more preferably 10.0 vol% or lower, still more preferably 9.0 vol% or lower, even still more preferably 8.0 vol% or lower, and yet even still more preferably 5.0 vol% or lower. By reducing the content of the unburned carbon particles 2 having a small particle diameter in the fly ash, for a cement composition

containing the fly ash, deterioration in fluidity caused by adsorption of an admixture or the like on the unburned carbon particles 2 having a small particle diameter can be suppressed, and workability can be improved. In addition, by reducing the content of the fine unburned carbon particles 2 in the fly ash, the fine unburned carbon particles 2 are not likely to float along with bleeding water during casting, and color unevenness can be suppressed for a cement composition containing the fly ash.

[0023]

In the fly ash, the content of particles having a particle diameter of 90 μm or more measured by a Laser diffraction particle size analysis method is preferably 15.0 vol% or lower, more preferably 13.5 vol% or lower, and still more preferably 12.0 vol% or lower. By reducing the content of the coarse particles having a particle diameter of 90 μm or more in the fly ash, deterioration in fluidity can be suppressed, and color unevenness can be suppressed for a cement composition containing the fly ash.

[0024]

In the fly ash, the content of particles having a particle diameter of 75 μm or more measured by a Laser diffraction particle size analysis method is preferably 20.0 vol% or lower, more preferably 19.5 vol% or lower, and still more preferably 19.3 vol% or lower. By reducing the

content of the particles having a relatively large particle diameter of 75 μm or more in the fly ash, deterioration in fluidity can be further suppressed, and color unevenness can be further suppressed for a cement composition containing the fly ash.

[0025]

In the fly ash, the content of particles having a particle diameter of 30 μm or more measured by a Laser diffraction particle size analysis method is preferably 15.0 vol% or higher, more preferably 18.0 vol% or higher, and still more preferably 20.0 vol% or higher, and is preferably 55.0 vol% or lower, more preferably 54.0 vol% or lower, and still more preferably 52.0 vol% or lower. In the fly ash, the content of particles having a relatively large particle diameter which contains a large amount of deformed particles is reduced, and a large amount of the spherical completely molten particles 1 are contained. As a result, for a cement composition containing the fly ash, deterioration in fluidity can be suppressed.

[0026]

In the fly ash, the content of particles having a particle diameter of 20 μm or more measured by a Laser diffraction particle size analysis method is preferably 35.0 vol% or higher, more preferably 38.0 vol% or higher, and still more preferably 39.0 vol% or higher, and is

preferably 70.0 vol% or lower, and more preferably 69.0 vol% or lower. In the fly ash, the content of particles having a relatively large particle diameter which contains a large amount of deformed particles is reduced, and a large amount of the spherical completely molten particles 1 are contained. As a result, for a cement composition containing the fly ash, deterioration in fluidity can be suppressed.

[0027]

In the fly ash, the content of particles having a particle diameter of less than 10 μm measured by a Laser diffraction particle size analysis method is preferably 30.0 vol% or lower, more preferably 29.5 vol% or lower, and still more preferably 29.0 vol% or lower, and is preferably 10.0 vol% or higher, and more preferably 12.0 vol% or higher. By reducing the content of the fine unburned carbon particles 2 in the fly ash, deterioration in fluidity caused by adsorption of an admixture or the like on the fine unburned carbon particles 2 can be suppressed, and color unevenness caused by the fine unburned carbon particles 2 floating along with bleeding water can be suppressed for a cement composition containing the fly ash.

[0028]

In the fly ash, it is preferable that an ignition loss is 6.0 mass% or lower. The ignition loss of the fly

ash relates to the content of unburned carbon, and it can be presumed that, in a case where the ignition loss is low, the content of unburned carbon in the fly ash is also low.

The ignition loss of the fly ash is more preferably 5.8 mass% or lower, more preferably 5.6 mass% or lower, and still more preferably 5.5 mass% or lower. By setting the ignition loss of the fly ash to be 6.0 mass% or lower, the content of unburned carbon is low, deterioration in fluidity can be suppressed, and color unevenness can be suppressed as compared to a cement composition containing fly ash in which the content of unburned carbon is high.

The fly ash satisfies a numerical value of an ignition loss of fly ash Type III described in JIS A6201:2015 "Fly Ash for Use in Concrete". In addition, the fly ash may satisfy a numerical value of an ignition loss of fly ash Type I, II, or IV described in JIS A6201:2015 "Fly Ash for Use in Concrete".

[0029]

By setting the ignition loss of the fly ash to be 6.0 mass% or lower, even in a case where the fly ash contains unburned carbon, and when the fly ash has a specific particle diameter distribution in which the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is lower than 38 vol% and in which the content of

particles having a particle diameter of less than 5 μm measured by the analysis method is 12 vol% or lower, deterioration in fluidity can be suppressed, workability can be improved, and color unevenness can be suppressed.

[0030]

In the fly ash, it is preferable that the content of Fe_2O_3 as a chemical composition is 7.1 mass% or lower. Iron (Fe) in the fly ash forms crystal phases with (Si) or (Al) in the fly ash. Examples of the crystal phase in the fly ash include quartz (SiO_2), cristobalite (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), hematite (Fe_2O_3), and magnetite (Fe_3O_4). Particles having a relatively large particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method are slowly cooled at a lower cooling rate than that of particles having a small particle diameter of less than 45 μm . Therefore, the amount of the crystal phase in the particles having a relatively large particle diameter of 45 μm or more tends to be more than that of the particles having a small particle diameter of less than 45 μm . The crystal phase in the fly ash includes black or reddish brown hematite (Fe_2O_3) or black magnetite (Fe_3O_4), and the color tone of the fly ash changes depending on the content of the crystal phase. In concrete in which a cement composition containing the

fly ash is used, the fly ash floats to the surface along with bleeding water, and the gradation (color unevenness) of the color tone may appear such that portions that appear black or portions that appear white are present in the gray color tone of the concrete. In a case where the content of Fe_2O_3 as a chemical composition in the fly ash increases, it is presumed that the content of the crystal phase in the fly ash, which causes a change in the color tone of the concrete surface such as hematite or magnetite, increases.

In the fly ash of the present invention, the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is lower than 38 vol%, the content of particles having a particle diameter of 45 μm or more is relatively low, and the content of particles having a particle diameter of less than 45 μm in which the content of the crystal phase is presumed to be low, is high. In a case where the content of Fe_2O_3 as a chemical composition in the fly ash according to the present invention is 7.1 mass% or lower, it is presumed that the content of iron which forms crystal phases such as black or reddish brown hematite or black magnetite is low, and the amount of the crystal phase in the fly ash is low. In the fly ash according to the present invention, the content of the crystal phase which causes a change in the color tone of concrete surface is

low. Therefore, color unevenness can be suppressed. In this specification, the content of the crystal phase in the fly ash is obtained by a method of measuring the amounts (mass%) of the crystal phase and the amorphous phase in the fly ash described below in Examples, and refers to the content of the crystal phase in the fly ash calculated in consideration of the total amount G_{total} (mass%) of an amorphous phase including unburned carbon. The content of iron (Fe) in the crystal phase refers to the amount of iron (Fe) in the crystal phase calculated in consideration of the total amount G_{total} (mass%) of the amorphous phase including unburned carbon, and will also be referred to as "the amount of iron (Fe) in the crystal phase" in this specification.

[0031]

The content of Fe_2O_3 as a chemical composition in the fly ash is derived from coal as a raw material. The content of Fe_2O_3 as a chemical composition in the fly ash is more preferably 7.05 mass% or lower, still more preferably 7.00 mass% or lower, and even still more preferably 6.95 mass% or lower, and is typically 3.00 mass% or higher. The content of Fe_2O_3 as a chemical composition in the fly ash refers to the iron content (iron oxide (III): Fe_2O_3) in terms of oxides measured according to JIS R5204 "Chemical Analysis Method of Cement by X-Ray Fluorescence".

[0032]

In the fly ash, it is preferable that the content of hematite (Fe_2O_3) is 0.75 mass% or lower, the content of magnetite (Fe_3O_4) is 1.25 mass% or lower, and the content of iron (Fe) in the crystal phase is 1.45 mass% or lower. Hematite (Fe_2O_3) is black or reddish brown, magnetite (Fe_3O_4) is black, and the fly ash containing a large amount of hematite or magnetite changes in color tone. In concrete in which a cement composition containing the fly ash is used, the fly ash floats along with bleeding water. As a result, the gradation (color unevenness) of the color tone may appear such that portions that appear black or portions that appear white are present in the gray color tone of the concrete. In a case where, in the fly ash, the content of hematite is 0.75 mass% or lower, the content of magnetite is 1.25 mass% or lower, and the content of iron (Fe) in the crystal phase is 1.45 mass% or lower, the content of hematite or magnetite in the fly ash, which causes a change in the color tone of the fly ash as one of the factors causing color unevenness, is low, and color unevenness can be suppressed.

[0033]

In the fly ash, it is more preferable that the content of hematite (Fe_2O_3) is 0.74 mass% or lower, the content of magnetite (Fe_3O_4) is 1.24 mass% or lower, and the

content of iron (Fe) in the crystal phase is 1.42 mass% or lower. In the fly ash, it is still more preferable that the content of hematite (Fe_2O_3) is 0.72 mass% or lower, the content of magnetite (Fe_3O_4) is 1.23 mass% or lower, and the content of iron (Fe) in the crystal phase is 1.39 mass% or lower. In the fly ash, it is even still more preferable that the content of hematite (Fe_2O_3) is 0.70 mass% or lower, the content of magnetite (Fe_3O_4) is 1.22 mass% or lower, and the content of iron (Fe) in the crystal phase is 1.37 mass% or lower.

In the fly ash, the content of hematite (Fe_2O_3), the content of magnetite (Fe_3O_4), and the content of iron (Fe) in the crystal phase vary depending on coal as a raw material or forming conditions of the fly ash. In the fly ash, the content of hematite (Fe_2O_3) is typically 0.30 mass% or higher, the content of magnetite (Fe_3O_4) is typically 0.20 mass% or higher, and the content of iron (Fe) in the crystal phase is typically 0.21 mass% or higher.

[0034]

In the fly ash, the content of hematite (Fe_2O_3), the content of magnetite (Fe_3O_4), and the content of iron (Fe) in the crystal phase can be measured by Rietveld analysis using a powder X-ray diffractometer. As the powder X-ray diffractometer, for example, D8 Advance (manufactured by Bruker AXS GmbH) can be used. In this specification, the

amount of iron (Fe) in the crystal phase is obtained by a method of measuring the amounts (mass%) of the crystal phase and the amorphous phase in the fly ash described below in Examples.

[0035]

For the fly ash, it is preferable that an average particle diameter (D50) corresponding to a cumulative frequency of 50% in a volume particle diameter distribution measured by a Laser diffraction particle size analysis method is 15.0 μm or more and 30.0 μm or less, a ratio (D30/D50) of a particle diameter (D30) corresponding to a cumulative frequency of 30% in order from the smallest diameter in the volume particle diameter distribution measured by the analysis method to the average particle diameter (D50) is 0.50 or higher, and a ratio (D70/D50) of a particle diameter (D70) corresponding to a cumulative frequency of 70% in order from the smallest diameter in the volume particle diameter distribution measured by the analysis method to the average particle diameter (D50) is 1.85 or lower.

For the fly ash, the average particle diameter (D50) is 15.0 μm or more and 30.0 μm or less, the particle diameter ratio (D30/D50) is 0.50 or higher, and the particle diameter ratio (D70/D50) is 1.85 or lower. As a result, the particle diameter distribution has a sharp

shape, the particle diameters are similar to each other, the content of particles having a large particle diameter including large amounts of the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5, which are factors causing deterioration in fluidity or color unevenness, is low, and the content of the unburned carbon particles 2 having a small particle diameter is low. For a cement composition containing the fly ash in which the average particle diameter (D50) is 15.0 μm or more and 30.0 μm or less, the particle diameter ratio (D30/D50) is 0.50 or higher, and the particle diameter ratio (D70/D50) is 1.85 or lower, deterioration in fluidity can be suppressed, and color unevenness can be suppressed.

[0036]

For the fly ash, the average particle diameter (D50) corresponding to a cumulative frequency of 50% in the volume particle diameter distribution measured by a Laser diffraction particle size analysis method is more preferably 16.0 μm or more and 29.5 μm or less, and still more preferably 17.0 μm or more and 29.0 μm or less. In a case where the average particle diameter (D50) of the fly ash is in the above-described range, the content of particles having a large particle diameter including large

amounts of the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5 is low, and the content of the spherical completely molten particles 1 is high. In addition, the content of the fine unburned carbon particles 2 is low. Therefore, for a cement composition containing the fly ash, deterioration in fluidity can be suppressed, and color unevenness can be suppressed.

[0037]

The particle diameter ratio (D_{30}/D_{50}) of the fly ash is more preferably 0.51 or higher and still more preferably 0.52 or higher. In addition, the particle diameter ratio (D_{70}/D_{50}) of the fly ash is more preferably 1.84 or lower. As the particle diameter ratio (D_{30}/D_{50}) and/or the particle diameter ratio (D_{70}/D_{50}) approaches 1, the shape of the particle diameter distribution becomes sharper, and the particle diameters become more similar to each other. In the fly ash, the content of particles having a large particle diameter including large amounts of the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5, which are factors causing deterioration in fluidity or color unevenness, is low, and the content of the unburned carbon particles 2 having a

small particle diameter is also low. Therefore, for a cement composition containing the fly ash, deterioration in fluidity can be suppressed, and color unevenness can be suppressed.

[0038]

For the fly ash, it is preferable that an average particle diameter (D50) corresponding to a cumulative frequency of 50% in a volume particle diameter distribution measured by a Laser diffraction particle size analysis method is 15.0 μm or more and 30.0 μm or less, and a ratio (D10/D50) of a particle diameter (D10) corresponding to a cumulative frequency of 10% in the volume particle diameter distribution measured by the analysis method to the average particle diameter (D50) is 0.2 or higher and 0.5 or lower. In the fly ash in which the particle diameter ratio (D10/D50) is 0.2 or higher and 0.5 or lower, the content of the unburned carbon particles 2 having a small particle diameter is low, and the particle diameters in the particle diameter distribution are relatively similar to each other. As a result, the content of the spherical completely molten particles 1 is high. Due to the ball bearing effect of the completely molten particles 1, fluidity can be improved, and workability can be improved for use in concrete or the like. In addition, in the fly ash in which the particle diameter ratio (D10/D50) is 0.2 or higher and 0.5 or lower,

the content of the unburned carbon particles 2 having a small particle diameter is low, and the particle diameters in the particle diameter distribution are similar to each other. As a result, in a cement composition containing the fly ash, the fine unburned carbon particles having a small particle diameter is not likely to float along with bleeding water, and color unevenness can be suppressed.

[0039]

For the fly ash, it is preferable that an average particle diameter (D50) corresponding to a cumulative frequency of 50% in a volume particle diameter distribution measured by a Laser diffraction particle size analysis method is 15.0 μm or more and 30.0 μm or less, and a ratio (D90/D50) of a particle diameter (D90) corresponding to a cumulative frequency of 90% in the volume particle diameter distribution measured by the analysis method to the average particle diameter (D50) is 1.5 or higher and 4.5 or lower. In the fly ash in which the particle diameter ratio (D90/D50) is 1.5 or higher and 4.5 or lower, the content of the coarse particles having a large particle diameter including large amounts of the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5 is low. For a cement composition containing the fly ash, deterioration in fluidity caused by

mixing of deformed coarse particles can be suppressed. In addition, in the fly ash in which the particle diameter ratio (D90/D50) is 1.5 or higher and 4.5 or lower, the content of particles having a low bulk specific gravity and a relatively large particle diameter is low. As a result, for a cement composition containing the fly ash, the particles having a low bulk specific gravity and a relatively large particle diameter is not likely to float along with bleeding water, and color unevenness can be suppressed.

[0040]

[Cement Composition]

A cement composition according to one embodiment of the present invention comprises: the fly ash according to the embodiment of the present invention; and cement.

The kind of the cement is not particularly limited, and examples thereof comprise normal Portland cement, high early strength Portland cement, moderate heat Portland cement, and low-heat Portland cement, etc.

[0041]

The content of the fly ash is preferably higher than 1 mass% and 35 mass% or lower and more preferably 2 mass% or higher and 32 mass% or lower with respect to the total amount of the cement composition. In a case where the content of the fly ash is in the above-described range with

respect to the total amount of the cement composition, the fluidity of mortar or concrete in which the cement composition containing the fly ash is used can be improved, and the workability can be improved. In addition, fine unburned carbon particles or coarse particles having a low bulk specific gravity does not float to the concrete surface along with bleeding water, and color unevenness can be suppressed.

[0042]

The content of the fly ash with respect to the total amount of the cement composition is set to satisfy the content of Type A, Type B, or Type C fly ash described in JIS R5213:2009 "Fly-Ash Cement". In the case of Type A, the content of the fly ash may be higher than 5 mass% and 10 mass% or lower with respect to the total amount of the cement composition. In the case of Type B, the content of the fly ash may be higher than 10 mass% and 20 mass% or lower. In the case of Type C, the content of the fly ash may be higher than 20 mass% and 30 mass% or lower.

[0043]

The fly ash is not necessarily used for fly-ash cement, and may be used as an admixture for a cement composition. The amount of the fly ash used may not satisfy the content of the fly ash described in "Fly-Ash Cement" defined in JIS.

[0044]

In addition to the fly ash and the cement, the cement composition may contain an admixture such as gypsum, a water reducing agent, a water reducing agent, or an high-performance AE water reducing agent.

[0045]

[Method of preparing Fly Ash]

A method of preparing fly ash according to one embodiment of the present invention comprises: a step of removing at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method from raw material fly ash such that a content of the particles having a particle diameter of 45 μm or more is lower than 38 vol% with respect to 100 vol% of a total amount of the fly ash; and a step of removing at least a part of particles having a particle diameter of less than 5 μm measured by the analysis method from the raw material fly ash such that a content of the particles having a particle diameter of less than 5 μm is 12 vol% or lower with respect to 100 vol% of the total amount of the fly ash. The step of removing at least a part of particles having a particle diameter of 45 μm or more from the raw material fly ash and the step of removing at least a part of particles having a particle

diameter of less than 5 μm from the raw material fly ash can be performed using an air classifier, or a sieve, or the like. In the case of air classification, for example, an air classifier such as TURBO CLASSIFIER manufactured by Nisshin Engineering Inc. can be used.

[0046]

With the method of preparing fly ash according to the embodiment of the present invention, the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, the coarse unburned carbon particles 5, and the fine unburned carbon particles 2, which are factors causing deterioration in fluidity and color unevenness can be removed by classification, which is a relatively simple method, without performing steps such as carbonization or crushing. With the preparing method according to the embodiment of the present invention, coarse particles and fine unburned carbon can be removed by classification, and the obtained fly ash contains a large amount of the spherical completely molten particles 1. With the method of preparing fly ash, due to the ball bearing effect of the spherical completely molten particles 1, fly ash capable of suppressing deterioration in fluidity and suppressing color unevenness can be obtained.

[0047]

In a case where fly ash in coal ash obtained from,

for example, a coal-fired power plant is used as a raw material, in order to obtain fly ash having a specific particle diameter distribution, the method of preparing fly ash comprises: a step of removing at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method from raw material fly ash such that a content of the particles having a particle diameter of 45 μm or more is lower than 38 vol% with respect to 100 vol% of a total amount of the fly ash; and a step of removing at least a part of particles having a particle diameter of less than 5 μm measured by the analysis method from the raw material fly ash such that a content of the particles having a particle diameter of less than 5 μm is 12 vol% or lower. With the preparing method according to the embodiment of the present invention, in a case where fly ash is used as a raw material, fly ash having a specific particle diameter distribution can be prepared, and the fly ash suitable for admixing with cement can be prepared.

Examples

[0048]

Next, the present invention will be described in more detail with Examples but is not limited to the Examples.

[0049]

Preparation of Fly Ash

(Examples 1 to 5)

Fly ash of Comparative Example 1 obtained from a coal-fired power plant was used as raw material fly ash. Using an air classifier (trade name: TURBO CLASSIFIER, manufactured by Nisshin Engineering Inc.), at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method was removed from the raw material fly ash such that the content of the particles having a particle diameter of 45 μm or more is lower than 38 vol% with respect to 100 vol% of a total amount of the fly ash. At least a part of particles having a particle diameter of less than 5 μm measured by the analysis method was removed from the raw material fly ash such that a content of the particles having a particle diameter of less than 5 μm is 12 vol% or lower with respect to 100 vol% of the total amount of the fly ash. As a result, fly ash for admixing with cement of Example 1 having a laser diffraction particle diameter distribution shown in Table 1 was prepared.

[0050]

(Examples 6 and 7)

Fly ashes for admixing with cement of Example 6 and 7 having laser diffraction particle diameter distributions

(vol%) shown in Table 1 were prepared as with Examples 1 to 5, except that fly ash of Comparative Example 2 obtained from a coal-fired power plant was used as the raw material fly ash.

[0051]

(Comparative Examples 1 to 2)

The fly ashes obtained from a coal-fired power plant were used directly as the fly ashes of Comparable Examples 1 and 2. In the fly ashes of Comparative Examples 1 and 2, the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method was higher than 38 vol% with respect to 100 vol% of the total amount of the fly ash. Specifically, the fly ashes of Comparative Examples 1 and 2 had laser diffraction particle diameter distributions (vol%) shown in Table 1. In addition, Fig. 1 is an SEM picture showing the fly ash of Comparative Example 1.

[0052]

(Comparative Examples 3 to 4)

The fly ash of Comparative Example 1 obtained from a coal-fired power plant was used as the raw material fly ash. Using an air classifier (trade name: TURBO CLASSIFIER, manufactured by Nisshin Engineering Inc.), at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size

analysis method and at least a part of particles having a particle diameter of less than 5 μm measuring by the analysis method were removed from the raw material fly ash such that the content of the particles having a particle diameter of 45 μm or more is 38 vol% or higher with respect to 100 vol% of a total amount of the fly ash or such that the content of the particles having a particle diameter of less than 5 μm measured by the analysis method was higher than 12 vol%. Specifically, fly ashes for admixing with cement of Comparative Examples 3 and 4 having laser diffraction particle diameter distributions (vol%) shown in Table 1 were prepared.

[0053]

(Comparative Examples 5 to 6)

The fly ash of Comparative Example 2 obtained from a coal-fired power plant was used as the raw material fly ash. Using an air classifier (trade name: TURBO CLASSIFIER, manufactured by Nisshin Engineering Inc.), at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method and at least a part of particles having a particle diameter of less than 5 μm measured by the analysis method were removed from the raw material fly ash such that the content of the particles having a particle diameter of 45

μm or more is 38 vol% or higher with respect to 100 vol% of a total amount of the fly ash or such that the content of the particles having a particle diameter of less than 5 μm measured by the analysis method was higher than 12 vol%. Specifically, fly ashes for admixing with cement of Comparative Examples 5 and 6 having laser diffraction particle diameter distributions (vol%) shown in Table 1 were prepared.

[0054]

[Measurement of Particle Diameter distribution of Fly Ash]

The particle diameter distribution of the fly ash for admixing with cement of each of Examples and Comparative Examples was measured by a Laser diffraction particle size analyzer (manufactured by Nikkiso Co., Ltd., trade name: MICROTRAC MT-3300EX). The results are shown in Table 1.

[0055]

[Measurement of Ignition Loss of Fly Ash]

The ignition loss of the fly ash for admixing with cement of each of Examples and Comparative Examples was measured according to "JIS A 6201: 2015 "Fly Ash for use in Concrete 8.3 Ignition Loss". The results are shown in Table 1.

[0056]

[Particle Diameters corresponding to Cumulative

Frequencies of 10%, 30%, 50%, 70%, and 90% in Volume
Particle Diameter Distribution]

Using a Laser diffraction particle size analyzer (manufactured by Nikkiso Co., Ltd., trade name: MICROTRAC MT-3300EX), particle diameters corresponding to cumulative frequencies of 10%, 30%, 50%, 70%, and 90% in order from the smallest diameter in the volume particle diameter distribution of each of Examples and Comparative Examples were measured. The particle diameter corresponding to a cumulative frequency of 50% in order from the smallest diameter in the volume particle diameter distribution measured by a Laser diffraction particle size analyzer was set as the average particle diameter (D50). In addition, the particle diameters corresponding to cumulative frequencies of 10%, 30%, 70%, and 90% were set as D10, D30, D70, and D90, respectively. Ratios D10/D50, D30/D50, D70/D50, and D90/D50 of the particle diameters corresponding to the cumulative frequencies of 10%, 30%, 70%, and 90% to the average particle diameter D50 were calculated, respectively. The results are shown in Table 2.

[0057]

[Measurement of Chemical Composition of Fly Ash]

The chemical composition (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO) of the fly ash for admixing with cement of each of Examples and

Comparative Examples was measured according to JIS R5204
"Chemical Analysis Method of Cement by X-Ray Fluorescence".
The results are shown in Table 2.

[0058]

(Measurement of Amounts (mass%) of Crystal Phase and
Amorphous Phase in Fly Ash)

The amount (mass%) of crystal phases and the amount
of an amorphous phase in the fly ash were measured by
Rietveld analysis using an internal standard material by a
powder X-ray diffractometer. As the powder X-ray
diffractometer, D8 Advance (manufactured by Bruker AXS
GmbH) was used. Measurement conditions, the internal
standard material, and Rietveld analysis conditions were as
described below.

Measurement Conditions

X-ray bulb: Cu

Tube voltage: 40 kV

Tube current: 40 mA

Measurement range of diffraction angle 2θ : start
angle=5°, end angle=70°/75°

* In a case where rutile type titanium dioxide was
added as the internal standard material and the end angle
was 70°, a peak shape of the titanium dioxide at about 70°
was not able to be correctly obtained. Therefore, the end
angle was set as 75° for a sample to which the titanium

dioxide was added.

Step width: 0.025°/step

Measurement time: 60 sec/step

Internal standard material: rutile type titanium dioxide

Rietveld Analysis Conditions

Rietveld analysis software: TOPAS Ver. 4.2

(manufactured by Bruker AXS GmbH)

Zero-point correction: not performed

Correction of height of sample surface: performed

Analysis target mineral: quartz, mullite (3:2), anhydrite, limestone, magnetite, hematite, and titanium dioxide (only a sample added as an internal standard material)

Preferred orientation function of hematite phase: assuming that preferred orientation of the hematite phase appears on a diffraction line of the (110) plane at a diffraction angle 2θ of about 35.5, refinement was performed using a March-Dollase function with an initial coefficient value as 1. Regarding the magnetite phase, it was assumed that preferred orientation did not appear.

[0059]

The measurement procedure of the crystal phase such as magnetite or hematite and the amorphous phase in the fly ash was as described below. Regarding the fly ashes—containing the magnetite or hematite phase, the

fraction of each crystal phase was not accurately obtained only based on XRD measurement data of a sample to which an internal standard material was added due to reasons described below. Therefore, the quantitative analysis was performed based on the XRD measurement data of both the sample to which the internal standard material was added and a sample to which no internal standard material was added.

(i) As the internal standard material, fly ash (sample 1) to which 20 mass% of rutile type titanium dioxide was added, and fly ash (sample 2) to which no internal standard material was added were prepared.

(ii) The fly ash (sample 2) to which no internal standard material was added was measured with a powder X-ray diffractometer. Fitting between the obtained powder X-ray diffraction pattern of the fly ash (sample 2) and each of theoretical profiles of quartz, mullite, anhydrite, limestone, magnetite, and hematite as the analysis target minerals was performed to quantitatively analyze the respective analysis target minerals in the fly ash. Next, the amounts (mass%) of the respective analysis target minerals were calculated by the analysis software.

The reason why the sample 2 to which no internal standard material was added was used for the quantitative analysis of magnetite and hematite is that peaks of

magnetite and hematite at a diffraction angle 2θ =around 35.5° ~ 35.6° or less are close to a peak of rutile type titanium dioxide at a diffraction angle 2θ =around 36.1° . In particular, the reason is as follows. In a case where rutile type titanium dioxide having a small particle diameter and a small crystallite size is used as the internal standard material, peak broadening occurs, and the vicinity of the bottom of the peak of rutile type titanium dioxide at a diffraction angle $2\theta=36.1^{\circ}$ overlaps with the peaks of magnetite and hematite. In particular, in a case where the content of magnetite or hematite is low, there is a large effect on the value determined by the quantitative analysis.

(iii) The fly ash (sample 1) to which rutile type titanium dioxide was added as the internal standard material was measured with a powder X-ray diffractometer. Fitting between the obtained powder X-ray diffraction pattern of the fly ash (sample 1) and each of theoretical profiles of quartz, mullite, anhydrite, limestone, hematite, magnetite, and titanium dioxide as the analysis target minerals was performed to quantitatively analyze the respective analysis target minerals in the fly ash (sample 1) to which the internal standard material was added. Next, the amounts (mass%) of the respective analysis target minerals were calculated by the analysis software.

(iv) Based on the value determined by the quantitative analysis of rutile type titanium dioxide of the sample 1, the total amount G_{total} (mass%) of the amorphous phase including unburned carbon was calculated from the following Expression (A). Total Amount G_{total} of Amorphous Phase = $100 \times (Y - X) / \{Y \times (100 - X) / 100\}$ (A)

In Expression (A), X represents the addition amount (20 mass%) of the internal standard material, and Y represents the value (%) determined by the Rietveld analysis of rutile type titanium dioxide.

(v) The total amount of the amorphous phase was quantitatively analyzed based on the content (mass%) of the crystal phase of the analysis target minerals in the sample 1. Next, the content of the crystal phase in consideration of the total amount of the amorphous phase was calculated from the following Expression (B) based on the contents (mass%) of the analysis target minerals of the sample 2.

Crystal Phase (in consideration of Total Amount G_{total} of Amorphous Phase) = Crystal Phase (Analysis Value of Sample 2) $\times (100 - G_{\text{total}}) / 100$ (B)

In Expression (B), G_{total} represents the total amount (%) of the amorphous phase determined by the quantitative analysis from Expression (A) based on the analysis value of the sample 1. Due to the above-described operation, regarding the hematite or magnetite phase in which accuracy

is not secured based on only the analysis data of the sample 1, the quantitative value of the fraction of each crystal phase in all the crystal phase was accurately obtained by reflecting the analysis result of the sample 2.

(vi) According to the following Expression (1), the content (mass%) of unburned carbon in the fly ash was subtracted from the total amount G_{total} (mass%) of the amorphous phase calculated from Expression (A), and the obtained value was set as the amount G_{FA} (mass%) of the amorphous phase in the fly ash. An ignition loss measured according to JIS A6201 "Fly Ash for Use in Concrete" was set as the content (mass%) of the unburned carbon in the fly ash.

Amount G_{FA} (mass%) of Amorphous Phase in Fly Ash=Total Amount G_{total} (mass%) of Amorphous Phase obtained by Rietveld Analysis-Content (mass%) of Unburned Carbon (1)

[0060]

The amount of iron (Fe) in the crystal phase was calculated as follows.

The amount of iron (Fe) in the crystal phase of the fly ash was calculated from the following Expression (2) based on a measured value 2 and a measured value 3, the measured value 2 being the content (mass%) of hematite in the crystal phase that was calculated in consideration of the total amount G_{total} (mass%) of the amorphous phase

including unburned carbon in the fly ash, and the measured value 3 being the content (mass%) of magnetite in the crystal phase that was calculated in consideration of the total amount G_{total} (mass%) of the amorphous phase including unburned carbon in the fly ash.

Amount of Iron (Fe) in Crystal Phase in consideration of Total Amount G_{total} of Amorphous Phase in Fly

Ash=[Measured Value $2 \times \{2\text{Fe}/\text{Fe}_2\text{O}_3 \text{ (111.6/159.7)}\}$]+[Measured Value $3 \times \{3\text{Fe}/\text{Fe}_3\text{O}_4 \text{ (167.4/231.5)}\}$] (2)

[0061]

Preparation of Cement Composition

The fly ash for admixing with cement of each of Examples and Comparative Examples and normal Portland cement were mixed such that the content of the fly ash was 20 mass% and the content of the normal Portland cement was 80 mass%. As a result, a cement composition containing the fly ash of each of Examples and Comparative Examples was prepared. The following evaluations were performed as to the cement composition containing the fly ash of each of Examples and Comparative Examples. The results are shown in Table 1.

[0062]

[Fluidity Evaluation-1: Evaluation of Fluidity of Cement Paste]

The cement composition, the high-performance AE water

reducing agent, and water were mixed in a Hobart mixer for 3 minutes, such that 1 part by mass of a high-performance AE water reducing agent (trade name: MASTERGLENIUM (registered trademark) SP8S, manufactured by BASF) as an admixture was added to 100 parts by mass of the cement composition containing the fly ash and that a water-cement ratio (W/C) was 30 %. As a result, cement paste using the cement composition containing the fly ash of each of Examples and Comparative Examples was obtained.

Immediately, the mixed cement paste was put into a cylindrical flow cone having an inner diameter of 50 mm and a height of 50 mm placed on polished glass. The cylindrical flow cone was pulled up 1 minute after mixing, and the cement paste was removed from the cylindrical flow cone. The longest length among the diameters of the cement paste having a circular shape and the length perpendicular to the longest length were measured, and the average value thereof was obtained as a flow value. In a case where the flow value was 140 mm or higher, the fluidity was evaluated to be superior. In a case where the flow value was lower than 140 mm, the fluidity was evaluated to be poor.

[0063]

[Fluidity Evaluation-2: Evaluation of Fluidity of Mortar]

The cement composition containing the fly ash of each

of Examples and Comparative Examples and standard sand of JIS R5201 were premixed at a mass ratio of 1:3 (cement composition: standard sand). 1 part by mass of a high-performance AE water reducing agent (trade name: MASTERGLENIUM (registered trademark) SP8S, manufactured by BASF) as an admixture with respect to 100 parts by mass of the cement composition containing the fly ash was added, and water is added such that a water-cement ratio (W/C) was 30 %, to the premixed powder and mixed in a Hobart mixer for 3 minutes. As a result, mortar in which cement composition containing the fly ash of each of Examples and Comparative Examples was obtained.

The flow value of the mixed mortar was measured according to JIS R5201:2015 "Physical Testing Methods for Cement 12.2 Measurement of Flow Value". In a case where the flow value was 145 mm or higher, the fluidity was evaluated to be superior. In a case where the flow value was lower than 145 mm, the fluidity was evaluated to be poor.

[0064]

[Evaluation of Color Unevenness]

The cement paste using the cement composition containing the fly ash of each of Examples and Comparative Examples which were evaluated in "Fluidity Evaluation-1" was cast on a metal pad, and was cured for 7 days in a wet

box at a temperature of 20°C and a humidity of 90% or higher. Whether or not there was a color difference on the surface of the cement paste was determined by visual inspection, and five positions having a color difference were selected in order from the largest difference in color. Using a color difference meter (trade name: CR-300, manufactured by Konica Minolta Japan, Inc.) a lightness value (L value), an a value, and a b value defined in the International Commission on Illumination (CIE) were measured at the five positions. ΔE_{ab} was calculated from the following Expression (3) based on a difference (ΔL) between a maximum L value (L_{max}) and a minimum L value (L_{min}) among the measured values at the five positions. Based on ΔE_{ab} , the degree of color unevenness was evaluated. Δa represents a difference (Δa) between a maximum a value (a max value) and a minimum a value (a min value) among the measured values at the five positions. Δb represents a difference (Δb) between a maximum b value (b max value) and a minimum b value (b min value) among the measured values at the five positions. As ΔL or ΔE_{ab} become smaller, the color unevenness is evaluated to be suppressed.

$$\Delta E_{ab} = \{ (\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2 \}^{1/2} \quad (3)$$

[0065]

[Table 1]

	Particle Diameter Distribution (Vol%) measured by Laser Diffraction Particle Size Analysis Method							Ignition Loss (mass%)	Fluidity Evaluation		Color Unevenness Evaluation (Color Measurement)	
	90 μm or More	75 μm or More	45 μm or More	30 μm or More	20 μm or More	Less than 10 μm	Less than 5 μm		Paste Flow Value (mm)	Mortar Flow Value (mm)	ΔL Value (Maximum-Minimum)	ΔEab
Example 1	2.8	5.4	18.7	35.4	61.3	13.5	3.4	1.6	155.0	153.0	7.4	3.6
Example 2	0.7	2.0	13.8	27.3	50.9	17.9	3.1	1.4	164.0	165.0	5.2	2.8
Example 3	0.1	0.6	9.4	20.3	39.9	22.3	1.3	0.8	171.0	169.0	1.5	0.7
Example 4	12.0	16.7	35.0	51.0	68.9	14.5	3.4	2.4	147.0	148.0	9.0	11.6
Example 5	3.4	6.1	18.9	33.1	53.0	23.1	8.1	2.2	144.0	146.0	11.5	12.8
Example 6	8.4	11.8	27.9	39.5	53.4	28.7	12.0	5.2	142.0	146.0	12.8	12.4
Example 7	10.4	19.3	30.5	42.9	66.5	18.4	10.7	5.5	143.0	145.0	12.7	11.9
Comparative Example 1	15.6	20.8	39.3	50.8	63.4	21.7	8.9	3.3	138.0	141.0	20.4	30.4
Comparative Example 2	15.4	23.4	40.5	52.3	60.2	24.3	13.2	7.2	109.0	114.0	27.5	32.7
Comparative Example 3	16.1	24.4	39.8	54.8	70.1	17.0	6.7	3.0	137.0	139.0	15.5	18.8
Comparative Example 4	8.9	17.0	28.4	45.5	56.7	24.8	12.7	2.7	139.0	143.0	14.5	16.7
Comparative Example 5	15.4	25.8	41.7	53.5	65.1	19.8	6.2	6.6	117.0	124.0	25.6	31.8
Comparative Example 6	6.5	10.9	24.5	46.8	58.4	33.1	15.4	5.2	131.0	134.0	23.8	30.9

[0066]

[Table 2]

	Cumulative Particle Diameter (µm) in Particle Diameter Distribution (Vol%) measured by Laser Diffraction Particle Size Analysis Method					Particle Diameter Ratio				Chemical Composition (mass%)				Crystal Phase (mass%)		Content of Iron (Fe) in Crystal Phase (mass%)
	D10	D30	D50	D70	D90	D10/D50	D30/D50	D70/D50	D90/D50	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Hematite (Fe ₂ O ₃)	Magnetite (Fe ₃ O ₄)	
Example 1	4.9	14.4	24.3	36.5	70.5	0.20	0.59	1.50	2.90	55.38	23.96	6.78	2.70	0.69	1.21	1.36
Example 2	7.1	14.8	19.2	33.9	49.3	0.37	0.77	1.77	2.57	55.39	24.02	6.78	2.70	0.69	1.22	1.37
Example 3	7.0	17.1	24.8	21.5	43.8	0.28	0.69	0.87	1.77	55.41	23.99	6.65	2.76	0.66	1.20	1.33
Example 4	7.3	16.0	28.7	42.8	96.5	0.25	0.56	1.49	3.36	55.69	23.68	6.88	2.73	0.75	1.23	1.42
Example 5	5.4	15.6	18.7	31.5	69.9	0.29	0.83	1.68	3.74	55.61	23.77	6.83	2.74	0.72	1.25	1.41
Example 6	4.5	12.6	20.5	37.7	78.1	0.22	0.61	1.84	3.81	55.68	23.75	7.10	2.67	0.73	1.25	1.42
Example 7	4.8	14.0	26.8	44.3	92.2	0.18	0.52	1.65	3.44	55.30	23.80	7.05	2.67	0.75	1.22	1.41
Comparative Example 1	5.4	14.4	29.3	52.2	102.0	0.18	0.49	1.78	3.48	55.14	23.61	7.82	2.67	0.84	1.30	1.53
Comparative Example 2	5.9	14.8	32.1	55.4	108.1	0.18	0.46	1.73	3.37	55.74	23.69	7.63	2.39	0.80	1.28	1.49
Comparative Example 3	6.1	20.2	31.0	58.1	111.2	0.20	0.65	1.87	3.59	55.63	24.16	7.53	2.75	0.81	1.28	1.49
Comparative Example 4	4.4	17.2	26.6	43.8	81.7	0.17	0.65	1.65	3.07	55.58	24.05	7.18	2.65	0.79	1.32	1.51
Comparative Example 5	6.4	15.3	32.3	60.0	118.2	0.20	0.47	1.86	3.66	56.22	24.16	7.33	2.41	0.78	1.26	1.46
Comparative Example 6	3.8	9.3	27.8	40.0	76.3	0.14	0.33	1.44	2.74	55.98	23.96	7.05	2.40	0.77	1.30	1.48

[0067]

As shown in Table 1, for the cement compositions of Examples 1 to 7 containing the fly ashes of Examples 1 to 7 in which the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method was lower than 38 vol% and in which the content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12.0 vol% or lower, the paste flow value was higher than 140 mm, the mortar flow value was higher than 145 mm, fluidity was improved, and workability was improved.

For Examples 2 and 3, the cement compositions containing the fly ashes in which the content of particles having a particle diameter of 45 μm or more was 15 vol% or lower were used, both the paste flow value and the mortar flow value were higher than 160 mm, and fluidity was further improved.

For Example 3, the cement composition containing the fly ash in which the content of particles having a particle diameter of less than 5 μm was 3.0 vol% or lower was used, both the paste flow value and the mortar flow value were higher than 165 mm, and fluidity was further improved.

[0068]

As shown in Table 1, for the cement pastes containing

the fly ashes of Examples 1 to 7 in which the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method was lower than 38 vol% and in which the content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12.0 vol% or lower, the ΔL value and the ΔE_{ab} value were smaller than those of the cement pastes containing the fly ashes of Comparative Examples 1 to 6, and it was found that color unevenness was suppressed.

As shown for Examples 1 to 4, in the cement paste containing the fly ash in which the content of particles having a particle diameter of 45 μm or more was 35 vol% or lower and in which the content of particles having a particle diameter of less than 5 μm was 3.4 vol% or lower, the ΔL value and the ΔE_{ab} value were smaller, and color unevenness was further suppressed. In a case where ΔE_{ab} was 3.6 as in Example 1, the colors are identified to be the same at the impression level. In a case where ΔE_{ab} was 2.8 as in Example 2, in comparison of separation between colors, the color difference is hardly recognized, and the colors are generally recognized to be the same. In addition, in a case where ΔE_{ab} was 0.7 as in Example 3, color unevenness is suppressed such that a strict standard

for an allowable color difference can be set in terms of the reproducibility of visual recognition and determination.

[0069]

In addition, as shown in Table 1, in the fly ashes of Examples 1 to 7 in which the content of particles having a particle diameter of 45 μm or more measured a Laser diffraction particle size analysis method was lower than 38 vol% and in which the content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12.0 vol% or lower, the ignition loss was low at 6.0 mass% or lower, and the content of the coarse unburned carbon particles 5 and the fine unburned carbon particles 2 was low. Therefore, it was found that the ignition loss was reduced.

[0070]

As shown in Table 2, in the fly ashes of Examples 1 to 7, the content of Fe_2O_3 as a chemical composition was 7.1 mass% or lower, the content of Fe_2O_3 as a chemical composition in the fly ash was low, and the content of the crystal phase such as hematite or magnetite in the fly ash, which was a factor causing a change in the color tone in the fly ash, was lower than that of the fly ashes of Comparative Examples 1 to 6. As shown in Table 1, for the cement pastes containing the fly ashes of Examples 1 to 7

in which the content of Fe_2O_3 as a chemical composition was 7.1 mass% or lower, the ΔL value and the ΔE_{ab} value were lower than those of the cement pastes containing the fly ashes of Comparative Examples 1 to 6, and it was found that color unevenness was suppressed.

[0071]

As shown in Table 2, in the fly ashes of Examples 1 to 7, the content of hematite (Fe_2O_3) was 0.7 mass% or lower, the content of magnetite (Fe_3O_4) was 1.25 mass% or lower, the amount of iron (Fe) in the crystal phase calculated in consideration of the total amount G_{total} of the amorphous phase containing unburned carbon was 1.42 mass% or lower, and the content of the crystal phase such as hematite or magnetite in the fly ash, which was one of the factors causing color unevenness and a change in the color tone in the fly ash, was low. As shown in Table 1, in the cement pastes containing the fly ashes of Examples 1 to 7 in which the content of hematite or magnetite was low, the ΔL value and the ΔE_{ab} value were lower than those of the cement pastes containing the fly ashes of Comparative Examples 1 to 6, and it was found that color unevenness was suppressed.

[0072]

As shown in Table 2, for the fly ashes Examples 1 to 7, the average particle diameter (D50) measured by a Laser

diffraction particle size analysis method was 15.0 μm or more and 30.0 μm or less, the particle diameter ratio (D30/D50) was 0.50 or higher, and the particle diameter ratio (D70/D50) was 1.85 or lower. For the fly ashes of Examples 1 to 7, the shape of the particle diameter distribution was sharp, the particle size was similar to each other, the content of the coarse and deformed incompletely molten particles 3, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5, which were factors causing deterioration in fluidity or color unevenness, was low, and the content of the fine unburned carbon particles 2 was low. Therefore, in the cement compositions containing the fly ashes, fluidity was able to be improved, and color unevenness was suppressed.

[0073]

As shown in Table 1, for the fly ashes of Comparative Examples 1 to 6, the content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method was 38 vol% or higher, and the content of particles having a particle diameter of less than 5 μm measured by the analysis method was higher than 12 vol%. In the cement pastes containing the fly ashes of Comparative Examples 1 to 6, the paste flow value was lower

than 140 mm, and the fluidity was poor. In addition, in the mortars containing the fly ashes of Comparative Examples 1 to 6, the mortar flow value was lower than 145 mm, and the fluidity was poor. In addition, for the cement pastes containing the fly ashes of Comparative Examples 1 to 6, the ΔL value was high at 14.5 or higher, the ΔE_{ab} value was 16.7 or higher, and color unevenness was found to the extent that it was able to be recognized by visual inspection.

[0074]

As shown in Table 2, in the fly ashes of Comparative Examples 1 to 5, the content of Fe_2O_3 as a chemical composition was higher than 7.1 mass%. In the fly ash of Comparative Example 6, the content of Fe_2O_3 as a chemical composition was 7.05 mass%, the content of hematite (Fe_2O_3) was 0.77 mass%, the content of magnetite (Fe_3O_4) was 1.30 mass%, and the content of hematite or magnetite was high. As shown in Table 1, in for the cement pastes containing the fly ashes of Comparative Examples 1 to 6, the ΔL value and the ΔE_{ab} value were higher than those of the cement pastes containing the fly ashes of Examples 1 to 7, and color unevenness was not suppressed.

[0075]

As shown in Table 2, in the fly ash of Comparative Example 6, the content of Fe_2O_3 as a chemical composition

was low at 7.05 mass%, the content of hematite (Fe_2O_3) was 0.77 mass%, the content of magnetite (Fe_3O_4) was 1.30 mass%, and the contents of hematite and magnetite were relatively low. However, as shown in Table 1, the ΔL value and the ΔEab value were relatively large at 23.8 and 30.9, respectively. The reason for this is presumed to be as follows. In the cement paste containing the fly ash—of Comparative Example 6, the content of particles having a particle diameter of less than 5 μm measured by a Laser diffraction particle size analyzer was relatively high at 15.4 vol%. Therefore, in the cement composition containing the fly ash of Comparative Example 6, the fine unburned carbon particles floated along with bleeding water during casting, and color unevenness was not able to be suppressed.

[0076]

In addition, as shown in Table 2, for the fly ashes—of Comparative Examples 1 to 6, the particle diameter ratio ($\text{D}_{30}/\text{D}_{50}$) was lower than 0.65, the particle diameter ratio ($\text{D}_{70}/\text{D}_{50}$) was higher than 1.85, and it was found that the shape of the particle diameter distribution was broad, and the particle diameters varied. In addition, as shown in Table 1, for the fly ashes of Comparative Examples 2 and 5, the ignition loss was higher than 6.0 mass%, and the amount of unburned carbon was not sufficiently reduced to

suppress color unevenness and deterioration in fluidity.

[0077]

As shown in Fig. 1, the fly ash of Comparative Example 1, which was fly ash obtained from a coal-fired power plant comprised the spherical completely molten particles 1, the fine unburned carbon particles 2, the coarse and deformed incompletely molten particles 3 having a particle diameter of 45 μm or more, the coarse and hollow incompletely molten particles 4, and the coarse unburned carbon particles 5.

Industrial Applicability

[0078]

According to the present invention, fly ash that is increasingly produced as the power generation amount increases in a coal-fired power plant can be efficiently used, and fly ash, a cement composition containing the fly ash, and a method of preparing fly ash can be provided, the fly ash being capable of suppressing deterioration in fluidity to improve workability and suppressing color unevenness for use in mortar or concrete without increasing energy used in a complicated step or for preparing.

Reference Signs List

[0079]

1: Spherical completely molten particle

- 2: Fine unburned carbon particle
- 3: Coarse and deformed incompletely molten particle
- 4: Coarse and hollow incompletely molten particle
- 5: Coarse unburned carbon particle

CLAIMS

1. Fly ash,

wherein a content of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method is lower than 38 vol%,

a content of particles having a particle diameter of less than 5 μm measured by the analysis method is 12 vol% or lower,

a content of hematite is 0.30 mass% or higher and 0.75 mass% or lower,

a content of magnetite is 0.20 mass% or higher and 1.25 mass% or lower, and

a content of iron (Fe) in crystal phases is 0.21 mass% or higher and 1.45 mass% or lower.

2. The fly ash according to claim 1,

wherein an ignition loss is 6.0 mass% or lower.

3. The fly ash according to claim 1 or 2,

wherein a content of Fe_2O_3 as a chemical composition is 7.1 mass% or lower.

4. The fly ash according to any one of claims 1 to 3,

wherein an average particle diameter (D50)

corresponding to a cumulative frequency of 50% in a volume particle diameter distribution measured by a Laser diffraction particle size analysis method is 15.0 μm or more and 30.0 μm or less,

a ratio (D30/D50) of a particle diameter (D30) corresponding to a cumulative frequency of 30% in the volume particle diameter distribution measured by the analysis method to the average particle diameter (D50) is 0.50 or higher, and

a ratio (D70/D50) of a particle diameter (D70) corresponding to a cumulative frequency of 70% in the volume particle diameter distribution measured by the analysis method to the average particle diameter (D50) is 1.85 or lower.

5. A cement composition comprising:

the fly ash according to any one of claims 1 to 4;
and cement.

6. The cement composition according to claim 5,

wherein a content of the fly ash is higher than 1 mass% and 35 mass% or lower with respect to a total amount of the cement composition.

7. A method for preparing fly ash comprising:

a step of removing at least a part of particles having a particle diameter of 45 μm or more measured by a Laser diffraction particle size analysis method from raw material fly ash such that a content of the particles having a particle diameter of 45 μm or more is lower than 38 vol% with respect to 100 vol% of a total amount of the fly ash;

a step of removing at least a part of particles having a particle diameter of less than 5 μm measured by the analysis method from the raw material fly ash such that a content of the particles having a particle diameter of less than 5 μm is 12 vol% or lower with respect to 100 vol% of the total amount of the fly ash-;

a content of hematite is 0.30 mass% or higher and 0.75 mass% or lower,

a content of magnetite is 0.20 mass% or higher and 1.25 mass% or lower, and

a content of iron (Fe) in crystal phases is 0.21 mass% or higher and 1.45 mass% or lower, in the obtained fly ash.

8. A method for repairing fly ash according to claim 7, wherein a content of Fe_2O_3 as a chemical composition in the fly ash is 7.1 mass% or lower.