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Second Phases in Steel

New analytical methods can identify the types and amounts of complex precipitates in steel.

W. R. Bandi

For many years better analytical methods for the determination of second phases in steel have been needed, because these phases are often more closely related to the heat treatment and mechanical properties of the steel than the elemental composition. I discuss here some of the recent approaches to solving this problem.

Ever since steel was first manufactured, metallurgists have been searching for methods of changing its mechanical properties so that specific grades can be made for particular applications. Often such changes are brought about by the addition of one or more alloying elements to the steel, and at least 35 elements have been added for this purpose. Most of these elements can be present in solid solution in iron, but they often change the mechanical properties of the steel by combining with oxygen, nitrogen, carbon, or sulfur to form precipitates in the steel that are referred to as second-phase compounds. Sometimes the second phase will contain two metals such as nickel and titanium combining to form Ni_3Ti, but most often the second phases are oxides, nitrides, carbides, sulfides, carbonitrides, carbosulfides, and similar compounds. These compounds may be formed in the molten bath, during solidification, during rolling or forming, during heat treatment, and sometimes even during storage at ambient temperature.

Table 1 shows how precipitates can affect some of the mechanical and physical properties of steel. Only a portion of the approximately 200 precipitates found in low-alloy, high-alloy, and specialty steels and some of the important mechanical properties are listed. Often metallurgists can associate precipitates with additional changes in the mechanical, physical, and chemical properties of steel. No attempt has been made in Table 1 to note whether a particular precipitate has a detrimental or beneficial effect on the mechanical properties of steel because in many instances the effect can be either positive or negative depending on the amount, size, and distribution of the precipitate. Precipitate concentration can vary from as much as 10 percent (by weight) (cementite, Fe_3C) to as little as 0.002 percent [boron nitride (BN) and ferrous sulfide (FeS)].

The determination of where a precipitate is located in the iron matrix is of great importance in terms of what effect it can have on the properties of the steel. Even very small quantities of a precipitate located at a grain boundary can induce cracking or corrosion, whereas a larger amount of the same material located randomly throughout the steel will not have the same effect. Small particles of carbide or nitride arranged in rows will form a barrier to slip and dislocation movement in the crystals of the iron matrix and are therefore much more effective in conferring strength than randomly arranged particles.

The particle size of the precipitated phase is also important. As an example, the strength of a steel is changed more by particles of carbide and nitride that are 30 to 400 angstroms in size than by larger particles because these smaller particles are much more effective in preventing grain growth, and fine-grained steels are stronger. Frequently very large particles of carbide or nitride are detrimental to the steel, whereas small particles of the same compound can be beneficial.

The magnitude of the analytical chemical problem can be appreciated when one realizes that more than 50 nitrogen compounds can be present in simple and complex steels. These include simple nitrides such as titanium nitride (TiN) or more complex nitrides such as niobium carbonitride (NbC_xN_y), manganese silicon nitride [$(MnSi)N_2$], and aluminum oxynitride (AlO_xN_y). A like number of carbides and oxides and a smaller number of sulfides and carbosulfides may also be found in steels. There are thus several hundred compounds that can exist in the carbon, alloy, and specialty steels presently being produced in the United States. As a result, the identification and determination of second-phase compounds in steel have been a real challenge in the development of improved steels.

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Identification of Second Phases

The identification of second phases frequently requires the application of a variety of analytical chemical techniques. It has been necessary to use modern qualitative physical techniques in many instances because conventional quantitative microchemical methods were not applicable or reliable. However, recent developments in the identification and determination of second phases by less conventional or new chemical approaches have made quantitative analysis possible and also have increased the analyst's ability to identify more minor phases in the steel. These developments I intend to describe in some detail. Since the chemical methods are correlated with qualitative physical methods, it seems appropriate to outline the conventional techniques now in use before proceeding to the newer ones.

The optical microscope is used on a routine basis to examine the microstructure of steel, and most of the literature on structure-property relationships in steel includes optical micrographs. Although there is a continued and expanded use of metallographic methods, the need for information on second-phase particles smaller than 2000 angstroms (the limit of resolution of optical microscopy) has led to the use of other microscopic procedures. From a practical standpoint, particles smaller than 1 micrometer cannot be identified with a microscope.

Very fine particles of a phase in steel can be examined with a transmission electron microscope; the sample used is in the form of a very thin foil. When a thin foil is not practical, an extraction replica is used. In this technique second phases are extracted by a plastic or carbon film that retains them, along with the surface topography, for examination in the electron microscope. This technique is also useful in the examination of fracture surfaces that may contain second-phase particles. The scanning electron microscope can also be used to produce an image of the steel surface; with this instrument it is possible to detect particles as small as 50 angstroms.

The electron microprobe analyzer is also used to examine discrete second-phase particles. When the second-phase particle is large enough so that the x-rays from the particle can be differentiated from the radiation due to the primary steel alloy phase, then it is possible to identify the particle. Even more refined analysis to show the purity of the second phase is possible. As an example, (Mn,Fe)S and (Fe,Cr)$_3$C can be differentiated from MnS and Fe_3C.

Microscopic methods are not completely satisfactory for the identification of all phases because, although they reveal the presence and location of a precipitate in a crystal, they cannot discern which or how much carbide, nitride, or carbonitride is present. X-ray diffraction is sometimes used to gain this information, but it is sometimes quite difficult to differentiate among the carbide, nitride, and carbonitride of the same metal. The quantitative determination of a particular second phase usually requires a microchemical determination.

New Microchemical Techniques for the Determination of Second Phases

In most instances the microchemical determination of a particular phase begins with the isolation of a group of compounds from the steel matrix. The difficulty in determining small amounts of a specific second phase has already been discussed. It becomes even more difficult, for example, when small amounts of minute particles of a metal carbide must be handled in the presence of a much larger concentration of Fe_3C. For this reason chemists have recently resorted to solid-gas reactions in which small quantities of a specific chemically isolated phase or a group of chemically isolated phases react with a gas without prior separation of the Fe_3C and other phases. If a good system is built for the determination of evolved gases, such a procedure can be much more sensitive and specific than normal microanalytical methods because it eliminates many microanalytical operations. Preliminary investigations established that metal carbides (*1–4*) and metal nitrides (*3, 5, 6*) burn in oxygen (O_2) and evolve carbon dioxide (CO_2) and nitrogen (N_2), respectively, over specific temperature ranges. The temperature of combustion or decomposition is an indication of which carbide or nitride is present. Quantification is usually achieved by measurement of the amount of CO_2 or N_2 evolved.

Early work by Koch and Keller (*1*) and Klyachko and Yakovleva (*2*), consisting of combustion at fixed temperatures with conventional apparatus, was only partially successful in determining iron carbide. However, because of the availability of better differential thermal analysis (DTA) instruments and better methods for the measurement of gases, my co-workers and I have been successful in developing

Table 1. Effect of precipitated phases on some mechanical properties of steel; X, affects mechanical properties directly or indirectly; O, no effect; RE, rare earth.

Precipitate	Mechanical property affected						
	Strength	Formability	Toughness	Strain aging	Grain size and orientation	Hardenability	Brittleness during rolling
Carbides							
Fe_3C	X	X	X	X	O	X	O
VC, V_4C_3	X	X	X	X	X	X	O
TiC	X	X	X	X	X	X	O
Nb_4C_3, NbC, (Nb,Mo)C	X	X	X	X	X	X	O
Nitrides							
Fe_4N	X	X	X	X	X	O	O
VN and VC_xN_y	X	X	X	X	X	X	O
TiN and TiC_xN_y	X	X	X	X	X	X	O
α and β Si_3N_4	O	O	O	X	X	O	O
AlN	X	X	X	X	X	X	O
NbN (cubic)	X	X	X	X	X	X	O
BN	O	O	X	X	O	X	X
Oxides							
FeO	O	X	X	O	O	O	O
MnO	O	X	X	O	O	O	O
Spinels	O	X	X	O	O	O	O
Al_2O_3, aluminates	O	X	X	O	O	O	O
SiO_2, silicates	O	X	X	O	O	O	O
B_2O_3, borates	O	O	X	O	O	X	X
Sulfides							
FeS	O	X	X	O	O	O	X
MnS	O	X	X	O	X	O	X
γ-Ti_2S	O	X	X	O	X	O	X
$Ti_4C_2S_2$	O	X	X	O	X	O	X
RE_2O_2S	O	X	X	O	X	O	X
Other phases							
$(Ni_2Fe)_3Mo$	X	X	X	O	O	O	O
σ-FeMo	X	X	X	O	O	X	X

procedures in which gas-solid reactions are used for the analysis of inclusions (*3–15*). Thus far, we have quantitatively determined 35 carbides, carbonitrides, and nitrides by reacting these compounds with O_2 and measuring the CO_2 or N_2, or both, evolved during combustion or decomposition over a specific temperature range.

To accomplish the analysis we modified a DTA apparatus (R. L. Stone Company) by reducing the sample compartment volume; a sensitive system for evolved gas analysis (EGA) was connected to this apparatus for the determination of the gas evolved from the 1- to 3-milligram sample as it was heated (*3–14*). The DTA procedures record the difference in temperature between a reference material (usually aluminum oxide, Al_2O_3) and the sample as the two are program-heated. The DTA recording is accomplished by use of a pair of differential thermocouples arranged so as to sense changes in the heat content of the sample as compared with the reference material. A change in heat content occurs because of a chemical reaction, change of state, or phase change of the sample. A schematic diagram which may be used as a guide to build or modify DTA and thermal conductivity instrumentation is shown in Fig. 1. In the modified Du Pont instrument shown in part in Fig. 1, we achieved an increase in the EGA sensitivity by redesigning and reducing the bore of the ceramic tube from 16 to 1.3 millimeters.

Although the CO_2 can be measured by thermal conductivity in the O_2 carrier gas, before the measurement of the evolved N_2 in the O_2 carrier gas, O_2 and N_2 must be separated chromatographically. With this technique, 80 percent of the N_2 evolved every 3 minutes is included in the sample by use of an automatic sampling device and is separated and measured as part of a series of sequential analyses (*5, 6–9, 12, 13, 15*).

The thermal conductivity response is recorded on a 1-millivolt full-scale recorder, and the area under the CO_2 response or the family of N_2 peaks is related to the concentration of the evolved gas and therefore to the carbide or nitride.

To carry out an analysis with the instruments described, between 1 and 3 milligrams of residue isolated from 1 to 4 grams of steel is placed in a platinum pan resting on a thermocouple in the sample compartment. The residue is heated at the rate of 10°C per minute in a dynamic O_2 flow of 3 milliliters per minute. The DTA thermogram is recorded. Figure 2 is a complex example of the determination of seven carbides in a residue isolated from a niobium-bearing steel. It shows that the steel contained three different niobium carbides, two molybdenum carbides, a titanium carbide, and Fe_3C. A Du Pont curve resolver, which is normally used to resolve overlapping chromatographic peaks, was used to resolve the complex response into the individual gas evolution peaks. The instrument can be used to generate Gaussian responses of different shape and size in order to fit the EGA CO_2 response. (Lorentzian and other shapes may also be generated, but EGA responses have been observed to be Gaussian.) Justification for a resolution is based on known responses for possible compounds of niobium and molybdenum. A microchemical determination of molybdenum was necessary to confirm the correctness of the resolution. Figure 2 is a very complex response and is included to show the limits of the technique. Figure 3 is a more typical EGA response and shows the peaks obtained as part of a determination of nitrides in another steel. In Fig. 3 the N_2 evolved at the lowest, intermediate, and highest temperatures resulted, respectively, from the decomposition of ϵ-NbN, NbC_xN_y, and TiN.

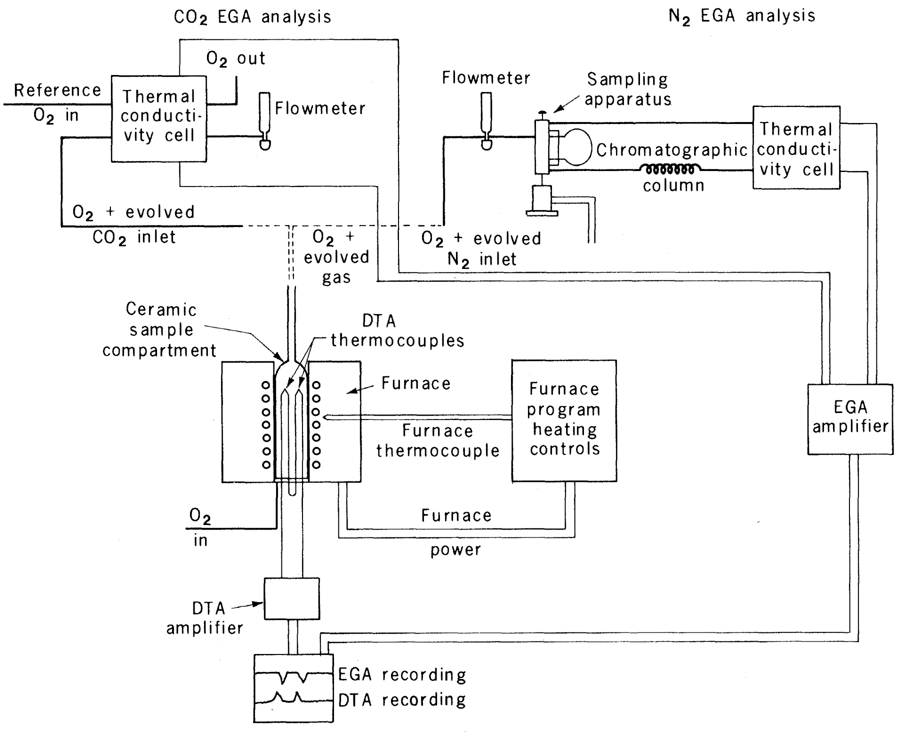


Fig. 1. Diagram of DTA-EGA apparatus.

Advantages of DTA-EGA

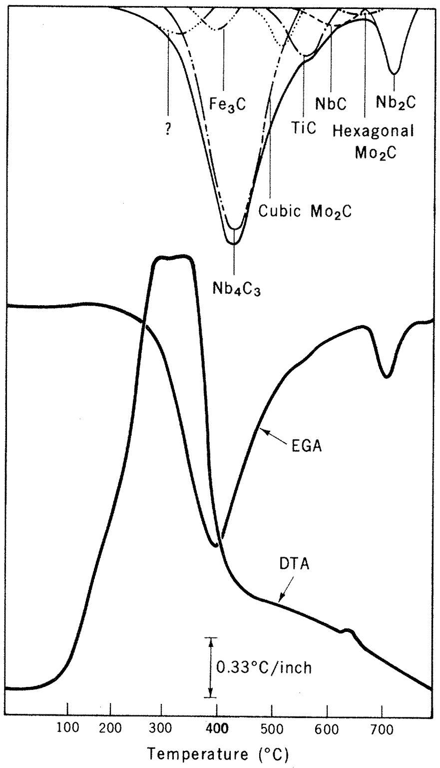
I have already pointed out that the use of DTA-EGA eliminates many of the chemical separations necessary in microchemical analysis. The separation of a few parts per million of a particular phase from a hundred thousand parts per million of Fe_3C is very difficult. Physical methods such as magnetic separation are often attempted because chemical separations of impure phases are not dependable (*16*). When the particles of the phase being determined are very small (~ 100 angstroms), normal filtration procedures cannot be applied. Moreover, published solubility data for the pure compounds are not always applicable to a very fine impure particle of a compound which has a large surface-to-weight ratio and possibly also some crystal defects. In addition, special precautions must be taken in a microchemical procedure to prevent the oxidation of very fine particles in air. Even if all the above difficulties are overcome, there is still some uncertainty about the interpretation of the results obtained with elemental analysis and x-ray diffraction. As an example, the chemist must use his best judgment in deciding whether the results indicate that TiN and V_4C_3 are present rather than TiC and VN. Such an interpretation can be even more difficult if the possibility of carbonitrides is also considered. Therefore, DTA-EGA not only saves analytical time, but it can also reduce the analytical errors.

The use of DTA-EGA also reduces the initial analytical time needed for the isolation of a residue. Because the gas analysis system is sensitive and because several carbides or nitrides can be determined from 1 milligram of isolated residue, less residue is needed than for an exhaustive chemical analysis.

With optimum isolation conditions, the

latest DTA-EGA instruments are capable of detecting the evolution of CO_2 and N_2 from as little as 0.001 percent TiC and 0.001 percent TiN, respectively. This sensitivity is equal to that attained for the determination of total titanium in the steel by standard chemical procedures.

Frequently phases can be quantitatively determined by DTA-EGA that are not even detected or identified by other chemical or physical methods. With reference to Fig. 2, an x-ray diffraction analysis revealed NbC, which was really NbC + Nb_4C_3, but did not identify Nb_2C, TiC, cubic Mo_2C, hexagonal Mo_2C, or Fe_3C. A second-phase compound usually has to be present in a concentration of at least 5 percent in an isolated residue before it is detectable by x-ray diffraction. Often Fe_3C or amorphous carbon from the decomposition of Fe_3C, or both, prevents the detection of important phases in the isolated residue.



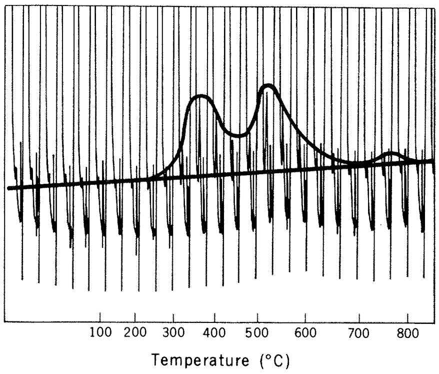


Fig. 2 (left). The DTA-EGA response for steel containing niobium and molybdenum. Fig. 3 (above). The EGA response of N_2 for niobium-bearing steel.

Because small amounts of second-phase compounds are more easily detected by DTA-EGA than by other techniques, phases can now be found in steels that were not suspected earlier. One of the initial surprises in the development of this method was the determination of three different types of NbN in the same steel. It was found that with certain heat treatments very small particles of hexagonal, close-packed hexagonal, and cubic NbN were all present in a particular steel. This finding was deduced from the composition of the steel, the microchemical analysis of the isolated residue, the DTA-EGA responses, the heat treatment, and the technical literature; but it was not possible to verify the forms of NbN by x-ray diffraction because the second-phase precipitates were too small (*9, 10*).

The Nb_2C (Fig. 2) was initially identified by DTA-EGA and verified on the basis of the composition of the steel and the determination of niobium in the isolated residue; Nb_2C was not observed by x-ray diffraction (*10*). Since the initial identification of Nb_2C, this carbide has also been found in several commercial high-strength, low-alloy steels, although it was not thought to be present. In more recent work, DTA-EGA results have shown that Cr_2C is present in heat-treated chromium-bearing steels in many more instances than had been reported (*15*).

Figure 2 shows that there is a difference of approximately 150°C in the combustion temperature of Nb_4C_3 and NbC; Nb_4C_3 is the defect structure of NbC and is often the form of the carbide found in steel. Only under optimum conditions is it possible to distinguish the change in the x-ray diffraction pattern caused by vacant carbon sites, which is responsible for the difference between cubic Nb_4C_3 and cubic NbC. If the particles in the precipitate are very fine, then line-broadening would prevent differentiation of the defect structure. Similarly the DTA-EGA results show that the normal vanadium carbide precipitated in steel is V_4C_3, and VC is only rarely found (*12*).

One of the outstanding advantages of DTA-EGA is that it can be used to differentiate easily between a metal carbonitride and the corresponding carbide, nitride, or carbide-nitride mixture. This differentiation is very difficult to accomplish by x-ray diffraction and other analytical procedures. For VC_xN_y, TiC_xN_y, $Cr_2C_xN_y$, and other carbonitrides, the simultaneous evolution of CO_2 and N_2 at a given temperature when the residue is heated provides for the easy discernment of these carbonitrides (*9, 12, 15*). The carbonitride NbC_xN_y differs from the carbonitrides mentioned above because it decomposes to NbON before giving up N_2; this carbonitride is easily detected when it is known that niobium is present in the steel (*10, 13*). It is possible, therefore, to establish by DTA-EGA the formula of the carbonitride in a precipitate. Results have been published for NbC_xN_y and $Cr_2C_xN_y$ (*13, 15*). The changes in the amount of carbon and nitrogen in the carbonitride precipitate brought about by changes in the heat treatment of the steel have been determined (*13*). In a similar manner, it is also possible to distinguish between a metal carbosulfide and a mixture of its carbide and sulfide.

Other changes in the composition of precipitates are also detectable by DTA-EGA. For example, (Nb,Mo)C, which was thought to be NbC on the basis of x-ray diffraction results, was observed to change into two phases (NbC and Mo_2C) when heat-treated (*10*). Also, the ratio of chromium to iron in $(Cr,Fe)_7C_3$ was observed to affect the combustion temperature (*15*).

One of the most effective uses of the DTA-EGA procedure is to quantitatively follow the changes in precipitate composition as a steel is heat-treated. Much can be learned about the mechanism of carbide formation and the rate of precipitation of a particular carbide by this technique. As an example, the formation, change, and disappearance of eight carbides have been recorded while a 10 percent nickel steel was aged (*14*). The identification of some of the carbides found by DTA-EGA, however, remains questionable because the results could not be confirmed by other methods.

Accuracy of Methods

As with every other analytical method, there are circumstances that affect the accuracy of the DTA-EGA procedure. As might be expected, one of these is the interference of one carbide or nitride with another present in the same isolated residue. For example, Nb_4C_3, (Nb,Mo)C, and V_4C_3 decompose over nearly the same temperature range; additional infor-

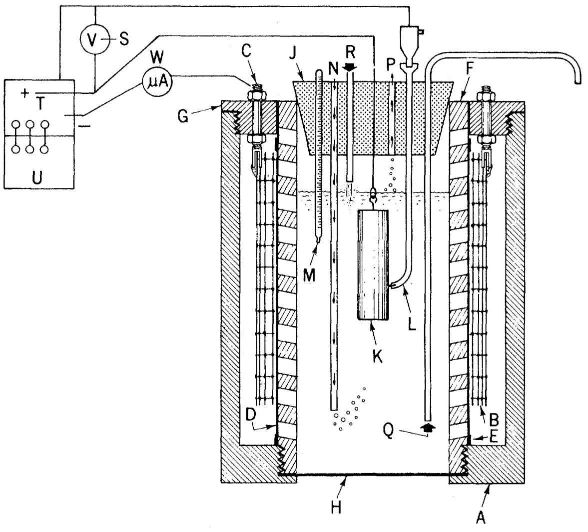


Fig. 4. Electrolytic cell for anodic isolation; *A*, Lucite cylinder; *B*, stainless steel cylinder cathode screen; *C*, threaded cathode connection; *D*, sausage skin (nitrocellulose membrane); *E*, rubber tape for sealing membrane; *F*, Lucite cylinder with holes for ion and electron transfer through the membrane; *G*, mounting ring for cathode screen; *H*, rubber gasket; *J*, rubber stopper; *K*, anode sample; *L*, calomel cell and probe; *M*, thermometer; *N*, argon inlet; *P*, argon outlet; *Q*, solution outlet; *R*, solution inlet; *S*, vacuum tube voltmeter; *T*, potentiostat; *U*, d-c power supply; *W*, microammeter.

mation is thus needed to ensure the correctness of the analytical result for these compounds. Sometimes it is only necessary to refer to the composition of the steel to resolve the problem. Often one can eliminate one of the possible constituents by showing that it is entirely present as another second-phase compound and therefore cannot be present as the suspected carbide. In other cases it is necessary to determine a particular metal in the residue in order to establish which phase is present. Conversely, the determination of the amount of a particular metal in the dissolved matrix can also be used to aid in establishing which carbide is present in the steel. Finally, x-ray diffraction examination of the residue may aid in determining which carbide is present. It is therefore clear that DTA-EGA identification without other information is sometimes questionable.

Another disadvantage appears to be that changes in the relative chromium and iron contents of compounds such as $(Cr,Fe)_7C_3$ will cause small changes in the combustion temperature and confusion in the identification of the compound (*15*). This misidentification appears to be a more serious problem than errors arising from changes in the size of the precipitated particles.

Often a steel contains so many metal carbides that there is a serious overlap in the thermal responses to the combustion of the carbides (*14*). Even though a curve resolver is used, the overlap reduces the certainty of identification and the accuracy of the determination.

The biggest disadvantage of the method, however, is that the accurate quantitative determination of the specific second phases is dependent on the successful chemical isolation of these phases from the steel matrix. Even though a smaller amount of isolated residue is required for DTA-EGA than for conventional microchemical analysis, the accuracy and dependability of DTA-EGA are related to the accuracy and dependability of the isolation procedure used to obtain the residue. Therefore, a discussion of the effect of the isolation procedure on the DTA-EGA results is necessary.

Three basic procedures have been used for these isolations. They are (i) anodic dissolution of the steel matrix in a specially constructed cell, (ii) treatment of the steel with halogen to preferentially dissolve the matrix, and (iii) treatment of the steel in dilute acids under controlled conditions so that the matrix and some of the chemically unstable phases are dissolved.

Koch (*16*) is the strongest proponent of methods of anodic dissolution. In this procedure the steel as the anode is suspended in a cell compartment. The electrolyte in the anode compartment is separated from the cathode by a permeable membrane such as sausage skin. A particular electrolyte and a specific voltage are selected on the basis of experimentation so that the steel matrix will dissolve but the second phase will be retained as a residue inside the membrane. Figure 4 is a diagram of a typical cell. Voltages can be adjusted so that the less stable phases are dissolved and only the electrochemically stable phases are isolated. Literally hundreds of electrolytes have been proposed (*16, 17*). In most instances the gas mixture, temperature, *p*H, and other cell parameters are closely controlled.

When anodic dissolution is used to isolate chemically unstable compounds such as Fe_3C, FeS, and MnO, both the number of oxides, nitrides, and carbides and the amount of precipitates such as Fe_3C and MnS which are isolated are so great as to reduce the effective sensitivity of the DTA-EGA method. Moreover, with more carbide and nitride present, there is usually more overlapping of the carbide and nitride responses and more difficulty in resolving the EGA responses. Therefore, anodic dissolution is not the best method for isolating stable nitrides and not generally the best method for isolating carbides. However, it is often the only method applicable for certain chemically unstable phases, and it is the best method for isolating intermetallic phases such as Ni_3Mo. Bandi *et al.* (*8*) have used it to isolate second-phase compounds from 18 percent nickel maraging steel and from 10 percent nickel maraging steel (*14*); DTA-EGA procedures were applied to the isolated residues.

Many workers have separated second-phase oxides, carbides, sulfides, and nitrides from the matrix by treatment with halogen and an organic solvent. Such a treatment usually dissolves compounds such as $(Ni_2Fe)Mo$ or Fe_2B. The mildest treatment used is an alcoholic solution of iodine, which was first proposed by Willems (*18*) almost 50 years ago. This procedure is still used with some modification for the isolation of chemically unstable phases such as Fe_3C (*11, 16, 19*), MnO (*18–21*), MnS (*20, 22, 23*), and FeS (*19, 20, 23*). It has been used more recently to isolate carbides such as Cr_2C, Cr_7C_3, and $Cr_{23}C_6$ (*15*). As with anodic dissolution, so many phases are isolated that the sensitivity of the DTA-EGA method is reduced.

Beeghly (*24*) proposed that bromine (Br_2) and alcohol or Br_2 and an aliphatic ester such as methyl acetate be used as a method for separating oxides and nitrides from steel. It is generally considered that treatments with Br_2 and nonaqueous solvents are the best methods for separating nitrides from steel because nitrides such as AlN and ZrN tend to hydrolyze in aqueous separation. These Br_2 mixtures are also widely used for the separation of stable oxide phases from steel but should not be used for the separation of carbides because too many carbides dissolve, leaving a residue of amorphous carbon. The large amount of amorphous carbon tends to dilute the sample and causes preignition of the nitrides so that Br_2 isolations are not ideal for the application of DTA-EGA techniques (*6*).

The isolation of small amounts of stable carbides and nitrides with dilute acid is ideal for the application of DTA-EGA because the sensitivity of the procedure can be used to the best advantage when many of the chemically unstable phases are dissolved. As an example, both MnS and Fe_3C (which may be abundant in steel) dissolve in acid.

Other Solid-Gas Reactions

In the preceding discussion, only the reaction of isolated residues with O_2 was mentioned. Other gases could be used. As an example, we and workers in two other countries have recently published results for the FeS and MnS content in steel by treatment of an anodically isolated residue with hot hydrogen (H_2) and determination of the hydrogen sulfide evolved from the decomposition of FeS by a sensitive spectrophotometric procedure (*23, 25*). The methods are very similar, and it was easy to determine less than 0.001 percent sulfur as FeS. Such a sensitivity is very difficult to accomplish by normal analytical methods. I have already expanded on the use of H_2 at elevated temperatures in the determination of other sulfides.

Several years ago attempts were made to determine nitrides, especially aluminum nitride (AlN), in steel by direct treatment of steel filings with H_2 over a selected temperature range (*26, 27*). In such a treatment ammonia gas (NH_3) evolves from the steel by reaction of H_2 with nitrogen, and the NH_3 is determined by a very sensitive spectrophotometric procedure. Since the original attempts to use this method, many workers have rejected it because it has been found that other nitrides interfere with the AlN determination (*27–29*). Moreover, the N_2 evolved from the decomposition of AlN can reprecipitate as another nitride or even as AlN before it diffuses from the steel (*27, 30*). Finally, the rate of diffusion of N_2 is dependent on the size of the steel filings (*27, 28, 31*) and the size of the nitride particles (*30*). However, it seems possible that many of these problems could be overcome if an isolated residue were used rather than a steel sample. Therefore, nitrides should be identifiable and determinable if an isolated residue were treated with H_2 at specific temperatures.

Steam has also been successfully used for the determination of second-phase boron compounds (*32*). This use is based on the discovery that boron oxides, which are isolated when the steel is treated with Br_2 and methyl acetate, react with steam to form boric acid at a much lower temperature than that at which BN reacts with steam. The resulting boric acid is swept out of the furnace by the steam, and boron is determined photometrically. As little as 0.0001 percent boron as the oxide or nitride can be determined by this procedure.

Recently, a procedure for the removal of carbon and carbides in a residue isolated in iodine and methanol has been reported (*33*). In this reaction a carbide treated with NH_3 at an elevated temperature is converted to the nitride, and hydrocarbons are evolved. All carbon, either amorphous or as a carbide, is removed by treatment with NH_3 at 800°C, but treatment with NH_3 at selective temperatures can be used to form nitrides from some carbides without attacking other carbides.

Other Instrumentation for Solid-Gas Reactions

The development of DTA-EGA methods in this country has been followed by developments in other countries (*34, 35*), and comments on these developments have also appeared (*36*). The most notable contribution seems to be the interfacing of a quadrupole mass spectrometer with a Du Pont DTA unit (*34*). Results for the decomposition of a number of nitrides obtained with this instrument are in agreement with those obtained by use of gas chromatographic methods.

Future Determinations

As new types of steel are developed, the demand for the determination of second phases will increase. As the development of new and better methods for determining second-phase compounds progresses, the information obtained can in turn be used to study mechanisms and rates of precipitation in new and existing steels. It seems that much of the work devoted to the development of chemical methods will be concerned with the reactions of gases with the isolated residue. The measurement of evolved gases by the use of mass spectrometry and other techniques will probably increase.

Because of the current effort to reduce the sulfur content normally present in steel and to change the sulfide morphology in high-strength, low-alloy steel used in such places as the Alaskan pipeline, it seems likely that a demand for the determination of a whole new group of sulfides such as rare-earth sulfides, rare-earth oxysulfides, titanium sulfides and carbosulfide, zirconium sulfide and carbosulfide, calcium sulfide, and magnesium sulfide will arise. This group of sulfur compounds does not cause as much fracture in cold weather as the normal manganese sulfide found in the steel will cause.

Efforts to change sulfide morphology of the steel will also result in changes in the concentration of oxides present in these steels. At present, carbon and low-alloy steels contain mostly aluminates and silicates which are routinely isolated in Br_2 solutions and eventually determined by emission spectroscopy. In steels in which rare earths, calcium, magnesium, zirconium, or titanium are used to change the sulfide morphology, it can be predicted that zirconates, titanates, Ce_2O_3, and $LaAlO_3$, and other unfamiliar oxides will be present. It will be necessary to determine these oxides so that their effect on the mechanical properties of the steel can be established. Twenty years ago, DTA instruments and quadrupole mass spectrometers were not commercially available for the determination of second-phase compounds, but it seems only a matter of time before this or some other newly developed instrumentation will be in common use in the steel industry.

Summary

The present and future relationship between the metallurgical development of new steels and the determination of second-phase compounds in these steels is emphasized on the basis of recent developments in the quantitative determination of these phases. Results of the application of DTA-EGA methods are presented as an example of this analytical approach, and the method used to measure the amounts of gases evolved from the reactions of second-phase compounds with O_2 is described in detail. The DTA-EGA method has also revealed phases that had not been found earlier in steels. Smaller amounts of second-phase compounds can be more accurately determined by this method than by any other procedure. Examples are cited for the reaction of O_2, H_2, steam, and NH_3 with second-phase compounds in the isolated residue, and the use of these reactions for the determination of second phases is discussed. A disadvantage of the DTA-EGA method is that it is dependent on the quantitative chemical separation of the second phase from the matrix steel by one of several methods. The relative merits of isolating second-phase compounds by electrochemical dissolution, by dissolution in halogen and alcohols or aliphatic esters, and by use of dilute acids are discussed in terms of their effect on the DTA-EGA determination.

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NEWS AND COMMENT

NSF: Pressures Mount to Provide Grants for Industrial Researchers

Senator Edward M. Kennedy (D–Mass.) has launched an effort to open the coffers of the National Science Foundation (NSF) to industrial researchers on an equal footing with scientists from academe.

The move is sending tremors of apprehension through university research administrators, who already feel themselves pinched by tight budgets and fear a further dilution of funds if the Foundation tries to support any appreciable number of scientists beyond its traditionally favored clientele in the universities. Their apprehension is heightened by the knowledge that Kennedy, as chairman of the Senate subcommittee on health and scientific research, exerts enormous influence over NSF's programs and budget.

At this writing, the prospects for immediate action on Kennedy's proposal remain uncertain. Kennedy's subcommittee recently approved a budget authorization bill that would direct NSF "to insure that researchers in the industrial sector are permitted to compete for [basic research funds] on an equal basis with researchers in the academic sector." That bill has not yet been approved by the parent Committee on Human Resources, where some members are said to be wary of the proposal to open NSF to industry, or by the full Senate. Nor is it clear how firmly committed Kennedy is to the equal-access proposal. Meanwhile, the House of Representatives has explicitly rejected an equal-access provision.

Thus, even if the Senate adopts Kennedy's proposal, the issue would have to be resolved by a House-Senate conference committee, where the outcome would be rated a toss-up. But whatever the fate of the proposal this year, the pressures for greater NSF support of basic research in industry seem destined to increase. "I doubt that we've seen the last of this one," commented one experienced staffer of the House Science and Technology Committee.

There is nothing in the statutes governing NSF that prohibits support of basic research in industry. But from the beginning, the founders and directors of NSF have viewed the agency's primary mission as the support of research and education at the nation's universities. In recent years, as the Foundation, under prodding from Congress, has ventured into greater support of applied research, it has encouraged industry to participate in such activities as the RANN (Research Applied to National Needs) program. But NSF leaders have steadfastly blocked industry from the basic research funds that comprise the core of the agency's activities.

Under present policy, NSF deliberately discriminates against unsolicited research proposals submitted by industrial scientists. Whereas it funds academic proposals primarily on the basis of "intrinsic scientific merit," it will fund industrial proposals only in "exceptional cases." The three exceptions are cases where the project is "of special concern from a national point of view and shows promise of solving an important scientific problem"; or "unique resources are available in industry for the work"; or "the project proposed is outstandingly meritorious." Only about 1 percent of NSF's basic research funds are awarded to industry.

Kennedy's interest in changing that policy is said to be motivated partly by the fact that a number of small- and medium-sized firms in his own state are clamoring for more capital to support research. Indeed, Kennedy's interest in the issue was stimulated in large part by a young physicist, Paul Horwitz, who took