ADVANCED SILICON NITRIDE & SIALON CERAMICS

Engineering & Industrial Applications of Syalons

As modern industry continues to demand stronger, harder, more wear resistant and heat resistant materials, which will operate cost effectively in hostile environments, it has become essential to seek alternative engineering materials.

The discovery of silicon nitride in 1857 by Deville and Whaler caused no excitement among the engineering fraternity of the day. Yet the announcement more than a century later, in 1972, that an alloy of this same material had been found stimulated enormous interest and triggered off investigations on a worldwide scale. The reasons why the two events were heralded in such dissimilar ways gives us an insight into the developments that have taken place in our major industries.

Modern industry requires stronger, harder, more wear resistant and heat resistant materials, which will operate cost effectively in more hostile environments than ever before. Today's aircraft engines require increasing thrust to weight ratios, which is generally achieved by both weight reduction and increased turbine inlet temperatures. The required operating temperatures of modern jet engines exceed the temperature limitations imposed by metallic turbine components. It has therefore become essential to seek alternative engineering materials.

In metal forming, escalating labour and capital costs mean that forming dies and rollers have to produce higher tonnages to greater tolerances than before. In extrusion and drawing operations for example, surface finish and metallurgical properties, combined with the need for highly toleranced often means that traditional die materials are no longer effective.

Wear resistance and resistance to chemical attack are of prime importance for today's high-technology materials. Power stations, which burn powdered fuel, suffer severely from burner tip erosion. Coal dewatering plants require highly abrasive resistant materials for their filtration systems and super hard nitride ceramics are replacing the more traditional tungsten carbide in many of these applications.

Restrictions on emissions for automotive engines and higher fuel costs have stimulated an interest in the use of super-hard light-weight inert materials in the automotive industry; in fact ceramics have become accepted in most industries.

From Silicon Nitride to Sialon

It became apparent in the 1960s and early 1970s that silicon nitride had some remarkable engineering properties. It exhibited good thermal shock, high strengths could be achieved, the material was oxidation resistant and thermodynamically stable. This material was an obvious candidate for the arduous applications in modern industry.

Unfortunately, silicon nitride did not lend itself to ease of fabrication. The best properties were only obtained from hot-pressed material, thus shapes could only be produced at extremely high cost by diamond grinding and even this material had relatively poor high temperature properties.

The discovery of an alloy of silicon nitride made independently in the UK by Jack and Wilson, and in Japan by Osama et al, brought the advantages of a material based upon silicon nitride, which was sinterable. Complex shapes could now be produced by conventional ceramics forming processes and then fired to high density products. These alloys, based upon silicon nitride, are known as sialons.

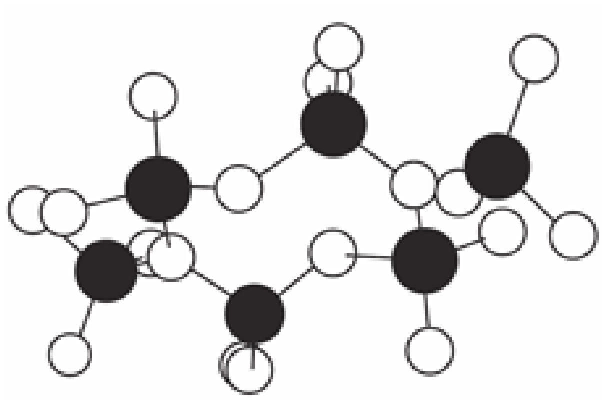
The current generation of sialons produced by **International Syalons (Newcastle) Limited** are extremely sophisticated ceramics: they have grown through research and development from patents granted in the early 1970s into a product range which has outstanding engineering properties.

What are Sialons?

Here the term sialon is reserved for the aluminium-silicon-oxyniride alloys of silicon nitride, which have been sintered into hard, high strength materials using yttrium oxide as a sintering aid.

As alloys of silicon nitride, sialons exist in three basic forms. Each form is iso-structural with one of the two common forms of silicon nitride, beta (β) and alpha (α) and with silicon oxynitride. The relationship between that of sialon and silicon nitride is similar to that between brass and pure copper. In the later case, copper atoms are replaced by zinc to give a better and stronger alloy than the mother metal. In the case of sialon, there is substitution of Si by Al with corresponding atomic replacement of N by O, to satisfy valency requirements. The resulting 'solution' (sialon) has superior properties to the original pure solvent (silicon nitride).

The fundamental structural unit of silicon nitride (Si_3N_4) is the SiN_4 tetrahedron, which is analogous to the SiO_4 structural units in silicates. The tetrahedra are linked together into a rigid three dimensional framework by sharing corners. The Si-N bonds are short and very strong. This strong, rigid, compact structure is responsible for many of the important properties of Si_3N_4.



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β-Sialon

β-Sialon is based upon the atomic arrangement existing in β-Si_3N_4. In this material, Si is substituted by Al with corresponding replacement of N by O. In this way up to two-thirds of the silicon in β-Si_3N_4 can be replaced by Al without causing a change in structure. The chemical replacement is one of changing Si-N bonds for Al-O bonds. The bond lengths are about the same for the two cases but the Al-O bond strength is significantly higher than that of Si-N. In sialon the Al is co-ordinated as AlO_4 and not as AlO_6 as in alumina (Al_2O_3). Therefore, in β-sialon the bond strength is 50% stronger than in Al_2O_3. Thus sialons intrinsically have better properties than both Si_3N_4 and Al_2O_3.

β-Sialon is produced by **International Syalons** using yttrium oxide (Y_2O_3) as a sintering aid and marketed under the trade name **Syalon 101**. During sintering at temperatures above 1400°C, the oxides react to form an yttrium-aluminium-oxynitride liquid which is necessary for densification. This then forms an intergranular glass on cooling. Syalon 101 is a fully dense ceramic characterized by high strength and toughness.

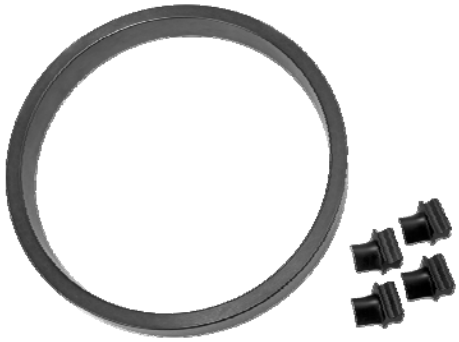
As a solid solution, the vapour pressure of β-sialon is lower than that of Si_3N_4 and as a result the sialon will form more liquid at a lower temperature with Y_2O_3. Sialon is thus more easily densified using normal sintering techniques. Furthermore, it should be noted that the lower vapour pressure of sialon reduces decomposition at high temperatures so that the sialon is thermodynamically more stable than Si_3N_4.

These β-sialons are particularly useful in applications such as non-ferrous molten metal handling, in which thermal shock resistance and chemical stability in contact with molten metals is required for use as components such as thermocouple protection sheaths and heater and riser tubes.

α-Sialon

The second form of Si_3N_4 with which sialon is iso-structural is α-Si_3N_4. The stacking structure in α-Si_3N_4 is different from β-Si_3N_4 in that the long 'channels' which run through the β structure are blocked at intervals. This gives rise to a series of interstitial holes. In α-sialons, Si in the tetrahedral structure is replaced by Al with limited substitution of N by O. Valency requirements are satisfied by modifying cations occupying the interstitial holes. In this way cations of yttrium (Y), calcium (Ca), lithium (Li) and neodymium (Nd) for example can be incorporated into the structure.

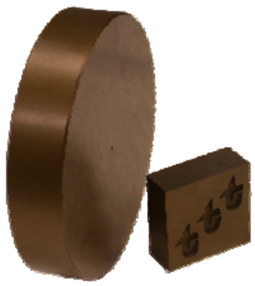
International Syalons market an α-sialon under the trade name **Syalon 050**. α-Sialons are intrinsically hard materials. Hardness can be simplistically related to bond energy density, which for α-sialons is high, giving extreme hardness. In addition, during sintering and subsequent heat treatment of α-sialons such as Syalon 050, the intergranular phase is taken up into the structure resulting in a dense, hard ceramics which is almost free of a grain boundary phase. This results in the material properties being retained at up to 1400°C. This is of great importance in wear mechanisms; hot hardness to above 1000°C is required for cutting tips, for example.



An important added advantage is oxidation resistance. The absence of a grain boundary phase in this ceramic means that the transport of diffusing species necessary for oxidation to take place at higher temperatures is restricted (there is limited liquid phase to assist transport), so that oxidation resistance is improved. These sialons have excellent resistance to abrasive wear and are having an impact as nozzles for shot blasting, particularly for highly aggressive grits. Also, the absence of a grain boundary phase makes them attractive candidates for high temperature applications, such as in gas turbines.

Composite Sialons

Sialons, due to their excellent sinterability, can be made into composite ceramics especially with other nitride ceramics. As such, **International Syalons** have developed a number of composite grades of sialon.



The first, **Syalon 501**, is based on β-sialon and is an electrically conductive grade which can be electro-discharge machined into complex shapes. It possesses many of the excellent properties of Syalon 101 and has found application as extrusion dies and die pressing dies.

Syalon 110 is a composite, again based on Syalon 101, which possesses improved resistance to attack by steel and outstanding thermal shock resistance. It has found application as a break ring for the horizontal continuous casting of steel.

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Typical Physical Property Data for Syalon Grades

Property	Syalon 101	Syalon 050	Syalon 501	Syalon 110
3 point RT Modulus of Rupture / MPa	945	800	825	500
3 point Modulus of Rupture at 1400°C / MPa	-	450	-	-
Weibull Modulus	11	8-13	11	10
RT Unit Tensile Strength / MPa	450	450	300	250
RT Compressive Strength / MPa	>3500	-	-	-
RT Young's Modulus / GPa	288	306	341	139
RT Hardness (HRA)	92	94	91	88
RT Hardness (Vickers $Hv_{0.3}$ / kg/mm^2	1500	2000	1370	1200
Fracture Toughness / $MPam^{½}$	7.7	6.5	5.7	3.5
Poisson's Ratio	0.23	0.27	0.31	0.19
Density / g/cc	3.23	3.23	3.95	2.65
Porosity / %	0	0	0	10
Thermal Expansion Coefficient (0-1200°C) / k^{-1}	$3.04x10^{-6}$	$3.2x10^{-6}$	$5.6x10^{-6}$	$3.04x10^{-6}$
RT Thermal Conductivity / W/(mk)	28.0	20.0	19.1	27.0
Thermal Shock Resistance / ΔT°C	900	600	400	800
RT Electrical Resistivity / ohm m	10^{10}	10^{10}	$7.24x10^{-6}$	10^{10}
Maximum Temperature Use / °C	1200	1400	800	1450

Typical physical property data obtained under test conditions. All properties have been measured by independent testing authorities. The values given only apply to the test bodies on which they were determined, and therefore can only be recommended values.

Corrosion Behaviour of Syalon 101 and Syalon 050 in Acids and Alkalis

Acid / Alkali	Concentration / %	Temperature	Exposure time / hrs	Reaction
Hydrochloric acid	33	Boiling	100	None
Nitric acid	69	Boiling	100	Weak
Sulphuric acid	98	Boiling	100	None
Hydrofluoric acid	100	Boiling	100	Strong
Sodium hydroxide	50	Boiling	100	None

Corrosion Behaviour of Syalon 101 and Syalon 050 in Molten Metals

Metal	Temperature / °C	Exposure time / hrs	Reaction
Copper	1150	10	Strong
Brass	950	50	None
Aluminium	950	1000	None
Tin	300	100	None

Typical corrosion data obtained under test conditions. The values given only apply to the test bodies on which they were determined and therefore can only be recommended values.

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Industrial Wear Applications

Syalon 101 and **Syalon 050** are characterised by excellent mechanical strength and hardness, making them ideal candidates for many extreme industrial wear applications.

Milling Media

International Syalons manufacture a range of grinding media for the preparation of industrial and analytical samples.

In trials, weight losses for **Syalon 101** bowls and media were about 14% of the reported weight losses for agate, alumina, zirconia and tungsten carbide, thus vastly reducing contamination of the sample as well as extending the media life.

In addition, milling efficiencies for Syalon 101 are also generally improved, meaning milling times are reduced.

Shot Blast Nozzles

Shot blasting is a method of surface preparation or cleaning. It involves blasting an abrasive grit, such as sand, alumina or chill cast iron, at high velocities at the surface to be treated.

Traditionally liners have been made from tungsten carbide. However, at the low angle impacts encountered in many blasting operations, tungsten carbide nozzles wear excessively due to the erosion of the relatively soft and ductile cobalt used to cement the carbide grains together.

Syalon 050 has a high hardness, fracture toughness and Young's modulus, resulting in excellent wear resistant properties, making it an ideal material for shot blast liners.

A standard 3/8" nozzle in Syalon 050 tested using chill-cast iron grit and operating at 100psi, performed for more than 1000 hours without appreciable wear.

Paper De-watering Foils

During the manufacture of paper a section of the process involves removing water from the fibre/water pulp. To do this, the pulp is spread over a fabric mat which travels over a series of suction boxes. These boxes apply a vacuum which draws the water out of the pulp as the fabric travels over them.

The suction boxes consist of a series of foils, which can be many metres long. The foils can be made of high density polyethylene (HDPE) or ceramic material. Ceramics are used in high speed applications. The foils are diamond ground to give a mirror finish, which is important for the quality of finish of the paper.

Initially alumina was the ceramic of choice. However, as machine speeds have increased, up to 100km/min, so the requirement for greater wear resistance has emerged. This is where **Syalon 101** comes in. Its excellent wear resistant properties, as well as thermal shock resistance, make it the ideal choice for modern high speed applications.

Molten Metal Handling Applications

Syalon 101 is world renowned for its exceptional performance in non-ferrous molten metal handling applications, particularly aluminium and its alloys. Increasing use is now also being found in the handling of molten copper and molten zinc.

Thermocouple Protection Sheaths

Syalon 101 thermocouple protection sheaths are becoming the industry standard in non-ferrous metal foundries. They possess outstanding thermal shock resistance, are non-wetting and suffer no degradation in contact with aluminium and its alloys.

Syalon 101 sheaths also allow constant temperature monitoring of the melt resulting in improved quality of the finished casting. For applications where the temperature exceeds 1200°C, **Syalon 050** is the preferred choice.

Heater & Riser Tubes

Syalon heater and riser tubes offer long life, improved process reliability and are cost effective. They too benefit from excellent chemical stability in many non-ferrous metals and are resistant to the build up of dross.

Level Sensors

Syalon 501 level sensors are used to monitor the level of the molten metal during die casting. They are uniquely characterised by high electrical conductivity combined with the excellent thermal shock resistance, corrosion resistance and non-wetting behaviour of Syalon 101 and can be used up to 800°C.

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Metal Forming Applications

Metal forming applications such as welding, extrusion and cutting can all benefit from **Syalon 101**s and **Syalon 050**s excellent mechanical and thermal properties and chemical stability.

Welding

In its most simple form a welding operation joins metal pieces together using a pool of molten metal. The first consideration of any welding operation is to create a weld which, as far as possible, has the same properties as the original metal. The join must also be created in such a way that minimum disturbance is caused in the area adjacent to the weld. Such welds are best done at high speed and in such a manner that the molten weld is completely shrouded from the atmosphere during the operation. Welding today encompasses many different techniques and methods, however speed and protection of the weld are required for all operations.

Welding methods are diverse but they all require the same high standard of material performance. Ceramics in welding must be able to withstand thermal shock at a variety of temperatures. They must have high strength to resist mechanical damage, which is often accidental. They must be resistant to ‘weld spatter’ and the consequent build-up of weld debris. They must also, for many applications, be electrically insulating and stable at high temperatures.

Weld Location Pins

Weld location devices are used in the resistance welding of captive nuts in automotive and commercial vehicle assembly. **Syalon 101** weld pins allow precise welding of nuts to sheet metal.

A major European manufacturer used steel pins for the location of nuts in a continuous resistance welding operation. On average, the steel pins lasted for 7,000 operations that is, a working shift, before wear and spatter build-up caused damage to the nut. By using Syalon 101 location pins, over 5 million operations have been completed without wear or damage occurring.

Welding Jigs & Fixtures

In addition to resistance welding, a number of other welding techniques successfully use Syalon 101. These include orbital welding, tungsten inert gas (TIG) welding, metal inert gas (MIG) welding, induction welding and plasma welding.

Orbital welding, often used in aerospace, employs small diameter gas shrouds to weld curved or cylindrical components. Syalon 101 gas shrouds have performed several thousand cycles, giving hundred-fold increases over conventional materials.

In the TIG welding of steel tubes in heat exchanger cores, Syalon 101 nozzles have outlasted alumina nozzles by a factor of 10 to one. The confined space in this operation creates severe welding conditions and Syalon 101s thermal shock properties and resistance to weld spatter are the key to the success of this operation.

Syalon 101 nozzles used in a plasma cutting operation had a life at least four times that of alumina and twice that of silicon nitride nozzles and the spatter build-up on the nozzle was easily removed.

Extrusion & Drawing Dies

Wire drawing, open die extrusion and hydrostatic extrusion, whether performed hot or cold, are all examples of metal flow through converging conical dies. Three independent variables affect the flow of material: the cone angle, the coefficient of friction and the ratio between the original diameter and the extruded diameter. These parameters have a strong influence on the extrusion or drawing force at any particular speed. Other influential variables include lubrication, temperature and the thermal properties of the die itself.

The material properties which make Syalon an excellent candidate for extrusion include hot hardness, high strength, good thermal shock resistance, high rigidity, chemical stability and good frictional properties.

Syalon 101 dies perform extremely well in the extrusion of copper, brass and nimonic alloys, with excellent resistance to wear and thermal shock giving extended die lives. Also, since Syalon materials do not contain a metallic phase, die pick-up can be eliminated, which results in improved continuity of the extrusion process, enhanced surface finish of the product, reduced scrap rates and increased productivity.

Single shot impact extrusion of nimonic components using Syalon 101 dies produced 30,000 components before excessive die wear was noticed. Tool steel dies had to be replaced at 750 components.

A major extruder of brass and copper in the UK has found that by using Syalon 101 dies, 250 tons of brass could be extruded compared to 100 tons through conventional dies. For copper, Syalon extruded 75 tons compared to 40 tons for a conventional die.

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Cutting Tips

On of the earliest successful applications for Syalon was as a cutting tip or throw away insert. Metal removal generates tremendous heat and even when a coolant is used temperatures of 1000°C at the cutting edge are commonplace. If a cutting tip has poor thermal conductivity, then the heat generated cannot be easily dissipated. The thermal damage is exacerbated by a high coefficient of thermal expansion and exaggerated crater wear develops leading to the rapid destruction of the cutting edge. This thermally induced wear is an important and neglected feature in metal removal.

Most turning operations involve ‘interrupted’ cutting, whether by design or accident. For example, in the turning of a roll of chill-cast iron, the existence of pin holes and local asperities makes the cutting action intermittent. Many cutting operations are by necessity discontinuous and as well as having suitable thermal properties, cutting tools must be tough.

In addition, work pieces are often hard and can be abrasive so the cutting tips should have high hardness values. Finally, the metallurgical properties of the work piece may be such that at the high temperatures generated a chemical reaction takes place between the tool and the work piece. So, chemical stability is also important.

This demanding set of requirements is met by **Syalon 050**. It is thermally stable up to 1400°C, thermal shock resistant, hard, tough and strong and chemically resistant to corrosion. In use Syalon 050 cutting tips reduced by 75% the machining time for turbine discs for the Rolls Royce RB211 engine.

Oil & Gas Applications

As existing supplies of oil and gas are depleted, these industries are being forced to explore ever more severe environments for future supplies. To help this exploration, Oil and Gas companies are utilising the excellent characteristics of Syalons, such as corrosion and erosion resistance, heat tolerance and light weight, to replace traditional metal components.

Hydrocyclones

In sub-sea oil extraction, hydrocyclone separators are used in the process of separating sand from the oil. Pressure differences in the slurry generates centrifugal forces which causes rotational motion of the fluid which in turn causes the dense sand particles to separate from the less dense material. The rotational flow results in severe abrasion on the materials used in the hydrocyclones.

Syalons possess the physical and chemical properties to perform well in this demanding environment where wear resistance is critical.

Metering Valves

Metering valves, used for metering the flow of often hot, abrasive slurries, again require a demanding set of properties. The high hardness, toughness and strength of **Syalon 050** results in excellent wear resistance, which when combined with its excellent thermal properties and chemical stability make it an ideal material for this application.

A 38mm diameter Syalon 050 metering valve, which cycled every 10 seconds, while metering a hot, abrasive slurry, out-performed inconel valves by a factor of 14 to 1 and out-performed silicon carbide valves by 7 to 1.

Chemical & Process Industry Applications

The chemical and process industries are continually seeking new advanced materials to help extend the life of critical components. **Syalon** ceramics are at the forefront of this search.

Mechanical Seals

Mechanical seals are used in the chemical and process industries as seals in rotating equipment, such as pumps and compressors. For example, in a pump when a shaft rotates the liquid can leak out between the shaft and the pump casing. In this case a mechanical seal would be used, which basically consists of a hard material embedded in the casing and a softer material in the rotating shaft. These are made to be in intimate contact.

The choice of seal materials depends on the material being pumped, its chemical reactivity, the temperature and the pressure. In many cases, **Syalon 101** makes an excellent choice for the hard seal material.

Impellers

Impellers are used in the chemical industry often for mixing or stirring highly corrosive chemicals and abrasive slurries. Traditionally impellers have been made from metal or plastic coated metals. These suffer badly from wear, thus contaminating the chemical, which in clean environments is unacceptable.

Syalon 101 is chemically stable to corrosion by many chemicals such as hydrochloric and sulphuric acids and alkalis such as sodium hydroxide. This behaviour combined with its excellent physical properties make Syalon 101 an ideal material for many demanding chemical applications.

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