

Panel Discussion*

Mr. Thomas—This session is to be a rather open discussion on topics covered earlier this afternoon. The speakers from this afternoon were excellent and covered a wide range of topics. Since there was not enough time for questions following each paper, the speakers are now ready to answer your questions. The members of this panel are also available to discuss related subjects and answer your questions.

Mr. Weiss—I should like to ask Messrs. Raybeck and Pasztor a question regarding their paper. Rooney et al.¹⁻³ found it necessary to construct special apparatus so that absolutely dry and moisture-free conditions could be maintained during the isolation of oxide inclusions from steel with alcoholic halogen reagents. They found that traces of water in the reagent, on the walls of the reaction vessel, or even exposure to air caused attack on iron and manganese oxides (FeO and MnO). In contrast to these precautions, and an elaborate procedure, is the open beaker method employed by Raybeck and Pasztor. Why should the bromine methylacetate reagent be less affected by water than bromine or iodine in methanol?

Mr. Raybeck—I am not sure why this should be so. We ran experiments on FeO and MnO using a dry bromine methylacetate reagent and one that was just reagent-grade which contained water. The experiments were run in open beakers, and we found no appreciable difference between the two reagents.

Dr. Melnick—Could this not be because the bromine methylacetate reagent is less polar than methanol? This, to me, would be a probable reason.

* Panel members: Arba Thomas, Armco Steel Co., Middletown, Ohio, chairman; K. W. Andrews, The United Steel Companies Ltd., Yorkshire, England; W. R. Bandi, U.S. Steel Corp., Applied Research Laboratories, Monroeville, Pa.; R. W. Bendure, Armco Steel Co., Research Laboratory, Middletown, Ohio; J. L. Hague, National Bureau of Standards, Washington, D. C.; K. F. J. Heinrich, National Bureau of Standards, Washington, D. C.; J. P. McKaveney, Crucible Steel Co., Research Laboratory, Pittsburgh, Pa.; L. M. Melnick, U.S. Steel Corp., Applied Research Laboratories, Monroeville, Pa.; L. C. Pasztor, Jones & Laughlin Steel Co., Research Laboratory, Pittsburgh, Pa.; R. Raybeck, Jones & Laughlin Steel Co., Research Laboratory, Pittsburgh, Pa.; and M. K. Weiss, Republic Steel Corp. Research Center, Cleveland, Ohio.

¹ T. E. Rooney and A. G. Stapleton, *Journal of the Iron and Steel Inst.*, Vol. 131, No. 1, 1935, p. 249.

² T. E. Rooney et al, *Iron and Steel Institute Special Report No. 25*, Section VI, Part 6A, 1939, p. 141.

³ T. E. Rooney et al, *Iron and Steel Institute Special Report No. 16*, Section IV, Part B, 1937, p. 109.

Mr. Bandi—Workers in England use the alcohol iodine method for the isolation of sulfides from steel. Perhaps Dr. Andrews could tell us more about this technique and about his own experience.

Dr. Andrews—Most of the known isolation techniques are also used to isolate sulfides from steel. However, most reagents decompose the sulfides, at least partially. I know the alcoholic bromine and iodine methods do, and I think the electrolytic methods do, too.

Mr. Thomas—We have heard many papers this afternoon on the isolation and determination of nonmetallic compounds in steel. Would someone care to relate the effects of nonmetallic compounds on the properties of steel in the various grades of steel?

Dr. McKaveney—Not being a metallurgist, I have difficulties in fully answering this question. I know, however, that in medium alloy steels such as Type 4340, nitralloy, etc., the silicates and aluminates are most damaging to fatigue strength, ductility, and notch toughness. The determination of these oxides, therefore, is important to the metallurgist and to metallurgical control.

Dr. Melnick—Besides oxides, the determination of nitrides is also important. The addition of aluminum and vanadium can prevent strain aging by forming aluminum and vanadium nitrides, thus tying up nitrogen. Hot shortness is prevented by adding manganese and titanium to form these sulfides in preference to iron sulfide. It should be remembered that inclusions are not always damaging but often are desirable to obtain certain properties in steel.

Dr. Andrews—I should like to add that, in addition to aluminates and silicates, particles of aluminum oxide also have a detrimental effect on the fatigue strength of steel. In some steels which were rolled or forged, we observed alumina particles which did not flow with the steel and, because the particle did not yield, produced a cavity around it. If there are soft or plastic inclusions such as manganese sulfide in the steel, they will flow around the hard particle and fill the cavity so that it no longer appears as a void. We believe, however, that these cavities, whether filled or void, are the beginning of cracks. This is nothing new, of course, and I mention it only to further illustrate examples in answer to the question.

Another interesting thing about inclusions is that they could set up local stress areas. These stresses could be sufficient to create local fatigue areas. For example, if a steel cools down and this steel contains titanium nitride inclusions, stresses could be set up by the different thermal expansion between the steel and the inclusion, which could create local fatigue. We are engaged in calculating the stresses due to differential thermal expansion between inclusions and the metal. It is hoped that this will tell us more about the effects of inclusions on the properties of steel.

*Mr. Wilson*⁴—Could the panel tell me what the simplest extraction

⁴ A. Finkl & Sons Co., Chicago, Ill.

procedure is for oxide inclusions in medium alloy steels, such as 4340, 8620, etc., and what method it would recommend for a medium-size research laboratory that wants to study and identify oxide inclusions in these types of steel? These steels are intended for free-machining applications, and we want to relate variations in types and amounts of oxide inclusions to variations in free-machining.

Dr. McKaveney—In our experience the primary oxide in fully killed steel is aluminum oxide, Al_2O_3 , and, for most practical purposes, it suffices to determine it. The quickest method for determining Al_2O_3 is to determine the acid-insoluble aluminum in a 5-g specimen of steel. The acid-insoluble aluminum is assumed to be Al_2O_3 . One can then subtract the oxygen equivalent to Al_2O_3 from the total oxygen determined by vacuum fusion, and the difference corresponds to the rest of the oxides, mainly silicon dioxide (SiO_2). As a rule, 90 to 95 per cent of the residue is Al_2O_3 .

Mr. Bandi—In my opinion, a cheap and quick method is the bromine methyl acetate procedure, but this method is only applicable to fully killed steels. Rimmed and semikilled steels contain a great number of oxides which are soluble in that reagent or in water. If the steel is killed with either aluminum or silicon, Al_2O_3 or SiO_2 is obtained. If the steel is not killed, there will be MnO and, in this area, manganese silicates and aluminates which can be water soluble or soluble in other reagents. One must be very careful and not apply a method to a type of steel for which it is not intended.

Mr. Pasztor—Perhaps we could better help you if you would tell us what information you are seeking.

Mr. Wilson—We want to compare machinability tests in various types and batches of steel.

Mr. Pasztor—In that case you are probably more interested in sulfides than oxides. Although certain oxides, such as silicates, may be of interest, sulfides determine the properties in machinability tests. Free-machining steels are low in oxygen. Sulfur is added to give the desired properties for free machining.

Mr. Wilson—I must disagree with that statement. Although the sulfides have a definite effect on the machining properties of steel, silica, alumina, and other oxide inclusions also affect these properties. The steels we are studying have about the same sulfur level and distribution and yet are markedly different in their machining properties.

*Miss Gladys Chalfonte*⁵—I am also interested in machinability studies, and I support the statement on the effect of oxide inclusions on machining properties. I am more interested in additives, such as selenium, bismuth, and tellurium, as well as other elements and their combination with oxygen, than in sulfides. We have also observed quite differing machining properties for steels containing approximately the same level and dis-

⁵ U.S. Steel Corp., Applied Research Laboratory, Monroeville, Pa.

tribution of sulfur. I believe that the great variations in their machining properties are due to the small amounts of additives such as bismuth, selenium, tellurium, etc., and their combinations with oxygen. Is there any connection between the oxides formed with these additional elements and the properties of a steel?

Dr. Andrews—I have a comment on leaded steels. We did some X-ray microradiography on steels containing lead and manganese sulfide and found Al_2O_3 particles surrounded by lead and manganese sulfide drawn out into lens-shaped forms with the hard Al_2O_3 particle in the center and the triangular spaces filled with lead or manganese sulfide. Additions of tellurium or bismuth result in complicated compounds which form an envelope surrounding the inclusions.

Mr. Weiss—In reference to Mr. Wilson's question as to a simple extraction procedure for oxide inclusions, I don't think that a simple extraction procedure is really what is needed here. From the magnitude of this problem, and from our own rather limited experience in determining structural constituents in free-machining steels, I venture to say that a thorough study is needed, using all the tools which are available. Besides the usual sulfides and oxides, there are complicated compounds resulting from the addition of bismuth, tellurium, and selenium. One must be very careful when selecting a method for isolating the metallurgically important compounds from the matrix because many of these compounds are rather unstable chemically. Furthermore, for subsequent identification and analysis it will be necessary to separate the residue into groups (oxides, sulfides, if this is possible), and this is not easy. I do not believe that isolation methods alone will provide all the needed information. Instead, information from electron probe microanalysis, X-ray microradiography, optical and electron microscopy, isolation methods, X-ray and electron diffraction, and others must be used in order to get a better understanding of the problem. I don't think that a simple test procedure will contribute much toward solving a difficult problem, and, although isolation methods have greatly contributed toward a better understanding of some metallurgical questions, they also have their limitations.

*Frank Byrne*⁶—Are the so-called nonstoichiometric compounds, which were mentioned earlier, really nonstoichiometric compounds, or are they undissolved fragments of imperfect crystals?

Dr. Andrews—I think nonstoichiometric compounds are real. In the case of titanium or vanadium carbide there is a VC or V_4C_3 . In many cases we can equate carbon, nitrogen, or vacancies to each other and can fill them between certain limits. This is particularly true of the nitrides and carbides and even more exact in phases such as M_3X and M_2X , which are nitride phases. FeO is the most noted case. The stoichiometric compound FeO does not exist, and the Fe:O ratio varies between certain

⁶ Westinghouse Research Laboratories.

limits. Another example is certain sulfides which are nonstoichiometric and for which we have good solid-state explanations. There may be difficulties in interpreting the data from isolated particles, but these nonstoichiometric compounds can be synthesized, and there is no doubt as to their existence.

Mr. Bandi—Are these not defect structures in the case of V_4C_3 ?

Dr. Andrews—Yes, they can be regarded as defect structures. In practice, and VC is a noted one, the available spaces around the metal atom are not completely filled by carbon atoms but only 75 to 100 per cent of the space is occupied by carbon atoms. The noted hexagonal case is where epsilon carbide varies between Fe_2C and Fe_3C . This is just due to the fact that one can maintain a structure with the minimum sites filled, yet one can only fill to the maximum; so one can end up with a structure somewhere in between. This makes things more complicated for the analyst to say what, precisely, it is.

Mr. Hague—I should like to comment on this session in general. I was very much interested in seeing Dr. Andrews' slides this afternoon. Some years ago, we at the Bureau studied stability ratios for Types 321 and 347 steels and used X-ray diffraction to work out some of the problems. We observed the same slippage in parameters which I thought I detected in Dr. Andrews' slides. We were able to show that one had to take both carbon and nitrogen into consideration in figuring the stability ratios for Types 321 and 347 steels, and one could not make a complete analysis with X-ray diffraction alone. This was brought out again during this symposium. Methods such as Beeghly's bromine methyl acetate method for the isolation of nonmetallic compounds has helped us in the past, and the new applications, which were presented during this meeting, are interesting. The electron probe microanalyzer offers a new possibility to analyze very small areas *in situ*, and the use of differential thermal analysis-effluent gas analysis, which was discussed by Dr. Melnick, has given us a new way to answer some of the problems which we could not do in the past except by inference.

Mr. Raybeck—I should like to ask Dr. Andrews how he identified vanadium nitride. We seem to be having difficulties identifying vanadium nitride by X-ray diffraction in our laboratory. We synthesized vanadium nitride in the laboratory and also purchased vanadium nitride, yet our X-ray diffraction results always show the compounds to be vanadium carbide containing 14 per cent carbon. Is there a distinct difference between these two compounds so that X-ray diffraction can be used to distinguish them?

Dr. Andrews—The structures for vanadium carbide and vanadium nitride are very similar, since their lattice parameters are close together. Using a focusing camera, we were able to distinguish between them quite easily. This is not an uncommon problem. Usually one must expect both the

carbides and nitrides of vanadium, titanium, and columbium when these elements are present in the steel. Titanium carbides and nitrides are easiest to resolve. I should add that the nitrides and carbides of vanadium, titanium, and columbium are obtained as separate phases, that is, they do not occur together in the same particle. I think the nitride forms in the melt and the carbide is precipitated out on cooling.

Mr. Pasztor—Dr. Andrews, have you ever observed V_3N in your isolates?

Dr. Andrews—Yes, I have; V_2N or V_3N are hexagonal, for both carbides and nitrides. Vanadium always dissolves molybdenum, which often results in complex solid solutions.

*T. D. McKinley*⁷—The electron probe microanalyzer has been put to many uses in the past few years. I am interested to hear about the extension of the probe to the detection of soft X-rays, either for lighter elements or for examining small volumes. I know it can be done, but the question is how well can it be done? Once certain problems in instrumentation are overcome, there will still be a number of problems to be solved such as line shifts, profile shifts, etc. Would Dr. Heinrich comment on some of these problems?

Dr. Heinrich—The present difficulties with quantitative analysis in the normal wavelength range will be increased by going to the longer wavelength. It is difficult to compare absolute intensities of lines if these lines are really bands of varying shape, position, and width. It is also questionable whether the intensity of the relationship is as simple as one assumes, because valence areas are involved in the formation of these lines. On the other hand, there is still a lack of fundamental data. One difficulty that is usually encountered is that the X-ray absorption coefficients are not fully known even in the region from 1 to 8 Å for nickel, copper, and gold, which are currently used as filters. It will take a lot of painstaking work to fill the many empty pockets in areas where the physicist, who began this work, is no longer interested and the chemist, who now needs to work with it, has not yet done so.

*G. Rengstorff*⁸—In studying the formation of inclusions by deoxidizing with silicon and aluminum, I have observed a complex aluminum iron oxide called hercinite. In the work which I did it seemed to appear quite frequently, not as an equilibrium phase, but as something which occurs during the early stages of the deoxidation process. There was no mention of this compound in any of the papers presented during this session. Is the absence of this compound due to the materials studied, because of the extraction techniques employed, or does this compound not exist in steel?

Mr. Bandi—I think this is due to poor extraction techniques, which could destroy this compound either by acid or water leaching. We do not know enough about this yet.

⁷ E. I. duPont de Nemours & Co., Inc., Wilmington, Del.

⁸ Battelle Memorial Inst., Columbus, Ohio.

Dr. Andrews—We found this structure with a microscope in the micro-structure and regard it as a spinel-type oxide. There are many phases which look very much like it under the microscope, but hercinite can be recognized by its lattice parameters.

Mr. Pasztor—First of all, we do not have a method for isolating complex oxides. Secondly, referring to the paper we presented this afternoon, after isolation we analyze the metal contents spectrographically. Therefore we cannot say whether or not complex oxides are present, nor what type, but can make only a statement as to what metals are present in the residue.

Mr. Raybeck—If reagents attack this oxide, I should like to suggest trying direct chlorination. We were able to isolate fayalite from steel by direct chlorination, and this might be a possible approach for you. The method is rather simple. The sample is chlorinated in a platinum boat and carbon is burned off in air leaving the oxides behind.

Dr. McKaveney—I should like to ask Mr. Beeghly about the prismatic type of aluminum nitride and his experience with the bromine methyl acetate method for isolating nitrides. What is the difference between the prismatic type versus needlelike aluminum nitride crystals?

*H. Beeghly*⁹—Looking through the literature, one finds that aluminum nitrides can be either a very stable or a very unstable compound. In steels, particularly in fine-grain steels containing 0.02 to 0.05 per cent aluminum, the aluminum nitride seems to be rather unstable. This we observed by dissolving this type of steel in hydrochloric acid, and there was little nitrogen left in the residue. The ester halogen method was developed to extract nitrides from steel without decomposing them. In testing the ester halogen method, we prepared steel from pure iron and added aluminum to it to form nitrides for our studies. By heating the steel to 2000 F and cooling it quickly, we could not recover aluminum nitride with the ester halogen method either, but when the steel was cooled slowly, we could. With larger amounts of aluminum, approximately 0.5 to 0.75 per cent, and heating to even 2500 F, by cooling rapidly we were able to recover aluminum nitride which seemed to be relatively soluble. This illustrates that under different conditions we were able to obtain different types of aluminum nitride which were either more or less stable. During the past few years several patents were issued to manufacturers of very stable aluminum nitrides. These are used to make laboratory crucibles which are stable indefinitely in air. Other publications also show stable aluminum nitride compounds, and it is reasonable to expect that some of these stable nitrides can be formed in steel.

*Steven Eisner*¹⁰—Assuming that the particles which were extracted by the various methods are the same as in the matrix, have studies been made to verify that the particles were not changed during extraction, such as

⁹ American Chemical Society, Washington, D. C.

¹⁰ Behr-Manning Co., Troy, N. Y.

metallographic observations or the use of electron microscopy to observe the edges of the particles before and after extraction?

Mr. Bandi—Most of our work was directed toward the identification by X-ray and electron diffraction, but on occasion we had optical or electron microscopic pictures taken. These were photographs of oxides which showed sharp needles before and after extraction.

Dr. Melnick—It is possible to take photomicrographs before and after dissolution, but I question the absolute value of such photographs and studies. When taking photomicrographs, a specimen has to be prepared and usually etched before even looking at it under a microscope. Therefore, one cannot be certain whether or not a particle was attacked by the etchant.

Dr. Andrews—Microscopic observations have been used, and I think this provides an interesting observation. A specimen can be observed under the metallograph, and the extracted particles can then be observed under a petrological microscope, and the shape and size and detail such as edges of particles can be compared. Also, small particles can be seen with the electron microscope before and after extraction. If certain particles which were seen in the steel should not appear in the extracted residue, then one can conclude that these particles either were attacked, or were not recovered by the collection procedure used. In any case, one gets an idea as to whether or not the residue contains the same particles as were observed in the matrix. I think that microscopic observations should be used more often, since this is a direct observation and one can see what the dissolution method is doing.

*Don Ryan*¹¹—During this session newer methods for the isolation, identification, and determination of nonmetallic inclusions were discussed. Would members of the panel care to comment on what the value of the metallograph is? The metallograph has been used for many years, and I am wondering how it rates compared to these newer methods.

Dr. McKaveney—One has to be very careful when identifying inclusions with the metallograph. For years our metallographers in the mill identified the aluminum nitride particles I spoke of before as alumina. A good metallographer probably would not make that mistake, but the interpretation is not easy.

Mr. Bandi—Aside from difficulties in identification, there are many inclusions and other particles which one does not see with a metallograph.

Mr. Ryan—This is the reason I raised the question. Judging by the discussion, I should think it might be best just to rate the inclusions for size but not try to classify them as compounds. However, today all steels are rated and classified metallographically, and this may be of very limited value.

Mr. Bandi—I agree that the metallograph has limited applicability, but the extraction methods cannot always separate the various particles from

¹¹ National Forge Co., Irvine, Pa.

each other and thus provide complete identification. In order to completely describe inclusions in steel, one has to use all of the tools available, and even then it is not always possible to give a complete statement as to type, size, and distribution.

Mr. Weiss—Not being a metallographer, I may have missed your question, but I believe you were referring to the classification of inclusions using the J&K chart. As far as I know, the J&K chart does not identify inclusions as compounds but rather classifies them into groups, which are called *A*, *B*, *C*, and *D*. This means that the chart provides only a general classification but does not claim to identify compounds. I should think that a method capable of giving more accurate information would be desirable to have. On the other hand, the classification from the J&K chart gives some information, and this is better than no information at all.

Mr. Weiss—I have a general question for members of this panel. In reading various publications on the subject, I have the feeling that we are headed toward confusion in terminology. We talk about inclusions, nonmetallic compounds, microconstituents, etc. We often seem to be talking about the same thing, yet are calling it different names. Is anybody aware of attempts to standardize nomenclature?

Dr. Andrews—Microconstituents seem to cover the whole lot, but this could be subdivided to better describe metallurgically important phases. I agree that most of the time people call something a name, and they know what they are talking about, but the next person may not.

Mr. Bandi—I should like to classify them as phases rather than compounds, such as endogenous and exogenous oxides. This follows past standard practice of describing an inclusion depending on whether the oxide was formed by deoxidation practice or as a result of contamination from brick linings, etc.

Dr. Melnick—I think there is a need for standard nomenclature. Today we talked about nonmetallic compounds, but there also are intermetallic compounds in other phases. I think standard nomenclature would be desirable, but I am not aware of any attempts in this direction.

Mr. Pasztor—I should like to ask Mr. Beegly for his comments on that.

Mr. Beegly—As far as I know, there is no agreement or understanding on this matter. Generally, chemists speak a language that other chemists understand, and metallurgists speak a language that other metallurgists understand, but when chemists talk to metallurgists, or metallurgists talk to chemists, one usually doesn't understand the other. For example, if a chemist talks about a stable compound to chemists, he understands one thing, and the metallurgist thinks about something else. It is difficult to define in simple language all that is happening, and it is even more difficult to get different people to agree to some simple definition. I suspect it would be most difficult to arrive at common nomenclature, but it certainly would

be very helpful if authors would define the terms they use in understandable language so that it can be understood by all and the experiment duplicated by anyone who wishes to do so. Although there seems to be no easy way to arrive at standard nomenclature, I agree that an attempt should be made in that direction, and until something is done, each author should define his terms.