1. INTRODUCTION

The product gas resulting from the partial oxidation of carboniferous materials in a gasifier consists predominantly of CO, CO_2, H_2, H_2O, CH_4, and, for air-blown units, N_2, in various proportions at temperatures ranging from about 400 to 1000°C (750 to 1830°F). Depending on the source of the fuel, smaller concentrations of H_2S, COS, and NH_3 can also be present. The gas phase is typically characterized by high carbon and sulfur, but low oxygen, activities, and, consequently, severe degradation of the structural and functional materials used in the gasifier can occur. Therefore, there are numerous concerns about materials performance in coal gasification systems, particularly at the present time, when demonstration-scale projects are in or nearing construction and operation phases. This report focuses on a subset of materials degradation phenomena resulting from carbon formation and carburization processes, which are related to potential operating problems in certain gasification components and subsystems. More specifically, the report (1) summarizes the current state of knowledge regarding carbon deposition and a carbon-related degradation phenomenon known as metal dusting as they affect the long-term operation of the gas cleanup equipment downstream of the gasifier and (2) addresses possible means to mitigate the degradation processes. These effects are primarily associated with filtering and cooling coal-derived fuel gases at temperatures ranging from the gasifier exit temperature to as low as 400°C (750°F). However, some of the considerations discussed in the present report will be sufficiently general to cover conditions relevant to other parts of gasification systems.

There are several possible materials/systems degradation modes that result from gasification environments with appreciable carbon activities. These processes, which are not necessarily mutually exclusive, include carbon deposition, carburization, metal dusting, and CO disintegration of refractories. Each of these phenomena will be briefly described so as to define the particular uses of the terms in this report. There is a lack of unanimity in the literature regarding such definitions, and care must be used in evaluating reported observations that use these terms.

Carbon formation on solid surfaces occurs by deposition from gases where carbon activities (a_cs) exceed unity. The presence of a carbon layer can directly affect gasifier performance by restricting gas flow, particularly in the hot-gas filter, creating debris that may be deposited elsewhere in the system or that may cause erosive damage of downstream components, and/or changing the catalytic activity of surfaces. Several sources of information exist on carbon deposition that are relevant to the operation of gasifiers. Blast furnaces, catalytic processes such as Fischer-Tropsch syntheses for hydrocarbon production, and gas-cooled power reactors have all experienced detrimental effects as a result of carbon formation via the decomposition of CO (Boudouard reaction). In these systems, the principal problem is simply the disruption of normal operations caused by the formation and deposition of carbon.

There are also material degradation effects resulting from the formation of carbon layers. A principal one is the phenomenon of metal dusting,[1–4] which requires a high carbon activity ($a_c >> 1$) and proceeds by a combination of mechanisms. The high carbon activity obtained in the gas phase provides the driving forces for the formation of M_3C carbides and deposition of carbon. The carbon deposition reduces the a_c at the metal surface to unity, and the carbides (stable only when $a_c > 1$) then decompose to form metal particles and filamentous carbon in the form of a dust that can be carried away by the flowing gas. Pits and holes on affected surfaces can be observed in addition to general metal wastage. The degradation is typically observed at intermediate temperatures of about 400 to 900°C (750 to 1650°F). The steps involved in metal dusting are more fully described in Sect. 4. This phenomenon can be distinguished from carburization normally seen with high-temperature alloys. Carburization results in the formation of stable carbides on and within the solid exposed to a carbon-containing environment (even at $a_c < 1$). The formation of such carbides (normally M_7C_3, $M_{23}C_6$, or MC, where M = Cr, Mo, or Fe) can lead to loss of ductility, mechanical disintegration, and loss of oxidation resistance (see, for example, refs. 5–7). In some cases, this form of carburization has been reported to precede metal dusting,[3] but it is distinct from the actual degradation mechanism associated with the latter phenomenon. There are cases where such a distinction has not been made, and "metal dusting" has been used to refer to other carburization effects. The formation of filamentous carbon by disproportionation of carbon monoxide actually exploits the process of metal dusting.[8]

Deterioration of refractories used in coal gasification vessels can occur at temperatures below about 650°C (1200°F) when these materials (usually castable refractories) contain iron or iron alloys. An excellent review of this phenomenon, known as CO disintegration, can be found in ref. 9. Carbon deposition from the gas mixture is a necessary step in the process, which then leads to degradation that exhibits many of the same characteristics as metal dusting. Indeed, the basic mechanisms involved in both CO disintegration of iron-containing refractories and metal dusting appear to be the same, although, historically, the studies of the respective phenomena appear to have been conducted independently of each other.

Section 2 of this report summarizes the results of thermochemical calculations of carbon activities and stabilities of iron-containing phases for representative gasifier systems. These calculations show that, in all cases, a driving force for carbon formation on solid surfaces exists at the operating temperatures of the gasifier components, but that the requisite carbide phase necessary for metal dusting is not always thermodynamically favored. Section 3 briefly reviews possible materials and system factors that can influence the kinetics of carbon deposition. Section 4 is a summary of work related to metal dusting. It includes a description of the mechanisms for the processes leading to metal dusting based on what appears to be the most compelling experimental results and theoretical considerations. The relative susceptibilities of different alloys to metal dusting are also reported. The influence of system operating parameters on carbon deposition, carbide stability, and metal dusting is discussed in Sect. 5, and materials selection considerations for hot-gas cleanup sections of coal gasification systems are presented in Sect. 6. A systems analysis to determine what, if any, deleterious effects might occur as a result of possible process variations is beyond the scope of the present review. Thus, these considerations are not to be interpreted as recommendations unless such an analysis confirms their acceptability. It is concluded that experimental verification of the predictions based on thermodynamic information and assumptions regarding kinetics will be required, and approaches to this and other issues are described in Sect. 7. Private communications to the authors regarding the occurrence of metal dusting in operating gasifiers are summarized in Appendix A.