Sialons: A Study in Materials Development

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ABSTRACT

Although the combination of properties shown by silicon nitride has made it a leading ceramic contender for engineering applications, the technological problem is in fabricating dense components cheaply and to precise dimensional tolerances. One solution is to use the principles of ceramic alloying inherent in the production of 'sialons'—the acronym given to phases in the Si–Al–O–N and related systems that are built up of (Si, Al)(O, N)₄ tetrahedra in the same way that the structural units of the mineral silicates are SiO₄ tetrahedra.

The mutual replacement of silicon by aluminium and of nitrogen by oxygen in β-Si₃N₄ gives β'-sialons and allows variations in the covalent and ionic contributions to the interatomic bonding that, in turn, allow variations in properties. The products promise to be outstanding for engine components and are already commercially successful as cutting tools for machining metals. Other applications are in welding and extrusion, in molten metal handling, and for seals, bearings and wear parts.

α'-Sialons are derived from α-Si₃N₄ by replacing Si with Al and effecting valency compensation by accommodating additional metal cations in interstitial sites. Prospects for their technological application are at least as good as for β'-sialons. The replacement of Si and N by Al and O in silicon oxynitride, Si₂N₂O, is more limited but again produces useful and fully dense O'-sialon ceramics by pressureless sintering.

Dual-phase materials in which pairs of the completely compatible
phases $\alpha'$, $\beta'$ and $O'$ are combined have advantages over single-phase sialons.

The sialons include vitreous as well as crystalline materials and, in the glass systems so far studied, up to about one in four oxygen atoms can be replaced by nitrogen. The viscosity, hardness and density all increase with increasing nitrogen content, providing stronger and more refractory glasses.

1. INTRODUCTION

In each of its structural modifications, $\alpha$ and $\beta$, silicon nitride ($\text{Si}_3\text{N}_4$) has a unique combination of properties. It is strong, hard, wear-resistant, stable to higher than 1800°C, oxidation-resistant and, because of its low coefficient of thermal expansion, has excellent resistance to thermal shock. It is also less than half as dense as steel. These features were pointed out more than 25 years ago, but the greatest impetus to its development was its selection by the Advanced Research Projects Agency of the US Department of Defense in 1971 as the material for the ceramic gas turbine. The latter was specified to run at 1370°C—more than 300°C higher than existing nickel-based super-alloy engines—so giving higher efficiency, the capability of using poorer fuels, and less pollution of the environment.

After 14 years, and government funding in the USA, Germany and Japan of at least $400 million—with perhaps an equal expenditure by private companies in those countries—there is still no commercial ceramic engine. One reason for this is that the desirable properties are achieved only in fully dense silicon nitride, and the main technological difficulty is in fabricating dense, precisely shaped components. The material cannot be densified like an ordinary oxide or silicate ceramic merely by firing it. The strong interatomic covalent bonding between silicon and nitrogen means that self-diffusivity is small and, by the time the high temperature is reached at which the atoms move, the silicon nitride begins to decompose by volatilisation of nitrogen. It can be densified by hot-pressing at about 2 tsi ($\sim 30 \text{ MPa}$) in graphite dies heated by induction to 1800°C, but the process is limited to simple shapes and the hot-pressed product (HPSN) is so hard that the final shape must be obtained by expensive diamond grinding. Moreover, so-called 'fluxing agents'—usually oxides, for example of magnesium ($\text{MgO}$) or yttrium ($\text{Y}_2\text{O}_3$)—must be added to the silicon nitride powder to achieve densification.