GENERAL DISCUSSION

MR. V. N. KRIVOBOK\(^1\) (presented in written form).—The three papers by Ebling and Scheil; Buck, Heger, Phillips and Queneau; and by Binder and Brown are so closely related on the basis of their subject matter that it appears proper to discuss them as an entity rather than separately, although each one provokes separate and individual thoughts and questions.

My first desire is to mention the common denomination for all three papers and that is their merit. The reader is at once impressed with the mass of data, most carefully secured. I wish to stress also the excellence of the metallographic work and the minute care which was obviously exercised in preparation of the metallographic evidence.

A simultaneous study of the three papers poses at once an old, yet so important, question: namely, which laboratory test is to be accepted as a "reliable" one. The word "reliable" is selected advisedly to mean that such test or tests would characterize the quality of the steel as it goes into service, predict its performance in actual installation, and reduce all other tests to be only supplementary. What we learn in this connection is this: Mr. Buck finds that low-carbon stainless steels, including 18-8 Mo and 18-8 Mo Cb, exhibit satisfactory corrosion resistance in the copper sulfate-sulfuric acid test after certain prior treatments, while in the boiling nitric acid test these steels had satisfactory corrosion resistance only under certain conditions of pretreatment and were unsatisfactory after other pretreatments.

Mr. Ebling is fully aware of the importance of various test methods and of the variables likely to influence such test methods. In fact, Mr. Ebling’s description of such variables is masterful. In the evaluation of the alloys which Mr. Ebling studied, he accepted the copper sulfate-sulfuric acid test and in explanation of his selection writes as follows: “Since this solution is generally used and is found in many specifications, it should be adopted as a standard testing solution for intergranular attack.”

Mr. Binder has used four different corrosive media, but has the following to say: "If carefully conducted, the boiling 65 per cent nitric acid test has been shown by wide experience to be very dependable in that both consistent and reproducible results are obtained.”

Thus we find that three distinguished and careful investigators seem to differ not in their evaluation of testing methods, but in their preference for a specific test.

At first, it might appear that this conflict is regrettable and confusing. This observation leads Mr. Buck to make a very pertinent statement which is as follows: “This conflict in results [he refers to the copper sulfate and boiling nitric acid tests] emphasizes that the concept of satisfactory and unsatisfactory resistance to intergranular corrosion is entirely dependent upon the specific conditions of testing. Unless this is

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\(^1\)Metallurgical Engineer, The International Nickel Co., Inc., New York, N. Y.
recognized, the development of very useful materials may be thwarted by acceptance of the idea that laboratory corrosion tests are reliable indices of service performance for conditions differing from those under which the acceptance tests are made."

One must remember, however, that although the matters under study were similar, they were not identical. The results of the studies disclosed not only experimental truths, but also furnished the explanation for each observation and this explanation is that while intergranular corrosion after various pretreatments is quite similar, the cause of this corrosion is not identical.

This is particularly important in the case of the newest alloys, that is, of very-low-carbon content. We are now faced, so we are told, with the possibility of formation, under certain conditions of heat treatment, of sigma phase in addition to carbide precipitation. In the work of Buck it is shown that the copper sulfate technique is impotent and the use of the boiling nitric acid test is obligatory to detect the presence of sigma. The copper sulfate testing procedure is satisfactory in detecting harmful carbide precipitation.

A number of interesting observations are brought out in the paper by Ebhng. One of such is the statement which will be found on page 129 that with only one exception the weld metal showed no attack regardless of the previous heat treatment. This is not the first time this observation has been made. The author of this discussion has observed it on more than one occasion but has not as yet been able to formulate the proper explanation. The explanation by all authors would be awaited with interest.

In the same paper on page 131 we find the statement that the regular type 316 stainless steel does not respond very well to a stabilizing heat treatment. It is assumed, in view of the previous discussion, that by stabilizing heat treatment the author means an agglomeration of carbides. Further it is stated that this alloy may become sensitized and subject to intergranular attack even under such previously little appreciated condition as the slow cooling after the stabilizing heat treatment. Or even the sensitization at as low a temperature as 800 to 900 F. for 500 hr.—a rather long treatment—results in the complete loss in resistance to intergranular attack. May it not be proper to suggest, in the light of the work of Buck, that the formation of sigma phase rather than carbide precipitation may be the reason for the observed behavior? In making this suggestion one must have the data on the possible significance of carbon content as will be mentioned later in specific reference to the work of Mr. Binder and Mr. Ebhng.

An intriguing statement is to be found on page 134 of Mr. Ebhng's paper. This is in reference to one particular heat of type 316Cb steel which is stated to exhibit "abnormal behavior." It is not clear as to just what is meant by abnormal behavior and what is the criterion for judgment between the behavior that is normal and abnormal. If it is to be understood that this particular heat did not yield the same results as other heats, ostensibly of the same composition and ostensibly similarly heat treated, would it not be proper to follow this heat up and see what may be causing this abnormal behavior?

In this connection it is interesting to note that the first of the type 316 Cb heats, (Table IV of Mr. Ebhng's paper) is one of those that showed abnormal results. Could it be that the abnormal results of this heat are explained on the

basis that the higher carbon content prevents sigma phase during the "stabilizing treatment"? One might also wonder whether or not the low chromium content of this particular heat had anything to do with its abnormal behavior.

The last paragraph of the same paper records the fact that low-carbon type 316 alloys are not immune to intergranular attack if sensitized for long periods of time at certain temperatures. The exact reason for the intergranular attack is not specifically stated, and in view of our previous experience with the phenomenon of sensitization, one would be quite justified in assuming that this sensitization is brought about by carbide precipitation. The possibility of sigma formation as shown by Mr. Buck and others is clearly indicated, and it would seem desirable if Mr. Ebling would clarify his views concerning this possibility.

Mr. Binder in his paper has favored us with much in the way of interesting studies. It is interesting to note at once that there is reassuring correlation between his findings and those of Buck: namely, that stainless steels may be sensitive to intergranular corrosion because of the formation of intermetallic phase (sigma) or carbide precipitation, or both. The realization of the formation and possible presence of sigma phase under certain conditions of heat treatment should certainly be followed by studies of the phase relationship in these alloys with the ultimate hope of finding an alloy free of sigma phase. To be sure, sigma further complicates matters and one must hope that laboratory studies will be continued and will be followed in some manner by observations of service performance so that another big, bad wolf is not added to the much discussed and sometimes over-stressed carbide precipitation.

On page 152 of Mr. Binder's paper appears a statement that either by increasing the molybdenum content to 3 per cent or by adding columbium to the 2 per cent molybdenum in extra-low-carbon steels we cause intergranular attack. I am interested in knowing if any differentiation is intended between extra-low and normal carbon?

Examination of Table I shows that average corrosion rates for 18-8 Mo Cb alloys (Nos. N-110 and K-293) are practically the same. It is the fifth period values that are different in one case (heat treatment 2). One wonders if Mr. Binder is not emphasizing this difference.

I should like to ask for a bit of elucidation on the conclusions of Mr. Binder which are stated on page 169. It is stated that in steels containing about 0.06 per cent carbon, the susceptibility to intergranular corrosion is caused by carbide precipitation. Is it Mr. Binder's thought that in steels of 0.06 per cent or higher carbon, carbide precipitation only takes place and no sigma phase formation is to be expected? Is it also his belief that in extra-low-carbon steels containing 3 per cent molybdenum or in molybdenum-columbium steels with carbon up to 0.06 per cent, sigma phase is the only reason for intergranular attack?

One notices with satisfaction that apparently Mr. Binder does not consider it important enough to complicate his excellent paper by considerations of influence of such matters as variation in nickel and nitrogen contents on corrosion rates in boiling nitric acid. The nitrogen content of alloys L-295 and M-327 is given as 0.029 and 0.035 per cent, respectively. In a recent paper by the same author and his associates, increased rates of corrosion (by nitric acid) are attributed to nitrogen contents in excess of 0.02 per cent (for nickel between 9 to 10 and 11 to 12 per cent). Perhaps further experimentation and study of results justified the moderation of the original conclusions.
It was my privilege to discuss personally and in detail with Mr. Buck and his coauthors their excellent and fruitful paper. Most of the points discussed dealt with certain deductions which one might make after studying the work.

Further study of this interesting paper revealed additional value in it. The observation—and the suggestion—that the high nitrogen content of heat No. 35, namely, 0.11 per cent, may be responsible for the observed formation of sigma is very interesting. The writer, in his Campbell Memorial Lecture in 1934, observed the influence of nitrogen on changes in the structural constituents of chromium-containing alloys. As Mr. Buck suggests, this particular finding should be further investigated.

Mr. Buck disagrees with Mr. Ebling. According to Mr. Buck, a stabilizing treatment of low-carbon 18-8 Mo (see p. 74), namely, 2 hr. at 1625 F, appears to have merit: "12 of the 20 heats so treated responded to the extent that their corrosion rates were less than the acceptable limit of 0.002 in. per month."

Mr. Ebling feels that stabilizing heat treatment (1650 F. for 2 hr.) does not promote any beneficial results.

This difference in conclusions is complicated by the fact that Mr. Buck's work indicates obvious usefulness of the boiling nitric acid as compared with the copper sulfate test. Yet here is a case of copper sulfate showing the presence of a harmful constituent (whether it be carbides or sigma), while nitric acid did not. I believe that in answer to this query it will be pointed out that the time of sensitization in the two cases was vastly different. This all-important observation should enable us to differentiate between cases of welded construction—for which apparently the steel in question would be satisfactory—and service at elevated temperature in which case the same steel may or may not be appropriate, depending among other things on the actual service temperature.

The discussion of corrosion resistance of welded low-carbon stainless steels presented by Mr. Buck is very clear and useful. Of singular interest are the data which show that low-carbon molybdenum and columbium-bearing 18-8 is not as reliable as the same type of steel with higher carbon content. Those who anticipated finding a solution for the carbide precipitation problem in low-carbon type 316 stainless steel by additions of small amounts of columbium may want to study Mr. Buck's report very carefully.

(Subsequent oral discussion).—It is my studied opinion that the work described in the papers contains much data on theoretical studies of fundamental observations. The discussion of the papers was thoughtful, technical, and of considerable interest to research workers. It would be highly desirable to attempt a correlation of the data contained in the numerous papers. This correlation would prove to be, I am quite certain, a valuable addition to our literature on the corrosion behavior of stainless steels.

Quite recently—and in this I am voicing the thought of a colleague—a most interesting paper appeared in the December, 1948, issue of Metal Progress, entitled "The Austenitic Stainless Steels—American and British Practice Compared." Its author, a distinguished British metallurgist, F. H. Keating, raises a pertinent question, namely, why is it that in British and Continental practice stainless steels with carbon seldom below 0.09 or 0.10 per cent have rendered excellent industrial service? Why have we in the U.S.A. found it expedient or necessary to use austenitic stainless steels with carbon between 0.05 and 0.08 per cent; and now we attempt, and succeed, in producing steels with
carbon below 0.03 per cent. Where do we intend to stop? While in some applications a very low carbon content in stainless steels is justifiable, is it not timely for us to evaluate the British and Continental experience, and incidentally our own, and critically appraise our thinking as to under what conditions of service the necessity for such extraordinary low-carbon steels is a real one? We would find, I am certain, that such conditions are not numerous. It seems to me that this Symposium disclosed the dangerous tendency of emphasizing rather minute if not unmeasurable or reproducible differences in corrosion rates, attributing these differences to composition, primarily that of carbon, and creating the impression of the superiority of one kind of steel over the other which is not justifiable. While laboratory tests are of considerable interest and may provide valuable basic knowledge, we have to admit that the only indisputable corrosion test is that of active service record. Hence, it behooves us not to forget Mr. Keating's queries. Nor should we forget that the original purpose of this Symposium was to discuss the correlation between laboratory and service tests.

[See Messrs. Binders and Browns Closure, P. 179—Ed.]

MESSRS. H. F. Ebling and M. A. Scheel (authors).—Mr. Krivobok has done a fine job of discussing three papers dealing with the complex 18-8 molybdenum stainless steel alloy. He has raised questions regarding the causes for attack noted in the tests made by several investigators. These are good sound questions and it is difficult with our present knowledge or, we might say, “state of art” to reply with anything more than opinions. We are hampered in not having adequate tools for research. X-ray diffraction studies of the phases we are interested in knowing more about are difficult because usually the phase in question is too small for work of this kind. Our microscopic etching technique is progressing to the point of recognizing these phases, but identification is as yet uncertain and difficult. With this in mind we will try to answer some of Mr. Krivobok’s questions.

To begin with, we have confined our paper to test solutions specifically designed for intergranular corrosion testing. At the time these tests were proposed, the principal cause for intergranular corrosion was the precipitation of carbides. It is becoming more evident now that the cause for intergranular corrosion is not alone confined to carbide precipitation as we have heard in other papers presented as a part of this Symposium. We observed this fact about three years ago when it was noted that short-time sensitizing tests of low-carbon type 316 alloys never failed in the acidified copper sulfate test but showed poor corrosion resistance in the boiling nitric acid test. (Mr. Buck’s paper).

The conclusion we came to from these observations is that the acidified copper sulfate solution appears to attack alloy sensitized with respect to carbide precipitation. Since carbon apparently requires a large quantity of chromium to precipitate as a chromium carbide, it is suspected that the resulting chromium level adjacent to the carbides is lower than when other phases such as sigma are formed. Thus it appears that the acidified copper sulfate test is effective only when the chromium level of the areas in question are below a certain quantity. The nitric acid test attacks austenitic stainless steel alloys regardless of chromium level. It is observed that on fully-annealed specimens, nitric acid has a preferential intergranular attack for these alloys.

In reply to the effect of a stabilization heat treatment on regular type 316 alloys one must agree that it results in an agglomeration of carbides. However, an
equilibrium is established between the carbon in solution and the precipitated carbides. Apparently the amount of carbon remaining in solution after a stabilizing treatment is sufficient to cause sensitization of the alloy if it is slowly cooled or given a low-temperature sensitizing treatment. The question of whether intergranular attack is caused by carbide precipitation or some other phase is answered by the test results obtained in acidified copper sulfate solution.

In the tests using stabilization heat treatments on low-carbon type 316 followed by low-temperature sensitization at 900 and 1020 F., it was stated that no beneficial results were noted. This observation again was made with respect to results in the acidified copper sulfate test. In our own experience, and as we have seen in Mr. Buck's paper, the stabilizing heat treatment is beneficial with respect to tests made in nitric acid.

Mr. Russell Franks. —The four papers by: Buck, Heger, Phillips, and Queneau; Bloom and Carruthers; Brown, De Long, and Myers; Ebhng and Scheil take me back just 20 years to 1929 when the problem of intergranular corrosion in the present commercial 18-8 type of steel was being given a great deal of consideration. This problem is now well under control because of the knowledge gained in the application of these steels and the use of columbium and titanium to combat intergranular attack.

These papers have concerned the matter of which test or tests should be applied in determining the susceptibility of the 0.03 per cent carbon type of 18-8 steel, with and without molybdenum, to intergranular attack. It is acknowledged that carbon is one of the most influential constituents in the austenitic chromium-nickel steels in bringing about susceptibility to intergranular corrosion, and it goes without saying that if the carbon content is reduced to 0.03 per cent, improvement in susceptibility to this defect automatically takes place. The question we are faced with is whether this improvement will permit the steels to be used in the as-welded, and as-welded and stressed-relieved conditions even though the steels fail to pass the well-known nitric acid test but do pass the copper sulfate test after they have been given a sensitizing heat treatment. I don’t think that anyone who has had experience with these steels will doubt the fact that the nitric acid test has been of considerable value in appraising and improving the quality of the stainless steels, but even so I doubt whether we can safely predict service performance using nitric acid test results as the only basis.

It seems to me that we have now arrived at a point in the development of these extra-low-carbon stainless steels at which we must take another step. This step is to install equipment of the 0.03 per cent carbon 18-8 steel, and of the 0.03 per cent carbon, molybdenum-bearing 18-8 steel in the as-welded, and in the as-welded and stressed-relieved conditions and determine under service conditions whether the steels are usable. The service conditions to which I refer are corrosive environments at room temperature and at temperatures slightly above room temperature which generally represents the conditions ordinarily encountered in the chemical industry. I am not referring to temperatures in the range 800 to 1400 F. because at these temperatures the 0.03 per cent carbon steels without stabilizing elements have been found to exhibit susceptibility to intergranular corrosion when exposed to corrosion for long periods of time.

The authors of these papers should be
congratulated for their fine work on these important steels, and they are urged to continue their effort in order to establish the value of these 0.03 per cent carbon 18-8 steels.

Mr. M. H. Brown (author).—The immediate answer we are all seeking is whether the very-low-carbon stainless steel grades can be safely used as-welded, or in the as-welded and stress-relieved condition, for process equipment. I agree with Mr. Franks that we have reached the point where direct study through installation of actual operating equipment is in order and we are already making such installations in selected environments. However, we will never be in a position to define the limits to which the very-low-carbon grades, or for that matter the conventional carbon grades, can be safely employed until our understanding of the basic mechanisms involved is clarified through further research. Important progress has been recently made and we should intensify our efforts in that direction.

Mr. Stephen F. Urban.*—I think there are some fundamental observations that we have lost track of and that I should like to summarize in an attempt to clarify present inconsistencies. More specifically, the following observations are pertinent.

Normal carbon, regular 18-8 stainless steel, in its normally annealed state, will adequately pass the boiling nitric acid test and the copper sulfate test but will disintegrate in a very short time in both media if the material has been heated in the sensitization range to precipitate carbides. With normal annealing temperatures, stabilized grades like regular 18-8 are immune to failure in both the nitric acid and copper sulfate media. If we use annealing temperatures approximately in excess of 2050 F. up and dissolve quite a few of the carbides and subsequently sensitize, we again obtain rapid failure in both testing media. If, on the other hand, we use normal annealing temperatures and sensitize, we find that both the columbium and titanium-stabilized grades pass the copper sulfate test and that in nitric acid, the columbium grade is relatively insensitive while the titanium grade shows high corrosion rates.

Of course, there must be a reason for the foregoing set of observations and we have all been struggling with this job for some time to develop answers. I won’t go into all the details of the data but I should like to present some trends. What this situation amounts to is that the temperature range for carbides to precipitate unfortunately is overlapped by the temperature range where sigma forms, thus making analysis of the problem extremely difficult. Briefly, we have used Tioiano’s technique, and in the so-called sensitized state have found in the titanium-stabilized steel definite sigma. This, I believe, explains why this steel in the condition stated meets the copper sulfate test but exhibits a high corrosion in concentrated boiling nitric acid.

To establish something of the nature of what is going on, heat treatments intermediate between the annealed treatment and sensitization were used from which it was found that some of these were instrumental in producing in the so-called sensitized state a high resistance to nitric acid. More specifically, 1600 F. for any reasonable time was not too satisfactory. A temperature of 1800 F. seemed to behave erratically whereas a heat treatment from 2 to 4 hr. at 1700 F. yields a material that on subsequent sensitization yields in concentrated boiling nitric acid corrosion rates that are fully equal to those obtained with the columbium

* Director of Research, Titanium Alloy Div., National Lead Co., Niagara Falls, N. Y.
grade under the same conditions. In other words, for some unknown reason, the 1700 F. heat treatment stabilizes the austenite so it is not disposed to form sigma on subsequently lower heat treatments. Under these conditions, type 321 meets both the copper sulfate and the boiling nitric acid test.

Though partly related to the above but really a discussion of Mr. Brown's and co-workers' paper, I wish to make a few comments. Mr. Brown has stated that he and his group have obtained a very excellent correlation between the boiling nitric acid test and field service. This I do not question; however, I wish to point out that in so far as I am aware, Mr. Brown's correlation is based on straight 18-8 alloy, and I am not aware that he has a similar correlation between laboratory and field tests on the stabilized grades.

In further regard to the boiling nitric acid test and what I believe is related to the presence of sigma, it is specifically brought out in Mr. Buck's and co-workers' paper that in the sensitized state, the corrosion rates increase as the molybdenum content is increased in low-carbon 18-8; unless as shown by them, the treatment of 1625 F. is used prior to sensitization. In view of my foregoing remarks on titanium stabilized grade, I strongly feel that a 1700 F. heat treatment would be preferable. The work of Buck and coworkers ties in neatly with the paper published several years ago by Binder and coworkers which paper showed that the corrosion resistance of austenitic molybdenum-bearing stainless steels stabilized with columbium exhibited in the sensitized state low corrosion resistance to nitric acid. They showed that in the compositions they were dealing with, sigma formation was easy to attain but did not point out that this was the cause of poor corrosion resistance in boiling nitric acid. The same steels did pass the copper sulfate test.

Regarding the paper by Mr. Ebling and Mr. Scheil which deals solely with the behavior in copper sulfate solution of various compositions having various heat treatments, I feel that their work gives us much more data than we have had before on intergranular corrosion as evaluated by that specific medium. Regarding the test itself, I wonder whether they would care to comment on the use of 0.5 per cent boiling sulfuric acid solution that is not buffered with copper sulfate. My reason for bringing up this point is that where we were not sure as to whether we had a slight attack or no attack after 500 hr. in the standard copper sulfate solutions, we have been able to obtain definite evidence of attack within 48 hr. with 0.5 per cent of boiling sulfuric acid.

Mr. M. H. Brown (author).—With reference to Mr. Urban's question as to whether the presence of the sigma phase may not be partially responsible for increased corrosion rates in the nitric acid test of stabilized alloys in certain conditions of heat treatment, I think this is very possibly true. If so, the question is immediately raised as to how serious the presence of sigma may be under service conditions which do not involve nitric acid. We cannot supply information on this point since we have intentionally avoided the use of such material for service equipment. In a few instances grooving has occurred at the weld metal-parent metal junction in type 347 equipment. This effect is, of course, similar to that resulting from a very high annealing temperature followed by exposure in the sensitizing range, and is believed principally due to carbide precipitation. We have practically no service experience on type 321, but laboratory evidence indicates it to be more susceptible to such grooving than type 347.

In comment on Mr. Urban's comparison of the behavior of type 321 and type 347 in the nitric acid test, our results on
commercially annealed material are in agreement, that is, both showed low rates as annealed, but type 321 usually exhibited a very high rate after a sensitizing treatment whereas type 347 was relatively insensitive to such treatment. However, if the specimens were exposed for 2 to 4 hr. at 1600 F. or 1700 F., type 321 normally exhibited a considerably increased rate as compared to annealed material, but a subsequent sensitizing treatment had little further effect, whereas the behavior of type 347 was generally the same as in the annealed condition.

Mr. E. G. Holmberg⁶ (by letter).—After reviewing the papers of this Symposium, the writer is left with the feeling that a tremendous amount of good work has been done in an effort to understand better the limitations of the three principal methods employed to detect sensitization in austenitic type 18-8 stainless steels.

It obviously is the purpose of these tests to determine: (1) the efficiency of a heat-treating procedure, and (2) the effect of heating within the sensitizing range subsequent to heat treatment. The data obtained for exposure of the various austenitic stainless alloys to these test conditions should not be misconstrued to be an indication of how they will perform when exposed to media of an entirely different chemical composition. As shown in the paper presented by Messrs. Brown, De Long, and Myers, an increase in the percentages of silicon and molybdenum in the 18-8, 18-8 Mo and FA-20 alloys will result in each alloy having a lower corrosion resistance to 65 per cent boiling nitric acid; however, it is well known that these same additions are extremely beneficial in improving the resistance of these alloys to most concentrations of hot sulfuric acid.

The ability to obtain consistently reliable and reproducible data with the 65 per cent nitric acid corrosion test makes it the preferred method for determining the presence of precipitated carbides and intermetallic compounds responsible for intergranular corrosion in 18-8 type stainless steels. The mass testing of specimens in 65 per cent nitric acid, as described in the paper presented by W. B. De Long is of particular merit, as it will permit testing a large quantity of specimens at considerably less cost than the procedure recommended by A. S. T. M. Method A 262-44T⁸ and should encourage greater use of the 65 per cent nitric acid test in production control.

To the writer it seems a fallacy on the part of consumers to accept unstabilized stainless equipment that has not been quench-annealed from 1950 to 2000 F. after fabrication. Even though sufficient experience has been had with improperly annealed stainless equipment in handling a particular media to know it will not corrode intergranularly, it is always possible such equipment may be useful at a later date in another service where corrosion of this type will occur. The additional cost necessary to properly anneal expensive stainless equipment to be assured its future usefulness will not be limited is well justified.

Mr. R. H. Aborn⁷ (presented in written form).—Throughout all of the papers presenting data on intergranular corrosion tests, it is notable that there is little, if any, discussion of the mechanism of behavior of the various test solutions. Years ago, when we were concerned with evaluating the susceptibility of austenitic stainless steels to intergranular corrosion, we were intrigued with the behavior of copper in the CuSO₄-H₂SO₄ test. It appeared to us then that the most probable mechanism was that the copper ion was able to carry oxygen to

⁶ Alloy Steel Products Co., Linden, N. J.
⁷ Assistant Director of Research U. S. Steel Corp., Kearny, N. J.
plug the holes made by $\text{H}_2\text{SO}_4$ in the protective "film" or layer. This concept is supported by evidence that $\text{K}_2\text{Cr}_2\text{O}_7$, known to be an oxidizing agent, is a successful substitute for $\text{CuSO}_4$ in this test. Sometime later Schroeder and associates in the Bureau of Mines proposed that in order for an intergranular test solution to be effective, it must contain in addition to the corroding agent, a second agent capable of protecting the body of the grains themselves. Such a concept applied to the three solutions discussed in this Symposium seems to correlate well with the observed behavior. In the case of $\text{CuSO}_4$-$\text{H}_2\text{SO}_4$, the protective agent is the $\text{CuSO}_4$ or copper ion and the corroding agent is $\text{H}_2\text{SO}_4$; in the $\text{HF}$-$\text{HNO}_3$ test the protective agent is $\text{HNO}_3$ or NO$_3$ ion and HF is the corroding agent; in the boiling $\text{HNO}_3$ test, De Long's paper in this Symposium provides striking evidence that the corroding agents are the metallic ions, particularly Cr, resulting from solution of the metal, whereas the protective agent is again $\text{HNO}_3$ or the NO$_3$ ion. This interpretation clarifies the longstanding anomaly in the use of nitric acid, as under certain conditions it can aid in the formation of a protective "film" whereas under other conditions such as the boiling nitric acid test it can destroy the "film." It is possible that the addition of copper ions might offset this destructive action on the body of the grains and provide a more wholly intergranular corroding medium.

Our observations on the mode of attack of these three test solutions indicate that only the $\text{CuSO}_4$-$\text{H}_2\text{SO}_4$ solution is limited entirely to intergranular corrosion. By adjusting the $\text{CuSO}_4$ content to 1 per cent, the minimum practicable level to avoid general corrosion of 18-8 alloy by boiling 8 per cent $\text{H}_2\text{SO}_4$, we were able to show that $\text{CuSO}_4$ protects only that metal which contains more than about 12 per cent chromium inasmuch as this particular solution produces general attack on some type 410 steels. The $\text{HF}$-$\text{HNO}_3$ test and the boiling nitric acid test produce both general and intergranular corrosion apparently because the NO$_3$ component is unable to provide full protection to "normal" grains in the presence of the corroding components. Both of these solutions, of course, are more sensitive to a small degree of metal damage than is the $\text{CuSO}_4$ solution. This greater sensitivity of the $\text{HF}$-$\text{HNO}_3$ solution in comparison with the $\text{CuSO}_4$-$\text{H}_2\text{SO}_4$ solution is shown in the accompanying Fig. 1 from the work of J. J. B. Rutherford at this Laboratory in 1934. Owing to its greater sensitivity, the $\text{HF}$-$\text{HNO}_3$ solution will reveal intergranular attack over a broader range of depletion of chromium or temperature of exposure.

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8 Schroeder, Berk, and O'Brien, Bulletin 404, Railway Engineering Association, June, 1938.
However, because neither the HF-HNO₃ nor the boiling nitric acid solution produced pure intergranular corrosion, we standardized on the CuSO₄-H₂SO₄ solution as the most accurate medium with which to study intergranular corrosion, realizing that it was not as sensitive as the other two tests but for practical purposes provided an ample degree of sensitivity.

We believe that any laboratory test can only be interpreted in terms of the specific conditions of that test, and that the ultimate criterion of suitability of any given stainless steel product can only be its behavior under the actual conditions of intended service.

With reference to the test terminology in the paper by Messrs. Ebling and Scheil, I should like to recommend that test names be objective, with the aim of indicating, so far as possible, the type and nature of the test. We merely adapted the CuSO₄-H₂SO₄ test to our needs. As the concentrations of CuSO₄-H₂SO₄ are close to 1 per cent and 8 per cent, respectively, I suggest this modification be called the 1:8 CuSO₄-H₂SO₄ test, and it might be further abbreviated to copper-sulfuric test.

Mr. Francis B. Foley.—After listening to the discussion of the papers at these sessions I feel compelled to make the observation that in the great majority of cases purchasers of stainless steel know in advance for what purpose it is to be used and its suitability for that service. Their concern then is to be sure they are obtaining good material of the type they have ordered. The tests under discussion were designed to insure in so far as practicable, that the material is of a quality the purchaser has a right to expect. They are not tests which tell whether or not the material will withstand attack under conditions other than those imposed by the test conditions. These laboratory tests serve as a check on the metallographic structure and the chemical composition of the metal.

Messrs. F. K. Bloom and M. E. Carruthers (authors' closure).—In considering the many excellent papers presented at this symposium, it appears that several questions of long standing regarding evaluation tests, while not completely resolved, have at least been brought clearly into focus. In addition, several new and interesting metallurgical facts have been uncovered.

The work of Messrs. Larrabee and Fetner and of Comstock offer strong support to the oft-made statement that no single laboratory evaluation test is a reliable index of the likely service performance of stainless steels. This point deserves emphasis. Some of the corrosion tests now regarded as standard were intended originally only as a measure of the adequacy of the heat treatments applied to the material. The trend toward accepting these tests as a measurement of all-around corrosion resistance is clearly dangerous and can easily impose many unnecessary limitations on the use of these alloys.

The investigations of Binder and Brown; Buck, Heger, Phillips, and Queneau, as well as our own studies, show clearly that the present laboratory tests to evaluate susceptibility to intergranular attack may give appreciably different results. This is further reason, again, for caution in accepting any single test as an index of general resistance to corrosion.

The failure of these tests to correlate is due in part to the fact that some of the media, notably boiling nitric acid, will cause intergranular attack for reasons other than the presence of precipitated carbides. Binder and Brown present convincing evidence that one such cause is sigma phase present as a grain boundary film. This phase appears to be...
present in the 18-8 Mo and 18-8 Mo Cb alloys both in wrought form and in cast weld metal.

These three independent investigations also confirm that the very-low-carbon 18-8 and 18-12-3 Mo alloys can be welded without developing any evidence of intergranular attack in the heat-affected zone when tested in any of the standard media. This is an observation of considerable practical importance at a time when conservation of columbium is a foremost problem. As R. Franks points out, the next logical step in appraising these materials is to determine their usefulness in actual chemical service. Some data have already been presented on the successful performance of the alloys in one such application and information is now being accumulated for a variety of others.

In general, while one of the main objectives of the symposium was to present information correlating laboratory test results with actual field experience, surprisingly little information of this type appears available. The consumers of stainless steel are entitled to and can be expected to impose tests to insure that the material they employ is properly heat-treated to exhibit the best corrosion resistance. However, until field experience has proved that these tests are a valid measure of the suitability of the materials in all types of service, great caution should be used in interpreting the results; otherwise, new and useful alloys may be discarded before they ever leave the laboratory and are tried in actual service.

The earliest work on the columbium and titanium-containing alloys largely involved testing in the acidified copper sulfate type reagent. Had boiling nitric acid been employed as a test instead, the usefulness of these materials might well have been questioned. As Mr. Brown has mentioned, even the columbium-containing grade may show grooving immediately adjacent to the weld in this test medium. Because this attack occurs in a very narrow zone next to the weld metal, perhaps only a few grains in width, it has often gone unobserved.

**MR. M. A. SCHEIL (by letter).—**

Two heats of type 347, the same heats which were reported by Buck et al. in their discussion of welded test specimens, were tested in our laboratory. The following are the analyses of the two heats:

<table>
<thead>
<tr>
<th></th>
<th>Carnegie No. 103</th>
<th>Carnegie No. 53</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, per cent</td>
<td>0.06</td>
<td>0.026</td>
</tr>
<tr>
<td>Manganese, per cent</td>
<td>1.56</td>
<td>1.50</td>
</tr>
<tr>
<td>Phosphorus, per cent</td>
<td>0.014</td>
<td>0.016</td>
</tr>
<tr>
<td>Sulfur, per cent</td>
<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>Silicon, per cent</td>
<td>0.53</td>
<td>0.30</td>
</tr>
<tr>
<td>Chromium, per cent</td>
<td>18.44</td>
<td>18.52</td>
</tr>
<tr>
<td>Nickel, per cent</td>
<td>11.68</td>
<td>12.25</td>
</tr>
<tr>
<td>Columbium, per cent</td>
<td>0.96</td>
<td>0.40</td>
</tr>
</tbody>
</table>

These heats were supplied in three thicknesses. Test specimens were prepared by welding one heat to the other using similar gage sheets. Welding was done by two processes: (1) automatic submerged arc, and (2) manual arc.

Details of the welding process are listed below:

<table>
<thead>
<tr>
<th>Gage, in.</th>
<th>Type of Weld</th>
<th>Electrode</th>
<th>Diameter, in.</th>
<th>Number of Passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to (\frac{3}{4})</td>
<td>Submerged arc</td>
<td>25-20 + Cb</td>
<td>(\frac{7}{8})</td>
<td>5</td>
</tr>
<tr>
<td>(\frac{3}{4})</td>
<td>Submerged arc</td>
<td>19-9 + Cb</td>
<td>(\frac{7}{8})</td>
<td>16</td>
</tr>
<tr>
<td>1 to (\frac{3}{4})</td>
<td>Manual arc</td>
<td>25-20 + Cb</td>
<td>(\frac{7}{8})</td>
<td>2</td>
</tr>
<tr>
<td>(\frac{3}{4})</td>
<td>Manual arc</td>
<td>25-20 + Cb</td>
<td>(\frac{7}{8})</td>
<td>8</td>
</tr>
</tbody>
</table>

Welded specimens were tested in boiling 65 per cent nitric acid in two conditions: (1) as welded, and (2) stress annealed at 1200 F. for 2 hr., furnace cooled. The results are given in Table I.
GENERAL DISCUSSION

TABLE I.—WELDED SPECIMENS TESTED IN BOILING 65 PER CENT NITRIC ACID, IN. PER YR.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>As-Welded</th>
<th>Stress annealed at 1200 F., hr. furnace cool, after welding</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>1 to 7/8</td>
<td>1 to 7/8</td>
</tr>
<tr>
<td>No. 2</td>
<td>3/4</td>
<td>7/8</td>
</tr>
<tr>
<td>No. 3</td>
<td>7/8</td>
<td>1 to 7/8</td>
</tr>
<tr>
<td>No. 4</td>
<td>7/8</td>
<td>1 to 7/8</td>
</tr>
<tr>
<td>No. 5</td>
<td>7/8</td>
<td>1 to 7/8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specimen</th>
<th>No. 1</th>
<th>No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period 1</td>
<td>0.009</td>
<td>0.010</td>
</tr>
<tr>
<td>Period 2</td>
<td>0.007</td>
<td>0.008</td>
</tr>
<tr>
<td>Period 3</td>
<td>0.006</td>
<td>0.008</td>
</tr>
<tr>
<td>Period 4</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>Average</td>
<td>0.007</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Specimen No. 1 welded by automatic submerged arc-welding process.
Specimen No. 2 manual arc welded.
° "Knife-line" attack.

In the as-welded condition there was practically no evidence of any knife-line attack. After the stress-annealing treatment of 1200 F., heat No. 103 showed some knife-line attack regardless of gage or welding process. The knife-line attack was considerably less in the case of manual-arc welding than with the automatic submerged-arc welding. Heat No. 53 showed a slight knife-line attack on the 1-in. gage specimen using the submerged arc and the 5/8-in. gage using the manual arc.

Only one condition, as-welded, can be compared with the data presented in Buck’s paper.

In this case, the as-welded specimens were found satisfactory in the acidified copper sulfate test as well as in the boiling nitric acid test. The stress-annealed specimens differed greatly in the temperature of the heat treatment. Thus no comparison can be made with these results.

We have recently tested six heats of type 347 material which were welded with a 25-20 Cb deposit and a 19-9 Cb deposit and were then stress annealed at 1200 F. for 1 hr. Specimens were run in boiling nitric acid, acidified copper sulfate solution, and the nitric-hydrofluoric acid solution. In this condition the results of the boiling nitric acid test and the nitric-hydrofluoric acid test were similar in as much as both tests solutions revealed a knife-line

<table>
<thead>
<tr>
<th>Heat</th>
<th>Boiling Nitric Acid</th>
<th>Nitric-Hydrofluoric</th>
<th>Acidified Copper Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>0.013</td>
<td>Knife-line attack</td>
<td>No attack</td>
</tr>
<tr>
<td>No. 2</td>
<td>0.016</td>
<td>Knife-line attack</td>
<td>No attack</td>
</tr>
<tr>
<td>No. 3</td>
<td>0.019</td>
<td>Knife-line attack</td>
<td>No attack</td>
</tr>
<tr>
<td>No. 4</td>
<td>0.024</td>
<td>Knife-line attack</td>
<td>No attack</td>
</tr>
<tr>
<td>No. 5</td>
<td>0.019</td>
<td>Knife-line attack</td>
<td>No attack</td>
</tr>
<tr>
<td>No. 6</td>
<td>0.025</td>
<td>Knife-line attack</td>
<td>No attack</td>
</tr>
</tbody>
</table>

Note.—All specimens stress annealed at 1200 F. 1 hr. after welding.
° Boiling 65 per cent HNO₃, average rate of five 48-hr. periods in inches penetration per year.
° Boiling 10 per cent HNO₃ and 3 per cent HF by volume, 170 F. for 1 hr. Bend test.
° Knife-line attack adjacent to weld deposit.

or welding process. The knife-line attack was considerably less in the case of manual-arc welding than with the automatic submerged-arc welding. Heat No. 53 showed a slight knife-line attack on the 1-in. gage specimen using the submerged arc and the 5/8-in. gage using the manual arc.

Only one condition, as-welded, can be compared with the data presented in Buck’s paper.

In this case, the as-welded specimens were found satisfactory in the acidified copper sulfate test as well as in the boiling nitric acid test. The stress-annealed specimens differed greatly in the temperature of the heat treatment. Thus no comparison can be made with these results.

We have recently tested six heats of type 347 material which were welded with a 25-20 Cb deposit and a 19-9 Cb deposit and were then stress annealed at 1200 F. for 1 hr. Specimens were run in boiling nitric acid, acidified copper sulfate solution, and the nitric-hydrofluoric acid solution. In this condition the results of the boiling nitric acid test and the nitric-hydrofluoric acid test were similar in as much as both tests solutions revealed a knife-line

<table>
<thead>
<tr>
<th>Heat</th>
<th>Carbon, per cent</th>
<th>Manganese, per cent</th>
<th>Silicon, per cent</th>
<th>Chromium, per cent</th>
<th>Nickel, per cent</th>
<th>Coulombium, per cent</th>
<th>Thickness, in.</th>
<th>Weld Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>0.06</td>
<td>1.42</td>
<td>0.55</td>
<td>18.46</td>
<td>10.87</td>
<td>0.87</td>
<td>5/8</td>
<td>25-20 Cb</td>
</tr>
<tr>
<td>No. 2</td>
<td>0.06</td>
<td>1.56</td>
<td>0.44</td>
<td>18.25</td>
<td>10.41</td>
<td>0.68</td>
<td>5/8</td>
<td>25-20 Cb</td>
</tr>
<tr>
<td>No. 3</td>
<td>0.05</td>
<td>1.58</td>
<td>0.49</td>
<td>18.38</td>
<td>11.06</td>
<td>0.77</td>
<td>5/8</td>
<td>25-20 Cb</td>
</tr>
<tr>
<td>No. 4</td>
<td>0.06</td>
<td>1.70</td>
<td>0.44</td>
<td>18.74</td>
<td>11.01</td>
<td>0.75</td>
<td>5/8</td>
<td>25-20 Cb</td>
</tr>
<tr>
<td>No. 5</td>
<td>0.06</td>
<td>1.41</td>
<td>0.54</td>
<td>18.72</td>
<td>10.91</td>
<td>0.68</td>
<td>5/8</td>
<td>25-20 Cb</td>
</tr>
<tr>
<td>No. 6</td>
<td>0.07</td>
<td>1.81</td>
<td>0.57</td>
<td>18.74</td>
<td>11.18</td>
<td>0.83</td>
<td>5/8</td>
<td>19-9 Cb</td>
</tr>
</tbody>
</table>
attack in the stock adjacent to the weld. The acidified copper sulfate test did not reveal this condition. These test results are outlined in Tables II, III and characteristic photographs shown in Figs. 2, 3 and 4.

**FIG. 2.**—Knife-Line Attack After Five 48-hr. Periods in the Boiling 65 per cent Nitric Acid Test. (This is heat No. 6 reported in Table II.)

**FIG. 3.**—Attack on Bend Test Specimen After Testing in a 10 per cent Nitric—3 per cent Hydrofluoric Acid Solution at 170 F. for 1 hr. (This is heat No. 1 reported in Table II.)

**FIG. 4.**—No Attack After the Boiling 65 per cent Nitric Acid Test. (The specimen is heat No. 6 but was annealed after welding at 1950 F. 1 hr., air cooled and sensitized at 1200 F. for 1 hr. and air cooled. Corrosion rate is 0.014 in. penetration per year.)
CHAIRMAN H. L. MAXWELL.\textsuperscript{10}—In closing I would also emphasize the article by Keating that has been referred to. I have seen the way they operate over in England—their metallurgical use of high-carbon 18-8 steel is quite different from ours. It is true they use high-carbon stainless steel. They use quite commonly what they call an 18-8 alloy which is a 1 per cent tungsten and a 1 per cent titanium alloy 18-8. Their conditions of use of their equipment are very widely different from ours. They don't push their equipment nearly the way we do capacity-wise, and they don't expect to get the heat transfer performance that we get over here.

I want to take this opportunity to thank all who have taken part in the program.

\textsuperscript{10} Supervisor of General Consultants, E. I. duPont de Nemours and Co., Inc., Wilmington, Del.