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14.1 Introduction

The sol-gel technique is a method for fabricating non-metallic, inorganic materials. In contrast to mixed-oxide processes, the synthesis produces an inorganic material via liquid and gel-type intermediate stages (sol and gel). In solutions, appropriate precursors show cross-linking reactions similar to reactions observed in the production of organic polymers.

In sol-gel cross-linking, soluble precursors, unlike organic polymers, hydrolyse and subsequently condense.

Alkoxides and halogenides of the desired inorganic material that dissolve in water or other solvents, are appropriate precursors for these reactions, e.g. $Si(OEt)_4$ for fabricating SiO_2 . A clear solution of these precursors in alcohol or other solvents transforms into amorphous gel via colloidal sol after hydrolysis and condensation reactions are initiated. The point at which former liquid solidifies is referred to as the sol-gel transition.

Subsequent transformation of gel produces the pure oxide material, usually by means of drying, heat treatment, and/or sintering.

14.1.1

Background and Origin of Sol-gel Chemistry

Ebelmen (1846) is considered the first to have published on sol-gel reactions. He attempted to synthesise a metal alkoxide, $Si(OEt)_4$, by transforming $SiCl_4$ with ethanol. However, Ebelmen observed that the formerly clear solution for the reaction spontaneously transformed into a gel-type mass [1].

What had happened? $Si(OEt)_4$ and $SiCl_4$ are also excellent precursors for solgel synthesis. They hydrolyse spontaneously with water, and the humidity of the surrounding air is sufficient to initiate the reaction. Hydroxides form and, in condensation reactions, immediately transform into a Si-O-Si network that completely fills the reaction container – the solution solidifies.

Around 1930, the first products became available that were produced by solgel synthesis. Materials were mostly partially condensed alkoxysilanes used for protecting earthenware products.

Since 1960, more and more precursors and additives for colloidal and particulate ceramics have been produced by means of sol-gel techniques. The use of colloidal sols for coating processes spread.

14.1.2

Material Fabrication by Means of Sol-gel Techniques

Sol-gel is a multi-purpose technology for fabrication of materials. The liquid intermediate state allows different types of forming (cf. Fig. 14.1).

For example, a sol can be dried to gel, and subsequently heat treated, producing a dense ceramic. Specialised drying procedures, e.g. subcritical and supercritical drying, yield highly porous solids referred to as aerogels. Nano-particles are produced with spray-drying methods. Also, substrates can be coated with sols. Today, sol-gel technology is used primarily to produce such coatings.

The variety of applicable forming methods for processing sol generates a wide range of properties in final oxidic products. The only fixed property after selecting the composition of the sol is the composition of the final oxide. Possible products include pure oxides, e.g. SiO_2 from $Si(OEt)_4$ sol and TiO_2 from $Ti(OEt)_4$ sol, as well as mixed oxides and complex compositions, e.g. eight-component glass from $Si(OMe)_4 + Al(OsecBu)_3 + P_2O_5 + LiOEt + Mg(OMe)_2 + NaOMe + Ti(OBu)_4 + Zr(OPr)_4$ [2, 3].

Physical material properties such as density, porosity, hardness, etc. are determined mainly by the conditions during sol-gel synthesis.



Fig. 14.1 Available forming techniques in sol-gel technology. Representation following Iler, in Brinker/Scherer, Sol-Gel Science, 1990.

For sol, pH, above all, controls the shape of the produced nano-particles. It causes differently formed networks when the sol transforms to solid. A typical example is synthesis of SiO_2 sol for either dense or porous coatings, differentiated only by the pH of the sol.

A further example of the effects of varying synthesis conditions on the produced material is found in fabrication of either highly porous or dense oxides. The temperature and pressure during gel drying predominantly determine which of the two material types is produced.

The following notes cover the mechanistic processes during production of coatings by means of sol-gel technology. Descriptions focus on SiO_2 , the most common system in sol-gel chemistry. It should be considered that mechanistic processes in the SiO_2 system cannot generally be transferred to other systems. Sol-gel synthesis frequently uses transition metals, e.g. titanium, zirconium, aluminium, or heavy metals such as lead. Electronegativity is lower for transition metals than for silicon. The result is that hydrolysis and condensation reactions involving transition metals are much faster and more difficult to control than for silicon alkoxides. Furthermore, transition metals are capable of increasing the coordination sphere, whereas silicon always has a coordination number of four. Increased coordination spheres allow transition metals, in contrast to silicone, to form aquo and oxo complexes.

Complex sol-gel reactions of transition metals are covered in the corresponding technical literature [9a, b].

14.2 Sol-gel Coating Formation for SiO₂

14.2.1 Coatings with SiO₂ Sol from Salts of Silicic Acid

The simplest way of producing SiO_2 sol is by hydrolysis of a silicic acid salt, e.g. sodium silicate. Sodium silicate solutions produce stable, colloidal sol. Nano-particles in this sol form during the following condensation reaction:



with R=OH, ONaOK.

Nano-particles in the sol can be analysed accurately with spectroscopic methods, e.g. Si-NMR. Investigations showed that 80% of nano-particles in a 0.5-molar solution of K₂O-SiO₂ are of the following molecule type [4]:

(each corner represents a tetrahedrally co-ordinated silicon atom).

The sol can be applied as a coating by means of common techniques, e.g. dip coating, spin-on deposition, roller coating, slit coating, meniscus coating, and doctor coating techniques.

Independent of the specific coating technique, the solid layer forms from sol when the surface-to-volume ratio increases rapidly. This leads to spontaneous cross-linking reactions between the nano-particles. High temperature promotes the condensation. Ultimately, the gel forms a coating on the substrate.

The gel coating is usually hardened by an additional heat treatment, i.e. gel is transformed to a pure, dense SiO_2 coating by dehydration.

Although variations are limited in this system, the physical properties of the produced dense SiO_2 coatings are determined by process parameters. The key value is the pH of the colloidal solution. Parameters have to be adjusted precisely for each separate process.

14.2.2

Coatings with SiO₂ Sol from Si Alkoxides

Tetraethoxysilane (TEOS, Si(OEt)₄) is the most common precursor for sol-gel reactions. SiO₂ sol is usually produced from TEOS in ethanol. A solution of TEOS and ethanol is predefined, then, added water initiates hydrolysis and condensation.

Analysis of the individual reactions and formed nano-particles is far more complex than for sodium silicate. The main reason is that three parallel reactions occur when TEOS, or other alkoxides, are transformed:



with R = -H, -OEt, $-O-Si-R_3$.

All three are equilibrium reactions and, therefore, can react in the opposite direction, as well.

Identifying nano-particles formed in hydrolysis and condensation of TEOS or other Si alkoxides is very difficult. Even spectroscopic analysis cannot identify



Fig. 14.2 Graphical representation of simulated structures of selected model calculations, following Schaefer and Maekin [10, 11]. *D* values represent the fractal structure dimensions.

the molecules [5–9]. Therefore, a precise chemical description of the formed nano-particles is not available.

Theoretical calculations attempted to assess structures appearing in Si alkoxide transformations. They consider, for example, whether condensation reactions are determined by diffusion processes or rather by reaction rates [10, 11]. Figure 14.2 illustrates results of such calculations.

It is apparent that structures of formed nano-particles vary significantly. In fact, experiments with dispersion photometers confirmed the structures in Si alkoxide sol. The structures can be controlled by process parameters such as temperature, dosage rates, stirring intensity and, particularly, pH.

Alkaline media primarily produce dense, discrete nano-particles in the sol. Condensation reactions are controlled by reaction rates and show monomercluster growth, i.e. clusters form, and grow due to condensing monomers.

In acid media, very open, branched nano-particles form in the sol. Here, condensation is controlled by diffusion as a cluster-cluster growth, i.e. monomers initially form a large number of small clusters that subsequently condense.

How do different nano-particles in the sol affect subsequently produced coatings? Generally, every type of sol can be deposited to form an SiO_2 coating. Physical properties of the coating, however, are determined by the type of nano-particles in the sol. Discrete, dense nano-particles typically lead to porous coatings because, during coating processes, gaps form in between the particles.

Branched, open-structured nano-particles yield denser coatings. During coating, this type of nano-particles produces tight networks without developing any gaps.

Variations in porosity of coatings determine hardness, and also cause different refractive indices. These coatings are therefore interesting for optical applications, one of which is introduced in the following section.

14.3

Application Examples

14.3.1

Translating an Idea into a Product: Development of an Anti-reflection Coating for Glass

The anti-reflection coating development for glass is a good example of how features of sol-gel technology are used to invent a new product.

The principle behind the development is that every transparent material, e.g. glass or plastic, also reflects light. Reflections occur when light penetrating the transparent material is subject to changing refractive indices. The same happens with light that leaves the material. Reflection losses are calculated using optical laws. For white glass, they are in the range of approx. 8% of total light intensity.

Light reflections are particularly troublesome when mirror effects impair seethrough properties, e.g. on displays. Reflections are equally unwanted in applications that require the total energy of sunlight, e.g. solar collectors and photovoltaic modules.

On glass, a coating with an appropriate refractive index can reduce reflections considerably. The necessary optimal refractive index can be calculated. For white glass, the value is equal to n_D =1.22. When the coating thickness is adjusted to $\lambda/4$, reflections of light with a wavelength of λ disappear.

Figure 14.3 shows the principle of the anti-reflection coating.

The problem is, however, that there is no dense, stable material available with a refractive index of n_D =1.22. The refractive index of MgF₂ fluoride, n_D =1.38, comes closest to the desired value. MgF₂, therefore, is a commonly used material for anti-reflection coatings on spectacle lenses.

Sol-gel technology allows fabrication of nano-porous coatings, as described above. Refractive indices of porous coatings are very low. For example, the desired refractive index of n_D =1.22 for anti-reflection coatings is obtained with SiO₂ and a porosity of 57%.

The initial step in production of nano-porous SiO_2 coatings by means of solgel is a chemical preparation of an appropriate SiO_2 coating solution. As described in Section 14.2, an alkoxysilane is hydrolysed and condensed in an alkaline medium. Figure 14.4 illustrates individual stages of the synthesis.

Sufficient shelf life, essential for commercial use of the produced sol, is provided by modification and stabilising steps following after hydrolysis and con-



Fig. 14.3 Principle of anti-reflection coating on glass. 8% of light intensity is lost due to reflection when light passes through uncoated glass (left). A coating with a refractive index of n_D =1.22 (right) reduces reflections to zero for a particular wavelength.



Fig. 14.4 Left: schematic representation of sol synthesis for anti-reflection coatings. Right: SEM image of monodisperse particles, prior to coating sol modification and stabilising.

densation of the silanes. During synthesis, control of the process parameters temperature, stirring intensity, and dosage rates is challenging. Comprehensive knowledge of parameters influencing the product is crucial for successful transfer of synthesis to large-scale production.

Merck KGaA produces such coating sol on an industrial scale, based on a joint development with Flabeg Solarglas GmbH as well as ISC and ISE Fraunhofer Institutes. It is used for production of highly transmissive float glass for solar-energy applications (solar collectors and photovoltaic modules) [9e].

Here, the coating is applied by means of dip coating, however, other application techniques are applicable as well. In dip coating, the float glass is im-





Fig. 14.5 Transmission spectrum of anti-reflection coating. The lower graph represents the uncoated reference sample, the upper graph shows the behaviour of glass with an antireflection coating. Measurement: Fraunhofer Institute ISE.



Fig. 14.6 Comparison of anti-reflection coatings with porous SiO_2 (upper graph) and a multi-layer coating (alternating high- and low-refracting materials, intermediate graph). The porous SiO_2 anti-reflection coating cov-

ers the entire spectrum whereas the effect of the multi-layer coating only covers the visible spectrum of the sunlight. Measurement: Fraunhofer Institute ISE.

mersed in a cuvette containing the coating sol, and drawn out of the solution at a defined velocity. The sol film on the glass surface dries and forms the gel. The coating thickness is controlled precisely by adjusting the velocity at which the glass leaves the bath.

After drying, the coating is hardened at temperatures close to $T_{\rm G}$ of the glass. Figure 14.5 shows a typical spectrum of a coated glass pane.

The produced porous SiO_2 coatings have a refractive index of approx. 1.25, very close to the target value of 1.22. An important prerequisite for solar-energy



Fig. 14.7 Application of highly transmissive anti-reflective glass in solar-energy production. Photograph: Flabeg Solarglas GmbH.



production is that the anti-reflective properties cover the complete solar spectrum. Figure 14.6 compares the porous SiO_2 anti-reflection coating with coatings of alternately high and low refracting layers. These multi-layer coatings are used frequently for anti-reflection on glass, e.g. lenses.

For further increase of porosity and, thereby, reduction of refractive index, mechanical stability of the SiO_2 coating should be considered. Stability, of course, drops when coating porosity increases. For the presented example of an SiO_2 coating, abrasive wear resistance is sufficient for application as highly transmissive covering glass on solar collectors or photovoltaic modules (tested

according to DIN EN 1096-2). But certainly, it is not high enough for every type of application, e.g. automobile windscreens and side windows.

Figure 14.7 shows highly transmissive anti-reflection glass used as covering glass for solar collectors or photovoltaic modules. 5% of added usable sunlight corresponds to the integrated, normalised transmission increase across the total solar spectrum. Annual gross heat production for thermal solar collectors is increased by 10%, depending on collector design. Highly transmissive glass for photovoltaic modules yields a 3.5% gain in energy efficiency. Geographical position and climatic conditions have additional effects.

14.3.2

Application of Wet Chemical Coating Techniques for a Common Product Type: Pearlescent Pigments

Pearlescent pigments by Merck KGaA are an example of how wet chemical coating methods can be used for a common and established group of products. Numerous applications of materials with pearlescent pigments are found in everyday life, e.g. automotive paint coatings, printed packaging materials, wallpaper, textiles, plastics, and cosmetic products.

Here, a brief discussion of interference colours and gloss is presented prior to describing pearlescent pigment production.

14.3.2.1 Gloss and Colour

Why does an object seam to have a particular colour? When visible light hits a blue object, the object absorbs part of the light (red, green, and yellow part of the spectrum) and reflects the remaining light that then appears blue to the human eye.

Absorption and reflection cannot explain certain colour phenomena, e.g. iridescent colours of a thin oil film on water. Such phenomena occur at layer interfaces when the thickness of boundary layers is in the range of the light wavelength. Part of the light is reflected at the first boundary layer of the film, and is subject to a 180° phase shift. The other part of the light is reflected at the second boundary layer. The two reflected light waves superpose and interfere. Depending on film thickness, light intensity can either increase, or the two waves can destructively interfere. The result is that certain parts of the visible light intensity decrease, whereas others are reflected stronger, determined by the coating thickness. Iridescent colours of an oil film covering water are therefore caused by variations of film thickness.

Gloss, i.e. reflections towards a preferred direction, are prerequisites for formation of interference colours. However, there are different types of gloss. The human eye differentiates finest nuances from soft pearlescent shine to sparkling and twinkling. Generally, gloss is created by light reflected at a smooth surface. Rough surfaces cause diffuse reflections of light. The soft gloss of a natural pearl is created by alternately arranged transparent protein and partially reflecting calcium carbonate layers. Reflections from the surfaces of CaCO₃ layers originate literally from deep inside the material.

14.3.2.2 Production of Pearlescent Pigments with Interference Colours

Thin layers of non-fading, highly refractive material, e.g. TiO_2 , embedded more or less parallel in low refracting media such as paint are necessary for fabrication of pigments with pearl-like gloss and interference colours (Fig. 14.8). Alternatively, the highly refractive layer can also be applied to a transparent, laminar substrate material.

To date, monocrystalline titanium dioxide flakes are not yet available. However, deposition of thin TiO_2 coatings on laminar substrates is possible. Biotite (black mica) is an appropriate substrate, and is found in large quantities as a natural resource. It can be split into flakes, is transparent, chemically inert, and heat resistant. Use of biotite as a substrate for metal oxide coatings caused a breakthrough in the technology of pearlescent pigments. Figure 14.9 shows a photograph of the mineral and an SEM image of biotite flakes.

Merck KGaA uses wet chemical hydrolysis of a titanium salt solution in biotite suspension for coating pearlescent pigments. It involves the following procedure [9c]:

An aqueous, strong acid $Ti(O)Cl_2$ solution is continuously added to a biotite suspension. When a certain pH is reached, $TiO_2 \cdot xH_2O$ deposits on the biotite. The reaction continues until a predefined coating thickness is obtained.



Fig. 14.8 Principle of pearlescent pigments with interference colour (left): TiO_2 layers within paint coat. Alternatively, TiO_2 can be deposited onto laminar carriers (right).



Fig. 14.9 Photography and SEM image of natural biotite (black mica).



Fig. 14.10 Coating thickness of titanium oxide determines the interference colour (top). SEM image of TiO_2 coating on biotite (left).

During the described process, the initially unimpressive biotite suspension starts to show a dull gloss. As the reaction progresses, the gloss intensifies.

When the reaction is interrupted at this point and the suspension is filtered, rinsed, and heat treated, it produces a silver-white glossy effect pigment. The titanium dioxide is now 40–60 μ m thick. Silver-white pigments are the largest group of pearlescent pigments. Depending on the particle-size distribution of biotite used, the gloss is either satin, brilliant, or sparkling.

A remarkable phenomenon is observed when coating of biotite with titanium dioxide is not interrupted but continues past the stage of silver gloss. The biotite suspension then starts to show a gold-yellow gloss. During continued deposition reaction, the gold-yellow colour disappears and the colour of the suspension changes to copper red, then to lilac, glossy blue, turquoise, and finally green. When the reaction continues further, the play of colours starts afresh. The explanation is simple: The titanium oxide layers, in each case, reached a thickness at which the observed interference colours occur (Fig. 14.10).

Anhydrous, crystalline modification of the oxide coating forms during subsequent drying or heat treatment of the coated biotite. Titanium dioxide on the



Fig. 14.11 SEM image of biotite particle with $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ coating.

biotite flakes can crystallise as rutile or anatase. Generally, the rutile modification is preferred due to a higher refractive index and light fastness. On biotite, however, anatase forms even under conditions that would usually promote rutile formation. Pre-coating of biotite with tin dioxide, also a wet chemical process, improves crystallisation of TiO_2 to rutile.

Apart from titanium dioxide, other metal oxides can be deposited onto biotite. Iron oxide in hematite modification is applicable due to a very high refractive index. In this case, iron salt solution is hydrolysed in a biotite suspension and an iron hydrate coating forms on the biotite. Subsequent heat treatment dehydrates the coating. Hematite is red-brown and, thus, the effect and colour of this type of pearlescent pigment are caused by a combination of absorption and interference effects. The technique yields bronze, copper, and red tones.

Multi-layer coatings on biotite produce unique colour effects. These pigments can show a so-called colour flop, i.e. an observer sees either one or the other colour, depending on the viewing angle. Production is more complex but is based on the same principles of wet chemical coating processes described above. Figure 14.11 shows a SEM image of a biotite particle with a TiO₂/SiO₂/TiO₂ coating.

14.3.3 Effect Pigments on SiO₂ Flakes

A completely new class of effect pigments is created when, apart from the oxidic coating, the substrate material of a pigment is optically active, as well. This case requires a substrate with precisely adjusted, homogenous thickness.

Merck KGaA produces such substrate from SiO_2 by means of sol-gel technology. Figure 14.12 illustrates the principle. A Si precursor is used to deposit a SiO_2 sol coating onto a rotating belt. During drying, the sol layer transforms to

Si-precursor



Fig. 14.12 Production of artificial SiO_2 flakes by means of solgel coating (web coating technique).



Fig. 14.13 SEM image of SiO₂ flakes, produced by sol-gel coating technique. Left: SiO₂ flakes, right: SiO₂ flake coated with TiO₂.

gel. Then, the solid gel is removed from the belt in order to obtain SiO_2 gel flakes with constant thickness. Coating thickness can be adjusted by controlling the deposition process.

Heat treatment of the gel flakes yields completely oxidic SiO_2 flakes (cf. SEM image, Fig. 14.13).

Coating of these SiO_2 flakes with titanium oxide, as presented in Section 14.3.2.2, produces effect pigments with a strong colour change, depending on the viewing angle. The reason is that not only the substrate but also the coating



Fig. 14.14 Sample with effect pigment coating: Specimen appears blue, green, or lilac, depending on viewing angle.





Fig. 14.15 Principle of anti-wrinkle effect due to coated polydisperse SiO_2 spheres (left), SEM image of applied SiO_2 spheres.

produces interference colours. Figure 14.14 shows the results: A coated model, photographed from three different directions, appears blue, green, or lilac, depending on the viewing angle.

14.3.4 Coating of SiO₂ Spheres for Cosmetic Formulations

Wet chemical deposition methods described in Section 14.3.2.2 allow applications in further branches as well. For example, polydisperse SiO_2 nano-spheres are produced as additives for cosmetic formulations [9d].

Additives of inorganic particles for cosmetic formulations are long known and common, e.g. as fillers or for controlled rheological properties. However, particles with specific size distribution and appropriate coatings can be used to create special effects.

TiO₂/Fe₂O₃-coated polydisperse SiO₂ spheres provide a so-called anti-wrinkle effect. When added to cosmetic formulations, these custom SiO₂ spheres cause diffuse reflection of incoming light. A small skin wrinkle, clearly appearing due to light shadowing effects, brightens and becomes less obvious as reflections are scattered. Figure 14.15 illustrates the anti-wrinkle principle. The SEM image shows corresponding polydisperse SiO₂ spheres.

 TiO_2/Fe_2O_3 coatings are applied by the same means as biotite coatings, described in Section 14.3.2.2.

14.4 Conclusions

The broad potential of sol-gel coatings is demonstrated, considering anti-reflection coatings for glass, wet chemical coating techniques for pearlescent pigments and effect pigments, as well as coating of SiO₂ spheres for cosmetic formulations, as examples.

With conceivably increasing demand for upgrading and functionalisation of all types of surfaces, coating technologies are gaining importance. Sol-gel coating techniques will play a decisive role in applications where physical coating methods are either unfeasible or uneconomical.

Sol-gel technology is usually the first choice for coating small particles, for applications that require porous coatings, and for coating processes operating at room temperature.

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