

*Enhanced production of magnesium silicates from strained magnesia*¹

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Summary. Mechanically strained, in contrast to annealed, MgO produced greater yields of forsterite and protoenstatite by solid-state reaction with a quartz-cristobalite mixture at 1200–1400° C. The specific surfaces of the strained and of the annealed MgO were similar. The strained MgO was more hygroscopic and similarity of the surface free energies was thus unlikely. The difference in the amounts of silicates produced from the two types of MgO decreased as the temperatures of synthesis increased. This was ascribed to loss of strain energy by unavoidable annealing before and after these temperatures had been reached.

Similar results were obtained when hydrated silica was substituted for the quartz-cristobalite mixture, but more forsterite was produced.

MAGNESIUM reacts more readily with certain organic liquids if cut while immersed in them, because of mechanical activation associated with the formation of a highly stressed nascent surface (Shaw, 1948).

Naeser and Scholz (1958) showed that some solids, when crushed between rolls, became more hygroscopic, sinterable, or chemically reactive. These effects also were ascribed to mechanical activation, but it is difficult to assess the relative contributions made to them by stored strain energy and by increased specific surface. A contribution by strain energy is probable, because some materials left the rolls as scales, resulting from deformation, or even exploded, as from the abrupt relief of strain.

Later studies demonstrated that prolonged grinding could cause mechanical passivation to succeed mechanical activation. Indeed, the two phenomena could repeat themselves cyclically with time, perhaps because the crystal-lattices were alternately disturbed and healed (Naeser and Scholz, 1962; Naeser, Scholz, and Fiedler, 1962).

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Stress has been thought to influence both the formation and the stability of metamorphic minerals. Thus Harker (1950, pp. 148–151) postulated the existence of 'stress minerals', the stability fields of which could be extended by non-hydrostatic pressure. Turner and Verhoogen (1960, pp. 472–477) did not reject this concept, although it was in apparent conflict with thermodynamic reasoning. Moreover, they mentioned the possible acceleration of metamorphic reactions, not only by stored strain energy, but also because shearing could involve penetrative intergranular movement, the repeated renewal of surfaces of contact, and the increase of specific surface by grain-size reduction.

Many laboratory experiments show that the conditions surmised by Turner and Verhoogen do, in fact, promote remarkable chemical or polymorphic changes. Thus Parker (1914) produced mercuric iodide and potassium chloride by grinding together mercuric chloride and potassium iodide, and demonstrated comparable interactions within other pairs of salts. More recently, Dacheil and Roy (1960) effected many chemical or polymorphic changes, some of which seemed incompatible with the operation of purely hydrostatic pressures or with the development of localized high temperatures resulting from friction.

During grinding, e.g. in a mortar, nuclei of new crystalline phases become distributed through the powder and promote the continued formation of these phases. Moreover, shearing stress operates concurrently with the chemical reactions or polymorphic changes. However, in the experiments of Naeser and Scholz, or of the present investigators, the solids were crushed and their chemical or other properties examined after the application of stress had ceased.

Buerger and Washken (1947) found that the plastic deformation of MgO and other polycrystalline inorganic solids induced a subsequent recrystallization when a critical temperature was exceeded. For a particular solid, this temperature was lowered when the prior deformation was intensified. Griggs, Paterson, Heard, and Turner (1960) discussed these phenomena, and described experiments in which the recrystallization of calcite was thought to have been promoted by internal strain-energy, grain-boundary energy, or both.

McCrone (1949) reported the 'boundary migration' of polycrystalline organic compounds heated below their melting-points. The effect was ascribed to strain induced mechanically or thermally. Thus crystals formed rapidly from a supercooled melt exhibited 'boundary migration', while those developed by seeding the melt did not; presumably the latter crystals were relatively strain-free (cf. Williamson, 1958).

The recrystallization of strained metals and alloys, beginning from strain-free nuclei, is repeatedly mentioned in metallurgical literature. In particular, Yoshida, Liebmann, and Lücke (1959) described a monocrystal of aluminium that recrystallized only at the end previously strained.

Fordham (1949) found that strained crystals of ammonium nitrate appeared to grow relatively fast from solution, but only initially. The growth-rate may have declined later because dislocations became buried in the newly deposited material.

In conclusion, there is published evidence that the chemical and physical behaviour of solids is influenced by processes likely to introduce strain energy. However, changes in surface area or other uncontrolled variables may make the specific effects of the strain energy hard to assess.

The plan of the present investigation

An attempt was made to prepare two batches of MgO particles, not differing in specific surface or size distribution, of which only one contained strained particles. Even if the two batches have similar surface areas, similarity of their surface free energies cannot be assumed, as internal strain, representing defects, dislocations, and lattice-distortions, may manifest externally as enhanced surface energy (Gregg, 1958).

If abrasion or polishing is involved in the preparation of powders, surface free energies may be augmented because the external layers have less ordered structures than the interiors of the particles. These external layers have been regarded as amorphous (Beilby, 1921) but are often composed of crystallites (Samuels, 1960). The smaller the particles, the greater is the contribution of these layers to their volume and thus to their total free energy. However, the crushing techniques used in the present studies probably minimized the development of such layers.

The MgO particles were heated with silica at temperatures below those of the eutectics in the system MgO-SiO₂ (Schairer, 1957) and thus the magnesium silicates resulted from solid-state reactions.

X-ray diffraction techniques were used to detect strain, to identify the crystalline phases, and to estimate the quantities of the magnesium silicates synthesized.

Materials, equipment, and methods

Materials. The MgO was prepared by calcining MgCO₃ of chemical reagent purity at 1000° C for one hour, and then at 1650° C for 2½ hours.

The quartz was a very pure, well-crystallized, 'potter's flint'. The hydrated silica ($\text{SiO}_2 \cdot 0.16\text{H}_2\text{O}$) was of chemical reagent purity.

The MgO and the quartz, before being crushed between rolls to induce strain, were pressed separately into cylindrical pellets 1 in. diameter and ca. 1 in. high and then sintered in a gas-air pot furnace. The MgO and quartz were sintered for $2\frac{1}{2}$ hours at 1650°C and for 4 hours at 1450°C respectively. A part of the quartz changed to cristobalite, detected by X-ray and D.T.A. techniques.

Crushing equipment and techniques. The roll crusher consisted of two parallel horizontal electrically driven cylinders, faced with hardened steel, with a variable gap between them. The sintered pellets were passed five times successively between the rolls, which were brought closer together for each passage until they virtually touched. The crushed material was then sieved with a screen scheduled to pass particles of maximum diameter $44\ \mu$. Any over-sized material was passed between the rolls, at their closest approach, and sieved as before. The crushed batch is hereafter termed 'strained' material.

Detection of strain. Strain was detected by observing the broadening of suitable X-ray diffraction bands in the back reflection region. Such broadening can appear also when particles are sufficiently fine, but is unlikely to be significant as the Coulter Counter showed that the equivalent spherical diameters of the MgO particles varied from 2 to $30\ \mu$. Moreover, strain was not detectable in the original MgO or quartz powders when these had passed between the rolls at the closest approach. As inferred earlier, it was necessary to pelletize these materials before they became detectably strained by crushing.

The MgO of the crushed pellets showed a broadening of certain X-ray diffraction bands, which, if stacking faults were initially absent, could be ascribed to the mechanically induced strain. The crystalline silica (quartz and cristobalite) developed relatively little strain, probably because, in contrast to the MgO, it was brittle rather than plastic.

Removal of strain by annealing. Endeavours were made to anneal portions of the strained powders without causing appreciable sintering. In this way, it was hoped to obtain two batches of powder, having similar specific surfaces, of which one only consisted of strained particles. Appropriate annealing temperatures were found by the use of a high-temperature X-ray diffraction unit. The diffractometer was oscillated backwards and forwards in the region of a 'back reflection peak', while the temperature of the powder specimen was simultaneously increased. The initially broadened peak became narrower, and the temperature at

which it attained its normal width was arbitrarily selected as the annealing temperature. The effect of temperature and time on the rate of loss of strain energy was not examined in detail.

The peaks used corresponded to:

MgO	422,	d 0.8600 Å	(Swanson and Tatge, 1953, p. 38)
Low quartz	312	1.0816	(Swanson, Fuyat, and Ugrinic, 1954, p. 25)
Low cristobalite	421	1.0989	(Swanson and Tatge, 1953, p. 41).

In accord with the data obtained, the powders were annealed in silicon carbide electrical resistance furnaces for $\frac{1}{2}$ hour, at 1200° C for MgO and 1000° C for SiO₂, and allowed to cool in the furnaces. The development of further cristobalite, during the annealing of the SiO₂, was not detected by X-ray or D.T.A. techniques.

The annealing of the MgO caused some crystal-growth and sintering, made apparent by the development of growth-steps on the cleavage-surfaces of the particles, obvious in electron micrographs, by the decrease of the mean particle-diameter from 7.5 to 6.7 μ , estimated by the Coulter Counter, and by the decrease of the specific surface from 23.45 to 22.3 m²g⁻¹, determined by the B.E.T. technique.

Production of magnesium silicates

Mixtures of MgO and crystalline silica (quartz or cristobalite) or hydrated silica were made in proportions by weight corresponding to Mg₂SiO₄. The mixtures were MgO (strained) and crystalline silica (strained), MgO (annealed) and crystalline silica (annealed), MgO (strained) and hydrated silica, and MgO (annealed) and hydrated silica.

The dry powders were mixed by prolonged shaking, and not by grinding, and 5.855 g of each mixture was compacted into a pellet at 60 lb in⁻². A separate batch was mixed for each pellet. The lightest pressure capable of producing a coherent pellet was used, to minimize further comminution or strain. Standardized techniques of mixing and compaction were used for all samples.

Appropriate pellets were heated at 1400° C, and also at a succession of temperatures from 1200° C, by 25° C intervals, to 1350° C. Each heating involved two pellets, one made from strained and one from annealed reactants. The pellets were placed side by side on platinum foil in an electric furnace having silicon carbide elements and a temperature controller. The temperature rose by 60° C per hour to its peak, where it

was maintained for three hours. The pellets then cooled at the natural rate of the furnace.

Pellets consisting entirely of hydrated silica were heated simultaneously with those containing hydrated silica and MgO.

Quantitative estimation of magnesium silicates

X-ray techniques were used to estimate the yield of forsterite quantitatively by the method of known additions (Brindley, 1961, pp. 495–496). The heat-treated pellets were first ground under acetone in an automatic mortar for $\frac{1}{2}$ hour, 0.1, 0.2, and 0.3 g of 'standard' forsterite were then added to separate 1 g samples of the resulting powder, followed by mixing under acetone in an automatic mortar for 15 minutes.

The yields of protoenstatite were determined by using standard binary mixtures (Brindley, 1961, pp. 493–494). This required the construction of a calibration chart based on the behaviour of mixtures of forsterite and protoenstatite in which the forsterite varied by aliquots of 25 % by weight. The mixtures were made by 15-minute grinding under acetone in an automatic mortar.

The diffractometer traces scanned corresponded to forsterite 112, d 2.458 Å (Swanson and Tatge, 1953, p. 84), and protoenstatite 220, 121 (Smith, 1959, p. 516).

Integrated intensities were obtained graphically. Each sample was completely studied in a single day, to minimize the effects of instrumental variation.

The samples were packed in a rotating holder designed by Bratton (1961, p. 21; p. 70) and a constant weight of sample, and approximately the same degree of compaction, were used. These procedures reduced the tendency to particle-orientation.

Standard forsterite and protoenstatite were prepared from MgO and hydrated silica in appropriate proportions by weight, corrected for the presence of 2 % MgF₂ added as a mineralizer (cf. Sarver and Hummel, 1962). The mixed reactants were heated at 1000° C for one hour, allowed to cool, ground under acetone for 3 hours, and subsequently heated at 1300° C for 24 hours. Only forsterite or protoenstatite were identified in the appropriate standard materials by X-ray diffraction techniques.

The enhanced production of magnesium silicates

The amount of forsterite formed from either strained or annealed reactants increased with temperature, but relatively more forsterite was

produced from the strained reactants, particularly at the lower temperatures (figs. 1 and 2). This was observed irrespective of whether crystalline silica (quartz and cristobalite) or hydrated silica were reactants.

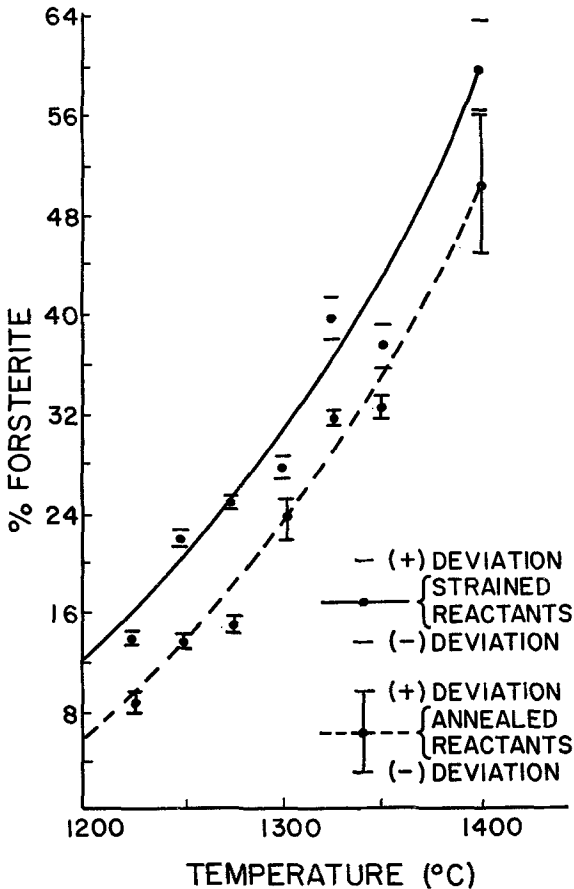


FIG. 1. Percent forsterite by weight formed from strained and from annealed reactants at various temperatures.

However, hydrated silica was relatively more effective in producing forsterite (cf. Alderman, 1959). The unreacted hydrated silica became a mixture of low-quartz and low-cristobalite after cooling, but the proportion of quartz was larger when annealed rather than strained MgO was the other reactant. The present experiments did not suffice to

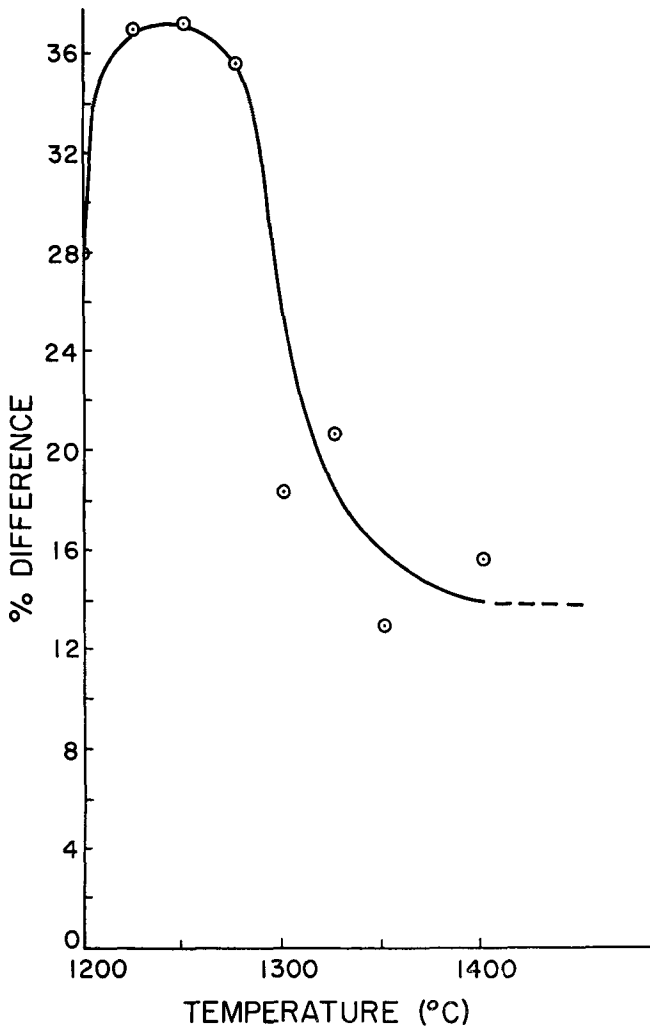


FIG. 2. Percent difference by weight in amount of forsterite formed from strained and from annealed reactants at various temperatures. The difference is expressed as a percentage of the weight of forsterite formed from the strained reactant at any given temperature.

suggest a reason for this. Pellets of hydrated silica, heated simultaneously with the MgO-silica mixtures, became poorly crystalline low-cristobalite after cooling.

Relatively little protoenstatite developed from the mixtures of MgO

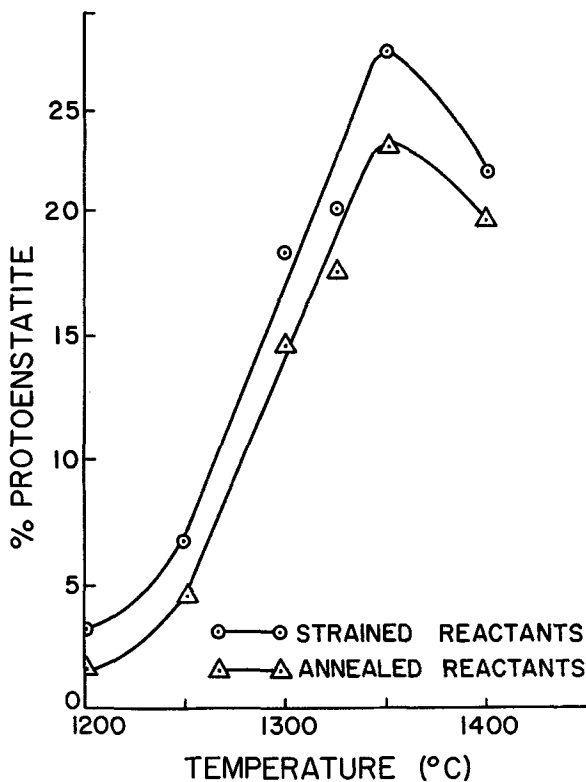


FIG. 3. Percent protoenstatite formed from strained and from annealed reactants at various temperatures.

and hydrated silica. More appeared where mixtures of MgO and crystalline silica (quartz and cristobalite) had been used, and the amounts were greater if the reactants had been strained (fig. 3). Forsterite was presumably the initial product of the solid-state reaction (Jander and Wuhler, 1936) and some of it reacted subsequently with SiO_2 to form protoenstatite. Thus an enhanced production of forsterite from strained, as compared with annealed, reactants could result in an enhanced production of protoenstatite also. The amounts of protoenstatite may be

expected to decline as the temperature of synthesis is increased (fig. 3) because the proportions of MgO and SiO₂ in the reaction mixture correspond to those of forsterite. Jander and Wuhrer (1936) showed that the production of forsterite from magnesium metasilicate is possible. Moreover, the reaction mixture became entirely forsterite after the prolonged heating at 1300° C used in the preparation of standards for the X-ray quantitative determinations.

Discussion

The strained, in contrast to the annealed, reactants produced more forsterite and protoenstatite, particularly at the lower temperatures of synthesis. Little strain was detectable in the crystalline silica (quartz and cristobalite) and, further, the enhanced yields of magnesium silicates were obtained also when hydrated, not crystalline, silica was used. Thus the strain energy in the MgO, rather than in the crystalline silica, was especially significant in promoting the formation of the silicates. It could, however, be argued that the greater specific surface of the strained MgO, rather than the stored strain energy, was really responsible. This is unlikely, as the strained and the annealed MgO differed little in specific surface. Further, the enhanced yields of silicates appeared especially in mixtures heated at temperatures not much above 1200° C. This temperature had been shown to be effective for the removal of strain from MgO by annealing and thus, in its vicinity, strain energy should be readily available.

The strain energy is a manifestation of the defects, dislocations, and lattice-distortions present in the MgO. The electron micrographs revealed sets of cracks parallel to the external cleavage-surfaces of the strained MgO particles. These cracks may be expected to be accompanied by dislocations resulting from crushing between the rolls. At least some of the cleavage-cracks were seen to survive the annealing-process, but the latter may be expected to reduce the density of the dislocations by causing them to move, combine together, or mutually annihilate each other.

Barr, Hoodless, Morrison, and Rudham (1960) showed that anion diffusion in NaCl was more significant before the dislocation density in the crystals had been reduced by annealing. Similarly, the enhanced mobility of ions, not necessarily anions, may contribute to the greater effectiveness of strained MgO in the formation of magnesium silicates.

According to Shaw (1955, Ph.D. thesis, University of California, quoted and discussed by Fyfe, Turner, and Verhoogen, 1958, pp. 84-86 ;

pp. 101-102), the formation of forsterite involves the migration of SiO_2 into or towards MgO , although some ionic mobility in the surface layers of the MgO may occur also. Migration of SiO_2 into strained MgO might well be facilitated if the dislocation density were relatively high. However, Hanoka (1961) found that surface diffusion seemed to play a significant role in the sintering of MgO at temperatures similar to those employed in synthesizing the magnesium silicates and thus, as suggested by Shaw (*op. cit.*), it may well be one of the mechanisms concerned in their production.

There was evidence that strain energy within MgO particles resulted in increased surface free energy. Strained MgO adsorbed water from saturated air at 25°C much more rapidly than did annealed MgO . For example, after 5 hours, the strained material had adsorbed ca. 3.0 % and the unstrained material only ca. 0.2 % by weight of water. These quantities were out of all proportion to the differing specific surfaces of the powders.

Thus the enhanced surface energy of the strained MgO may contribute to the augmented production of magnesium silicates, perhaps by producing a greater surface mobility. However, the enhanced surface energy may itself be supplied from the strain energy within the MgO particle, perhaps by the movement of dislocations towards the surface.

Determinations of the heats of solution of strained and of annealed MgO in 2.0 *N* HNO_3 revealed energetic differences greater than those to be expected because of the differences in specific surface. Such determinations cannot, however, be used to assess the amounts of strain energy available at the reaction temperatures to contribute to the formation of magnesium silicates. Some of this energy is lost by unavoidable annealing before and after these temperatures have been attained. A proportion of the energy so lost may be utilized in sintering MgO particles together, rather than in assisting them to react with SiO_2 , because the heterogeneity of the mixture leaves many MgO particles in mutual contact.

It is not known whether strain energy enhances the yields of magnesium silicates by promoting the formation of nuclei of the silicates, by assisting their subsequent growth, or by both mechanisms, although it is suspected that easier nucleation may be very significant.

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