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The Relationship between Particle Motion on a Graphite Surface and Tammann Temperature

In early studies, Bassett (*1*) used hot stage electron microscopy to follow the development of the growth of silver films vacuum deposited onto graphite at 300°C and 10^{-4} Torr. During the initial stages of deposition, he observed that small particles, 2–10 nm in size, moved in a random fashion over the graphite surface. However, after a short period of time, particle mobility came to an abrupt end. Sears and Hudson (*2*) suggested that the mobility was due to Brownian motion of the particles and, according to them, such motion took place over a chemisorbed layer of gas on the graphite. They argued that loss of mobility occurred when the particles and support came into true contact. This explanation was also invoked by Thomas and Walker (*3*) to account for their observations made by photomicrography of the behavior of several metals on graphite when heated in the presence of various gases. A much more detailed investigation of the motion and growth of small silver particles on graphite was conducted by Heinemann and Poppa (*4*), who concluded that particle migration played a major role in the overall sintering process of this particular system. A number of *in situ* electron microscopy studies have also been performed on the growth characteristics of other metals on graphite and amorphous carbon supports (*5–9*).

Previous investigations with the controlled atmosphere electron microscopy technique showed that when iron particles supported on graphite were heated in various gas environments, the particles became mobile on the surface at a definite temperature, 700°C (*10, 11*). Subsequent studies with other metals dispersed on graphite revealed that there was a characteristic mobility temperature which was related to the bulk melting point. From the plot presented in Fig. 1, it can be seen that the experimentally observed mobility temperature for 10-nm sized particles of various metals and oxides is approximately half their respective bulk melting points when the temperature is expressed in absolute units. It should be appreciated that particle motion has been observed in many other metal/graphite–gas systems, however, only those systems where the identity of the migrating species is known with some certainty have been included on this plot. For the most part, these mobility temperatures coincide with the Tammann temperature of these materials, which is calculated from 0.52 [bulk melting point (K)].

A literature search shows that a number of events have been found to take place at this temperature. Tammann (*12*) discovered that there was a minimum temperature at which a solid would undergo a solid–solid interaction. He suggested lattice mobility becomes appreciable at an absolute temperature which is a given fraction of the absolute melting temperature. For ionic solids, this fraction is about 0.3 for surface diffusion and 0.5 for bulk diffusion. In later years it was noted that the rate of sintering of oxides increased markedly at this point and was believed to be associated with a corresponding diminution in rigidity, or increase in plasticity of a solid (*13, 14*). It was also found that under these circumstances defects in the surface of a solid became mobile enabling the surface migration of ions to take place. It should be recognized, however, that the Tammann temperature does not represent a discontinuity of behavior, but rather a temperature in the vicinity of which a rapid change in the rate of movement of ions or atoms occurs. It is, therefore, not surprising to find that in a

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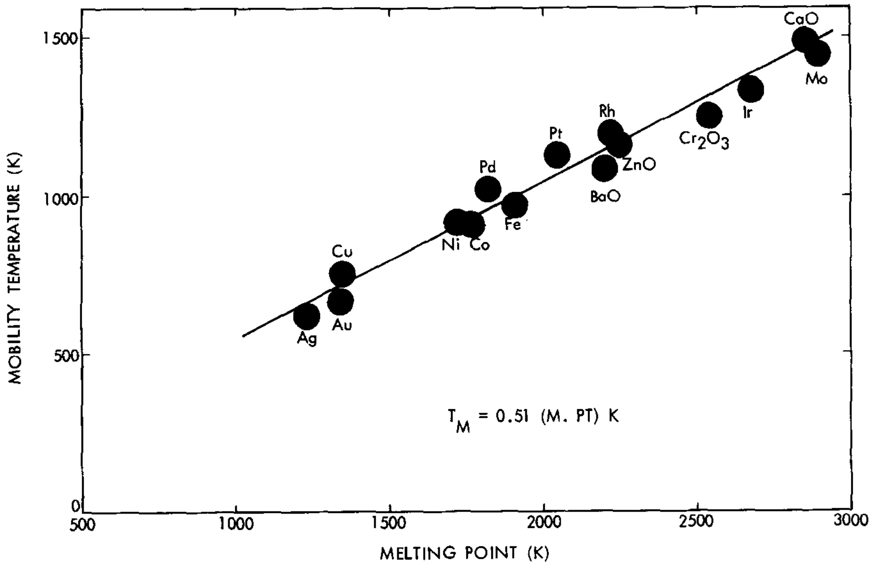

FIG. 1. Relationship between mobility temperature of particles supported on graphite and their bulk, melting points.

system where there are relatively weak interactive forces between a particle and support, that particle motion is observed at the Tammann temperature of the particulate material. Particle motion would not be expected in a system where there was a significant interaction between the particles and the support. Nevertheless, even in this case, one would anticipate an appreciable increase in the rate of sintering via the atomic migration mode (*15*) at the Tammann temperature of the particles.

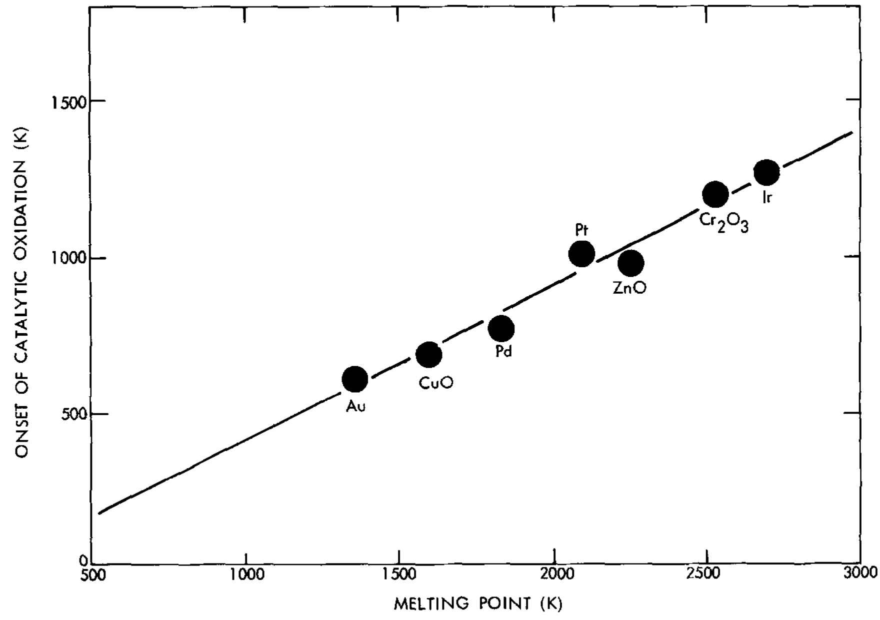

FIG. 2. Relationship between onset temperature of catalytic oxidation of graphite and bulk melting points of catalysts.

This effect can be further extended to the catalytic gasification of graphite. Since the reaction of graphite with molecular oxygen is highly exothermic (*16*),

$$\text{C (graphite)} + \text{O}_2\text{ (g)} \rightarrow \text{CO}_2\text{ (g)}\quad \Delta H = -94.0 \text{ kcal mole}^{-1}$$

there is every reason to believe that during this reaction active catalyst particle surfaces are at a higher temperature than that of the surrounding graphite surface. In an attempt to obtain an estimate of this extra heat, the following approach was adopted. The observed onset temperature for catalytic oxidation by the channeling mode taken from several CAEM studies of various catalysts has been plotted as a function of their respective bulk melting points (Fig. 2). If one assumes that the identities of the catalytic species is as shown on this plot, then it can be seen that a linear relationship exists between the two parameters, which has a similar slope to that given in Fig. 1. Indeed, a comparison of these two plots (Fig. 3) confirms this point and from the separation of the lines a value of 160 ± 20°C is derived. It suggested that this is the amount of heat generated at active particle surfaces due to the exothermic carbon–oxygen reaction and is sufficient to raise the surface temperature of such particles to the Tammann point, thus enabling particles to undergo a transformation in shape from a nonwetting to wetting condition, characteristics normally associated with the liquid state and necessary requirements for channel formation (*17*).

It is interesting to compare this value with that obtained by Luss and Amundson (*18*) using a model approach to calculate the temperature rise in a catalyst pellet during the combustion of coke, of 247°C, and the experimentally determined value of about 30°C for the removal of coke from a silica–alumina catalyst pellet (*19*). Cusumano and Low (*20*) used an infrared radiometric method to measure the heat generated at the surface of silica-supported nickel particles during exposure to oxygen. From these experiments, they estimated that the maximum temperature rise resulting from the reaction was between 144 and 215°C. The relative consistency of these

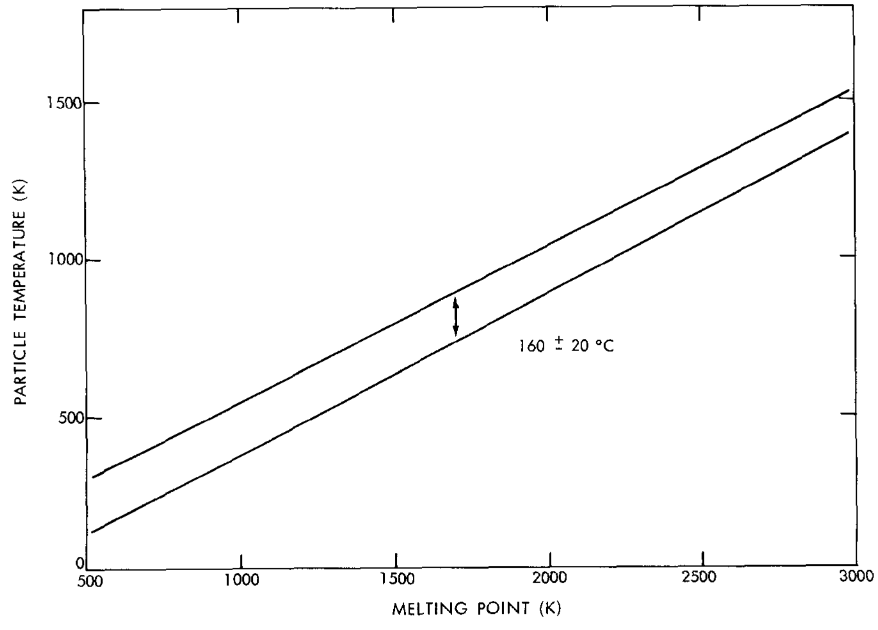

FIG. 3. Determination of extra heat generated at particle surface due to oxidation of graphite.

values does lend credibility to the present approach.

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