

chromium minerals, such as, chromite, etc.; (i) zirconium minerals, such as zircon, baddeleyite, etc.; and (j) nickel minerals, such as, granierite, etc. The metal oxides include, for example, ZnO, Al₂O₃, CdO, CaO, Cr₂O₃, CoO, ZrO₂, SnO₂, SrO, TiO₂, Fe₂O₃, FeO, CuO, PbO, NiO, V₂O₅, BaO, Bi₂O₃, BeO, MgO, Mn₃O₄, MnO₂, etc. Examples of compound oxides are CoO.Al₂O₃, CoO.nSiO₂, CoO.Cr₂O₃.Al₂O₃, Co₃O₄.SiO₂.Al₂O₃.Fe₂O₃.NiO.MnO, ZnO.SiO₂, CaO.WO₃, Fe₂O₃.MnO₂.Mn₃O₄, TiO₂.Al₂O₃, BaO.CrO₃, PbO.CrO₃, FeO.Cr₂O₃, etc. Of these preferable are oxides of transition elements and minerals containing the same. Examples thereof are ilmenite, rutile, pyrolusite, chromite, zircon and like minerals and Cr₂O₃, CoO, ZrO₂, TiO₂, Fe₂O₃, FeO, NiO, V₂O₅, Mn₃O₄, MnO₂, CoO.Al₂O₃, CoO.nSiO₂, CoO.Cr₂O₃.Al₂O₃, Co₃O₄.SiO₂.Al₂O₃.Fe₂O₃.NiO.MnO, Fe₂O₃.MnO₂.Mn₃O₄, TiO₂.Al₂O₃, BaO.CrO₃, PbO.CrO₃, FeO.Cr₂O₃ and like oxides.

The amount of powder used can be suitably determined within a wide range depending upon the use of the final foamed product and the kind of powder to be used. However, it is preferable to use the powder in an amount of about 0.1 to 20% by weight, most preferably in an amount of about 0.2 to 10% by weight, based on the weight of SiO₂ in the silica sol, although it is possible to use a greater amount of powder. The powder can be used singly or admixture with one another. It may be added directly to silica sol, or it may be added in the form of aqueous dispersion or paste.

Silica sol is then gelled. It is required in the present invention that the gelation be conducted at a pH of not higher than 7; otherwise the specific surface area of the resulting silica gel would be markedly reduced, with the consequent tendency of incomplete foaming during the subsequent firing step. Insofar as the gelation is conducted at a pH of not higher than 7, it may be conducted in usual manner. For example, silica sol having a pH of not higher than 7, preferably 1 to 3, is left to stand at room temperature or heated for gelation. It is preferable to conduct the gelation at an elevated temperature of 40° to 70°C in order to accelerate the gelation. The silica gel thus prepared is then washed with water and dried so as to be substantially free of sorbed water. By washing with water a water-soluble component such as Glauber's salt or like alkali metal salt can be removed from the gel. There is no need to wash it out completely but it is rather preferable to allow such salt to remain in the gel in an amount of not more than 10 weight percent, preferably 0.5 to 5 weight percent, based on the solid weight, since foaming of silica gel is accelerated without any adverse effect by the presence of such a small amount of remaining salt. In the drying for removing sorbed water, silica gel is subjected to heating and/or reduced pressure. Usually, silica gel is heated at about 80° to 150°C for about 2 to 10 hours. Preferably, the drying is conducted so as to produce the dried silica gel having a specific surface area of at least 450 m²/g, particularly 500 to 900 m²/g. The silica gel to be used in the invention preferably has a bulk density of 0.4 to 0.8 g/cm³ and a particle size ranging from 0.05 to 10 mm, particularly 0.1 to 5 mm.

According to this invention, the silica gel is subsequently fired for foaming. The firing is conducted at a temperature ranging from 1000° to 1600°C. In accordance with the present method the silica gel can be directly fired at the above temperature, or preferably pre-fired at 500° to 900°C and thereafter fired at 1000°

to 1600°C. The latter method is especially effective for silica gel having a large particle size of more than 0.18 mm with the advantage of giving a uniformly foamed product having a high degree of foaming which is more excellent in mechanical strength than a product obtained without pre-firing. It is preferred to conduct pre-firing at a temperature of 550° to 750°C to reduce the specific surface area of dried silica gel by 1 to 80%, more preferably by about 10 to 50%. Since larger reduction of specific surface area may result in insufficient foaming during firing, the pre-firing may preferably be such that the pre-fired silica gel still has a specific surface area of at least 400 m²/g. The reduction in specific surface area is determined by temperature and time, which may therefore be suitably selected. Determination of specific surface area referred to herein is conducted by BET method under the condition of 1-hour pumping treatment at 300°C. The adsorption gas used for the measurement was nitrogen gas for dried silica gel and ethylene gas for the foamed product obtained. When pre-firing is conducted before the firing step, water-insoluble inorganic powder to be added to silica sol should be stable under the gelling conditions and infusible, not decomposable and nonvolatile under pre-firing and firing conditions. The silica gel pre-fired is then fired at 1000° to 1600°C to effect foaming. The dried silica gel can be directly fired for foaming without pre-firing. In every case, preferably firing temperature is in the range of 1100° to 1500°C. Although the mechanism to form a foamed product has not been fully clarified, heating at the above-mentioned temperature vitrifies silica gel throughout its surface and partially closes the interior pores, while permitting the remaining hydroxyl groups to be released and expanded to water vapor, with the result that the vitrified silica gel undergoes expansion in its entirety. The firing step causes silica gel to expand to 1.5 to 10 times the original volume and the expanded mass is fixed in this state upon cooling. The firing atmosphere exerts hardly any influence on the expansion of the foamed product, so that firing may be conducted in various gases such as air, an inert gas, etc. or in vacuum. Heating may be conducted in an electric furnace, fuel oil furnace, gas furnace or some other suitable heating means. It is further possible to conduct firing in a molten glass or molten metal, which gives a unique glass or metal product incorporating therein a foamed product of this invention. Firing usually completes within a short period of 3 to 10 minutes, although longer time is applicable without any adverse effect. After firing, the product will be cooled by suitable means, for example, cooling to room temperature slowly or quickly.

The granular siliceous foamed product of this invention is a foamed body of silica having a substantially nonhygroscopic vitrified surface and including in its interior a great number of semi-closed pores defined by vitrified partition walls. Further the shape of the granular siliceous foamed product of this invention varies greatly depending upon the kind of silica gel, foaming conditions and the like and may be almost precisely spherical, ellipsoidal or more complicated. The size of the foamed product also varies over a wide range, which is generally at least 0.2 mm in shorter diameter and not greater than 25 mm in longer diameter. However, it is possible to obtain smaller or greater granules, for instance, small granules having a diameter of about 0.1 mm. Depending upon the uses, granules of the de-