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SELECTIVE OXIDATION SURFACE ANALYSIS ON METALS AND MINERALS

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ABSTRACT

Selective Oxidation Surface Analysis (SOSA) studies were made on (a) metal surfaces containing high molecular weight carbonaceous impurities (i.e. greases, oils) and (b) mineral particles containing adsorbed "surfactant collectors".

The principle of the technique consists of heating the sample in a stream of oxygen. The surface carbon species are selectively oxidized over characteristic temperature ranges and the effluent gas fed over a catalyst. The resulting carbon dioxide was continuously analyzed by an I.R. detection system. The method was shown to capable of differentiating and quantifying the various carbonaceous compounds.

SOSA could prove useful in the mineral and metallurgical industries.

INTRODUCTION

Carbon may be associated with a metal or mineral surface in two major forms. Primarily the carbon may be an integrated constituent of the surface film as for example in cemented carbide cutting tools or carbonated deposits on many salt type minerals which are formed by interaction of the crystalline lattice with atmospheric carbon dioxide. Secondary, the carbon may be physically or chemically adsorbed to the surface in the form of carbonaceous additives or impurities (i.e. hydrocarbon fatty acid soaps or greases).

In many industrial processes it is important to distinguish and quantify the various forms of the interfacial carbon. For example in many metal working operations such as aluminum or steel rolling or wire drawing; oils, greases and emulsion lubricant/coolants are used to aid metal deformation. Although most of the hydrocarbon film can be removed in subsequent degreasing operations, often trace amounts of carbonaceous impurities remain on the surface. This can have adverse effects on post treatment processes which may involve electrodeposition, phosphatizing, anodizing or vapour deposition.

In other mineral processing operations (i.e. flotation or grinding) it is essential to add long chain polar hydrocarbon additives which adsorb at the mineral/water interface. A knowledge of the quantity of additives adsorbed

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and the kinetics of adsorption are important parameters in studying the process efficiency.

Hence in recent years a considerable research effort has been devoted to surface carbon analysis to meet the needs of industry. Initially methods were derived based on the chemical extraction of carbonaceous material from the surface (ref.1) but these proved time consuming and only semi-quantitative (ref.2). More direct and routine techniques were later developed based on the principle of direct combustion on the carbon in oxygen (refs.3-5). The carbon was converted to carbon monoxide and oxidized to carbon dioxide using a catalyst. Finally the total amount of carbon dioxide produced was quantitatively analysed by IR, calorimetry or conductometric titration techniques. Methods have been standardized whereby the surface carbon is oxidized at (a) one specific temperature (i.e. ~550°C) (ref.3) (b) several temperatures (ref.2,4) or (c) by continuously heating from room temperature to some predetermined temperature.

Although such methods proved simple and inexpensive to use on a routine basis they suffered from a major disadvantage in that it was not possible to distinguish between carbon from different carbonaceous compounds. Hence the results give only a quantitative value of the total amount of surface carbon. In order to achieve more detailed characterization of surface carbon, research has been therefore directed to more sophisticated high vacuum instrumentation (i.e. Secondary ion mass spectrometry, Auger or X-ray photoelectron spectroscopy (ref.5,6)). Such methods are obviously more expensive and time consuming to employ on a routine basis.

However, recently Selective Oxidation Surface Analysis (SOSA) have been developed by the Swedish Institute of Metal Research, Stockholm. The method is based on the combustion and oxidation of surface carbon followed by analysis of CO_2 during continuous heating of the sample. This enables carbon from different carbonaceous compounds such as hydrocarbon, bicarbonates, carbonates, carbides and allotropic forms of carbon (graphite and amorphous carbon) to be distinguished. In this paper a range of applications of this novel technique are described.

METHODS

Principles of the analytical method

The analysis of the surface carbonaceous material is based on the oxidation of the surface film in a flowing high purity oxygen stream. A sample of the metal or mineral is placed at room temperature in a furnace which is heated at a constant predefined rate of 20 K/min up to 700-800°C. The carbon and hydrocarbons present on the metal surface oxidize selectively in specific temperature ranges, depending on thermodynamic and kinetic factors. The reaction products are then converted in an separate oxidation furnace containing a catalyst to CO_2 and H_2O. The concentration of these compounds are continuously analyzed using a high-sensitive I.R. detector system.

The approximate oxidation range of the various forms of carbon is shown in Fig. 1 and the principles of the method and layout of the equipment shown in Fig. 2.

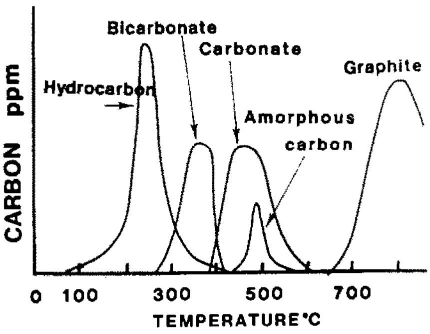

Fig. 1. Approximate oxidation range of various carbonaceous species

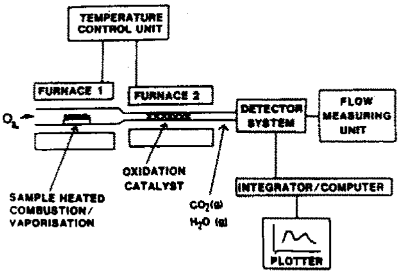

Fig. 2. Equipment layout

RESULTS AND DISCUSSION

In the present study results are presented showing the range of applicability of the technique in characterizing and quantifying carbonaceous films on various mineral and metal surfaces.

(A) Degreasing of low-carbon batch-annealed steel sheet

The oxidation curves for the steel sheet samples before and after degreasing with a trichloroethylene degreasing process for varying periods of time is shown in Fig. 3. Two peaks are evident in the SOSA plot, the peak at 200-300°C has been attributed to the rust protection oil and the peak at 300-400°C to the residual rolling oil emulsion.

The SOSA curves indicate that the degreasing efficiency increases with increase in operation time. In addition, it appears that the lower temperature peak is more effectively reduced than the higher peak suggesting that the degreasing process effectively removes the low molecular weight rust-protecting oil but only marginally removes the high molecular weight rolling oil. In fact after 15 minutes the major contaminant appears to be the residual rolling lubricant and to completely clean the surface it would be necessary to extent the degreasing time or change the solvent.

(B) Residual carbon film on the inside of copper tubes

A carbon film is thought to be formed in the soft-annealing operation by decomposition of the drawing lubricant. This has been reported to have an important influence on the pitting corrosion of the tubes. In Fig. 4 the oxidation curves of the as-drawn and as-annealed tubes is shown. From these curves it would appear that the surface carbonaceous material is reduced as a result of the annealing process. In addition, it is evident that the carbonaceous residual on the as-annealed sample consists mainly of hydrocarbon species and not carbon. This residue is oxidized at a substantially higher temperature range than for the tube drawing lubricant. It has been suggested that this residue consists of high molecular weight hydrocarbon formed by polymerization and cracking of the lubricant on the copper surface.

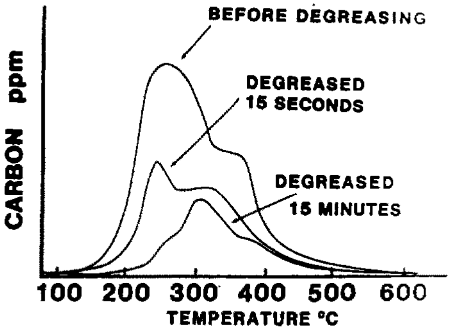

Fig. 3. Degreasing of steel sheet with trichloroethylene

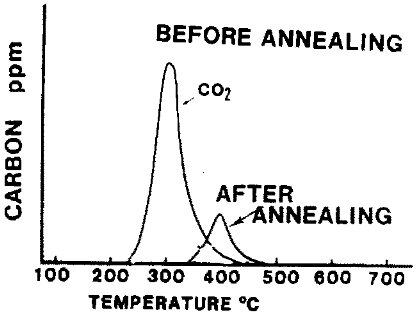

Fig. 4. Copper tube

(C) Adsorbed fatty acid/amine and sulphate collector adsorbed during froth flotation of salt type minerals

Many natural occurring salt type minerals are hydrophilic and it is necessary in the froth flotation process to add polar molecules to the pulp, to make the surface hydrophobic. This enables the mineral particles to collide and become attached to rising air bubbles and carried to the surface of the flotation cell. The mineralized froth can then be easily removed and separated from the pulp containing the less valuable mineral components. Such surface active agents are called collectors and a knowledge of the extent of which the mineral surface is coated with collectors is important in order to understand and control the process. For salt type mineral, fatty acid/amine and sulphate collectors are frequently used. In Fig. 5 the SOSA plot of fluorite (CaF_2) after dispersion in water and after microflotation in dodecylamine collector is shown.

The unprocess fluorite (Fig. 5a) clearly indicates the combustion of carbonaceous species on the surface occurring between 200°C and 700°C. These curves have been attributed to carbonate and bicarbonate, the carbonate oxidizing at the higher temperature range (>500°C). This was established from preliminary calibration experiments in which carbonate and bicarbonate was analyzed separately.

In Fig. 5b the adsorbed amine collector can be seen to oxidize at a relatively lower temperature range. The degree of surface carbonation and the concentration of adsorbed collector can be estimated from these plots knowing the molecular weight and quantity of carbon dioxide produced from the various carbon fractions. The method was found to be sensitive to μg levels of collector/g of mineral. Additional studies have been carried out on long chain fatty acids and sulphate collectors.

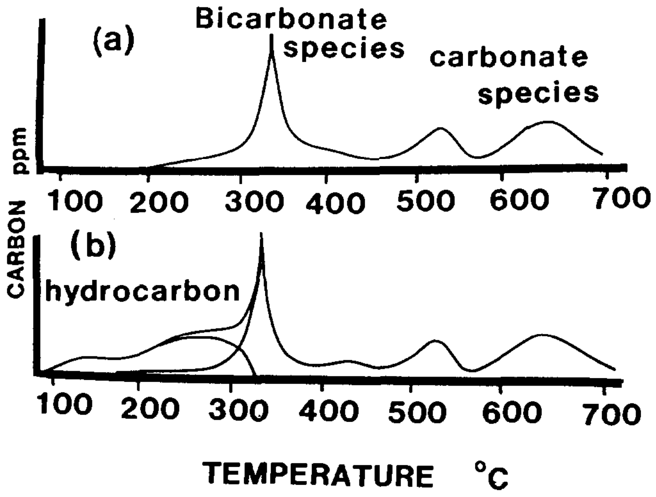

Fig. 5.
Fluorite particles

(a) dispersed in water without collector

(b) Floated with dodecylamine at pH 10.8 ($9x10^{-5}M$)

D) Adsorbed xanthate collector in sulphide minerals

In the case of sulphide minerals xanthate collectors are frequently used. In Fig. 6 a and b, galena (PbS) is shown after processing in water and flotation with isopropyl xanthate respectively. Again the galena surface can be seen to be heavily carbonated and the adsorbed xanthate collector oxidized at a relatively lower temperature range.

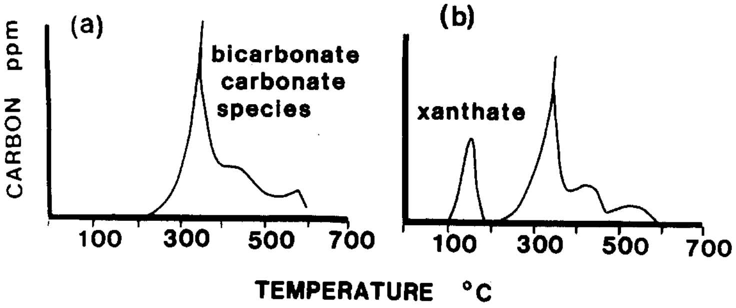

Fig. 6. Galena particles (a) dispersion in water, (b) floated with sodium isopropyl xanthate pH 8 ($5x10^{-3}M$). No frother.

CONCLUSION

Selective Oxidation Surface Analysis can be used to quantify surface carbon and enables the type of carbonaceous material to be characterized. It has been shown to be a useful method to study

(I) Surface carbonaceous reaction occurring during the annealing of copper tubes

(II) The efficiency of degreasing operations on annealed steel sheet

(III) The adsorption of hydrocarbon surfactant-collectors on mineral particles such as fluorite and galena

(IV) The degree of carbonation of the mineral surfaces.

Acknowledgement

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