INTRODUCTION

Sand provides the refractory medium for making moulds to shape metals and alloys by founding. An analysis of the founding process reveals that the moulding sand affects the entire process in the production of a sound casting, even to the stage of machining.

With increasing demand for quality castings which require better strength properties, more accurate dimensional control and higher degree of surface finish, various sands are being sought. Zircon sand has large reserves in the world including the placer deposits along the Indian Coast. The outstanding properties of zircon which make it highly desirable as a moulding medium are its high refractoriness, high conductivity, high density, low thermal expansion and chemical stability. Because of these high temperature characteristics, zircon finds increasing application especially in steel foundries.

It has long been recognized that zircons show considerable variation in physical properties even though there is little difference in chemical composition. Mineralogists, earlier, classified zircons into three groups on the basis of their optical properties, density and response to heat treatment. Subsequently, in addition to these properties a further criteria, based on chemical alteration by hydration, was utilized for distinction. Further work showed that grouping of zircons according to these properties could not be justified since samples with intermediate properties were also common. It was suggested that a genetic relationship exists between the three groups of constant composition and the differences in their physical properties was attributed to the effects of alpha-particle irradiation emanating from the decay products of uranium and thorium present within the crystal structure. It is now well established that the change in density, refractive index, etc., are due to the breakdown of the crystal structure. It has also been shown that for a set of zircons of the
same geological age, those containing high concentration of uranium and thorium exhibit higher structural disorders than those containing less amounts (Holland and Gothfried, 1955).

It is generally believed that nuclear radiation is the cause of the observed changes in the physical properties of certain minerals and the phenomenon has been termed metamictization. The term metamict is generally used in mineralogy to denote minerals initially crystalline, but amorphous later, losing their crystal structure in this process of change due to molecular rearrangement caused by radioactive emanations from uranium or thorium contained in the mineral. Metamictization occurs in structures which are originally weakly bonded. Even though they may have crystal faces, metamict minerals are generally amorphous to X-rays or yield a faint fuzzy pattern. Some metamict minerals like zircon give sharp electron diffraction pattern owing to retention of relict crystallinity sufficient to permit the relatively short wave electrons to yieldresolved patterns (Heinrich, 1958). The mineral gets converted to an isotropic form, with a decrease in specific gravity. Cleavage is absent and fractures are conchoidal. The mineral may be focus of fractures radiating into surrounding mineral grains. There are abnormal amounts of non essential water and a decreased resistance to chemical attack. The mineral may be pyrognomic-recrystallization occurs upon heating, usually at a definite temperature, with a considerable to minor evolution of heat and light to an aggregate crystalline pseudomorph, i.e., thermoluminescent.

PRESENT STUDIES

The disorganization of the crystalline structure may be measured by several methods — TL techniques, density measurements, X-ray diffraction, differential thermal analysis, etc. Kulp et al. (1952) have shown that the characteristic thermal curve for metamict zircon appears to consist of a doublet at a
temperature of 890 °C to 910 °C, suggesting crystallization of mineral to be a two stage process. According to Frondel (1953), the differential thermal curve shows a gradual water loss at 100 °C to 225 °C and a broad exothermic peak at 460 °C to 550 °C, followed by a single peak at 880 °C for reorganization of the metamict material. According to Holland and Gottfried (1955), for zircon completely undamaged by alpha radiation, the X-ray diffraction 2 θ angle (Cu Kα) for 112 plane is 35.635 while in metamict zircon it approximates to 35.1. The lattice expansion in metamict zircon is anisotropic with the ratio between the two 'a' dimensions, a1/a2 being 1.001 to 0.9735 while the 'c' dimension also expands from 5.974 Å for metamict material (zircon belonging to the tetragonal system). Berman (1955) has described transitions from zircon crystals appearing entirely "fresh" with sharp X-ray diffraction patterns to those that appeared completely metamict and gave no diffraction pattern. In the specimen that were somewhat metamict both the index of refraction and birefringence decreased; complete isotropy was reached in the totally metamict specimen.

Pellas (1965) has reviewed most of the recent measurements, and presented a modern comprehensive model of the metamictization process in zircon, further modification to which has been suggested by Vaz and Senftle (1971). When zircon is subjected to ionizing radiation, viz., alpha, beta and gamma radiation, electrons and holes are produced in the crystal lattice. On heating such a zircon, the trapped charge acquires sufficient thermal energy to escape from its trap, such that it can move in the conduction or the valence bond and recombine with the opposite charge. The emission of light during this recombination process provides the source of thermoluminescence. Natural charge trapping in zircons is the result of ionization by the radiation from the decay of radioactive inclusions in the crystal. According to Pellas (1965) the crystal structure of zircon is broken down into four
phases during the process of metamictization. Initially the radiation from the radioactive decay of the radioactive inclusions produces an expanded zircon phase that contains a high concentration of interstitials and vacancies. Further radiation damage finally results into a break-up of the ZrSiO$_4$ lattice into ZrO$_2$, SiO$_2$, and amorphous zircon. He further suggests that the concentration of the expanded zircon phase and the three final phases reach maximum concentration at different total alpha particle doses. In view of this model it is expected that the largest number of electron or hole traps would be associated with the phase containing the largest number of interstitials and vacancies. Hence, thermoluminescence of zircon should be maximum at an alpha dose at which the expanded zircon phase reaches a maximum. Krasnobayev (1964) found a sharp drop in natural thermoluminescence of zircon for alpha doses a hundred times less than that expected from Peilas model. The present investigation was undertaken to gather (i) further knowledge on damage mechanism of zircons and (ii) to ascertain the suitability of zircon sands vis-a-vis their colour and radioactivity for foundary usage.

**EXPERIMENTAL METHODS**

For the present study seven zircon samples, varying in colour from pink, to brown, light yellow to yellow and light green to green and dark green, were chosen. Further, for comparison, in some parts of this investigation, three known metamict varieties of zircon, viz., Naegite, Alvite and Crytolite were used.

**Density, Alpha Activity and Thermoluminescence Measurements:**

The values of density for different zircon samples were determined by using two quartz pycnometers of 50 ml capacity. Redistilled water free from air bubbles was used and precautions were taken to reduce the evaporation to a minimum.
Air bubbles adhering to the samples were completely removed by heating the pycnometer, containing the sample and \( \frac{3}{4} \) of its volume of water, to about 50°C under diminished pressure. Weighing was done with the help of an electrical balance, (E. Mettler, Zurich, Switzerland) which measures correctly up to four places of decimal. Corrections were made for the differences in the displacement of air by the volume of the contents of the pycnometers. Three different determinations were made on different portions of each sample and the difference did not exceed 0.0009. The results obtained were correct to the nearest unit in the third decimal place.

Alpha activity of the zircon samples was measured by using an alpha probe - SP647A manufactured by Electronics Corporation of India, utilizing a scintillation detector. This system was used in conjunction with the electronic 'Alpha Counting System ACS-31A' manufactured by the same company. The PM-tube was operated at a constant voltage of 950 volts throughout the experimental work. Weighed amount of the samples was taken for each observation and from a preliminary observation for each sample the counting time was chosen to reduce the counting error to less than three percent. The minimum counting time for such an accuracy amongst the samples studied came to the order of six hours. The gross alpha activities of the samples were determined by the "thick source counting technique" as adopted by Turner et al (1958), using a disc of 42 mm diameter.

Thermoluminescence of the samples was recorded with the experimental arrangement similar to that described by Kaul et al (1976). To avoid variation in TL-glow due to grain size, samples with grain size 80-100 mesh were thoroughly mixed and uniformly spread on the TL-oven. The heating rate for glow measurements was kept constant at 20°C/min and the glow curves recorded under the following conditions:

1) Natural TL measured for each sample.
ii) Different aliquots of the same sample were irradiated by different doses of gamma-rays from Co$^{60}$ source and induced TL measured.

iii) The samples were annealed at a constant temperature of 950°C for different periods of time, then quenched to the room temperature and TL measured after irradiation dose of 2.4 x 10$^6$ rads from Co$^{60}$ source.

iv) Samples were irradiated to a fixed gamma-ray dose of 2.4 x 10$^6$ rads from Co$^{60}$ source and induced TL measured.

v) Samples were annealed at 950°C for 30 hrs, then quenched to the room temperature and TL measured after irradiation dose of 2.4 x 10$^6$ rads from Co$^{60}$ source.

REFRACTORINESS OR SINTERING, DTA AND X-RAY DIFFRACTION MEASUREMENTS

Refractoriness is an index to the heat resisting properties of a material. This can be quantitatively indicated by criteria like melting point and fusion point of the material, which in general can be considered as any type of phase change. The term "Sintering" or "Sintering point" has also been used by different workers to indicate a measure of refractoriness of the material. As applicable to foundry sands, according to the AFS (1963), sintering point is the temperature level at which incipient fusion has occurred when the test specimen is subjected to controlled conditions of time and temperature.

The sintering point of the zircon samples was determined by taking a small amount in a porcelain boat and introduced into a tubular furnace. The temperature of the tubular furnace was gradually raised. Beyond 1000°C, the boat was withdrawn for every 25°C rise of temperature, and the sample scrutinised through a magnifying glass. The temperature at which the first indications of fusion were noticed
was taken as the sintering point of the sample.

Investigations for X-ray diffraction studies and Differential Thermal Analyses of the said zircon samples were carried out with a view to determine the extent of metamictization on the lines suggested by Holland and Gottfried (195) and Kulp et al (1952). In addition to this micrographs of polished sections of the zircon samples and the scanning electron micrographs of the aggregate samples were made for the investigations.

RESULTS

Results of the present investigations have been published and described in detail (Nerurkar et al, 1979). In brief it can be said that the colour of zircon samples can be correlated to their present alpha activity. The density of the zircon samples decreases with alpha activity following a sigmoid shaped curve. No natural TL is observed in green and dark green zircons. The TL emission reaches saturation, the magnitude of which seems to depend on the present alpha activity. The enhancement of TL emission on thermal treatment is also alpha activity dependent and has been related to the recovery of the deformed zircon fraction to normal zircon. This has also shown that the extent of metamictization is also the reason for lowering of the sintering point. The results of DTA show distinct variation between different samples and the metamict varieties. The X-ray studies give different 20 values for the samples implying their crystallinity, which is borne by the micrographs and the scanning electron micrographs. From the present investigations unsuitability of some zircon sands, due to their higher alpha activity, for foundry use is also borne out.
REFERENCES CITED