WETTABILITY OF GRAPHITE BY BARIUM FLUORIDE CALCIUM FLUORIDE EUTECTIC

by

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As a result of a screening program for desirable chemical and physical properties, the barium fluoride calcium fluoride eutectic (1, 2) was chosen for a study of graphite wettability.

Systematic studies by Zisman of the equilibrium contact angles of a wide variety of pure liquids on low and high energy solid surfaces revealed many interesting regularities (3). An empirical rectilinear relationship between the cosine of the contact angle, θ, and the surface tension exists. The contact angles between molten salts and graphite shows the same relationship and was demonstrated by the Oak Ridge Molten Salt Reactor Program (4). The plot of the cosine of the contact angle, θ, versus the surface tension of the liquid or molten salt indicates that the change from nonwetting ($\theta > 90°$) to wetting ($\theta < 90°$) takes place at a surface tension of about 190 dynes/cm.

As indicated by the empirical relationship of the cos θ versus surface tension, BaF_2-CaF_2 eutectic should not wet graphite as its surface tension is greater than 190 dynes/cm. This was observed first experimentally and later calculations of the surface tension of BaF_2 and CaF_2 substantiated this fact. Additions of 10 to 20% of CsF, RbF, and KF, whose surface tensions are less than 190 dynes/cm, were added to the BaF_2-CaF_2 eutectic. This enabled the salt mixture to wet the graphite. This was not a satisfactory solution as problems were encountered in physical and chemical properties of the resulting mixtures. Other salt combinations were unfavorable.

Several methods of pretreatment of the graphite were tried. Pretreatment of the graphite with BaF_2-CaF_2 eutectic water slurry was most successful. On the pretreated graphite, the molten BaF_2-CaF_2 mixture formed a contact angle $\theta \approx 30°$, compared to a contact angle $\theta > 90°$ on untreated graphite.

The relationship between surface energy and wetting behavior is related to the interface energy of the three surfaces available. They are the solid-liquid interface energy, solid-vapor interface energy, and the liquid-vapor interface energy. Analyses of these parameters and surface tension of the salts and graphite indicate the pretreatment causes a decrease in the solid-liquid interface energy, making spreading more favorable.

The contact angle is sensitive to surface changes. On graphite, it was found that normal machined graphite gave satisfactory results. Large variation was obtained between a piece of machined graphite compared to the same graphite with a band saw cut finish. The variation went from spreading ($\theta = 0°$) to a contact angle $\theta \approx 60$-$70°$. Variations of contact angles on normal machined graphite pieces were estimated to be a maximum of $\pm 10°$.

References

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