Discussion—Stainless Steels Session

Relationship Between Microstructure and Properties in Stainless Steels by F. B. Pickering

Question: Dr. H. D. Solomon[1]—You mentioned one of the main problems that occurs in ferritic stainless steels, namely, that grain growth tends to be very very rapid. Do you have any suggestions as to how these steels can be processed in such a way as to keep as fine a grain as possible?

Answer: Dr. Pickering—I think there are two ways at least for grain refining the ferrite stainless steels. In this context, I am referring to the fully ferritic steels that contain no austenite, because the presence of austenite at high temperatures can result in a refinement of the ferrite grain size. However, in fully ferritic steels, the conventional way to grain refine or inhibit grain growth is to introduce second phase particles that pin the ferrite grain boundaries. Such additions as titanium and niobium may be used, to form Ti(CN) and Nb(CN) particles, and I have evidence that under appropriate conditions these additions may prevent excessive grain coarsening until temperatures above 1200°C. The effect does, however, depend on the interstitial content, the grain coarsening temperature being lower with smaller interstitial contents. In this respect, one may express some minor concern when it is suggested that ultra-low interstitial contents are used because one wonders whether there will be sufficient carbo-nitrides formed to give adequate grain growth inhibition. Whilst the very low interstitial contents may be very desirable for corrosion resistance, toughness, and formability, there is always the possibility that, for example, the toughness advantage conferred by the low interstitial content may be more than offset by grain coarsening.

A second possible method of refining the ferrite grain size is by controlled processing, more specifically low rolling finishing temperatures. I believe this is being investigated, but I think there may be some problems because these ferritic steels recover rapidly to produce recovery type substructures. This lowers appreciably the driving force for recrystallization by reducing the stored energy, and so recrystallization is much retarded. In fact, many as-rolled materials show recovered rather than

[1] General Electric Co., Schenectady, N. Y.

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recrystallized microstructures. In this respect, certain alloying elements may retard recovery and so cause recrystallization to be more rapid, due to the retention of more stored energy. If such alloying elements also can produce second phase particles that inhibit grain growth, so much the better. In the absence of grain growth inhibition, then, there is always the danger that any refined grain size produced by controlled processing would be very susceptible to coarsening during subsequent heating; that is, during welding.

Question: Dr. Solomon—There is literature information, work specifically by Angle, that would lead one to believe that for Type 304 stainless steel with 0.08 carbon, the M_d temperature is perhaps as low as room temperature, perhaps only 25°C. And my experience is that it may be a bit higher. I wonder if you could comment on that?

Answer: Dr. Pickering—The M_s and thus the M_d temperature depends very much on the composition, the less alloyed the Type 304, the higher the M_s and M_d. M_d also depends on the amount of strain applied, increasing with increasing strain. My experience is that with Types 301 and 304 steels, the M_d temperature at true strains of up to about 0.4 was usually lower than 100°C, and we never observed an M_d of 250°C. However, in very pure metals one might expect somewhat higher M_d temperatures. In atomic energy application, I believe there is quite a lot of evidence that the M_s temperature is increased by irradiation. Whether the M_s is raised as far as normal radiation temperatures, so that martensite is formed actually during irradiation, is, I think, very questionable. The irradiation-induced martensite, so called, I think, formed during cooling irradiated material back to room temperature.

Question: G. Bodine[2]—I'd like to make a comment regarding the ferritic materials. A few years ago, I made an interesting observation on the 26-1 (E-Brite) composition in which I got into an area that I felt was maybe way too deep. This relates to strain rate effects and their influence on the transition temperature, and I had a series of 26-1 (E-Brite) materials that when subjected to the conventional modes of evaluating, the transition looked very ductile, and so forth.

In fact, the same piece of material in different conditions exhibited good ductility, even on impact drop weight testing. But when I got into ultra-high strain rate evaluation, we had a completely new ball game.

This, I believe and would suggest, would be an interesting field for microstructure correlation. When we employed explosive deformation, one could take the same materials that were all essentially ductile, by conventional means, and separate them into two piles: one like glass and one remaining ductile. Some of the preliminary work I did inferred that

[2] Combustion Engineering, Chattanooga, Tenn.

there's a whole new ball game in evaluating some of the subtle characteristics of these ferritic stainless steels.

Answer: Dr. Pickering—Whilst I have never been concerned with explosive forming, I can appreciate that the very high strain rate, coupled with the shock-wave effect, would lead to ferritic stainless steels of the 26-1 type behaving in a brittle manner. May I suggest that this could be due to two effects. The first is the increase in the yield or flow stress at very high strain rates such that the cleavage fracture stress is exceeded and the ductile-brittle transition temperature is markedly raised. Hence, the transition temperature could be above room temperature, and the material could be very brittle. I think increasing ferrite grain size and the presence of elements that raise the transition temperature would aggravate this effect.

The second feature is the propensity of fully ferrite structures to mechanical twinning at high strain rates, and I believe that elements such as chromium, molybdenum, silicon etc. increase the mechanical twinning tendency. In ferrite, twinning (or rather intersecting twins) can readily nucleate a cleavage crack and thus initiate brittle cleavage fracture. I also believe that twinning is a very common form of deformation during explosive forming. Both these effects may contribute to the extreme brittleness in some explosively formed ferrite stainless steels, particularly if the grain size was coarse.

Question: L. Thompson[3]—Would you please comment on the relative effectiveness of strain-induced HCP epsilon martensite as opposed to BCC alpha martensite as related to the strain hardening observed in unstable austenitic stainless steels?

Answer: Dr. Pickering—Our experience has been that epsilon martensite contributed virtually nothing to strain-induced plasticity, at least compared with transformation to alpha martensite. I believe there is evidence in the literature to confirm this. In the stainless steels we examined, where the stacking fault energy was low, the formation of epsilon martensite was quickly followed by alpha martensite, and it was the latter that produced to the improved stretch formability of the unstable austenite stainless steels.

Possibilities for Microstructural Control During Hot Working of Austenitic Stainless Steels by B. Ahlblom and W. Roberts

Question: Dr. Solomon—Have you looked at the influence of delta ferrite in steels that have been particularly balanced to have some delta

[3] General Atomic Co., San Diego, Calif.

ferrite at the working temperatures? Do you see any differences between the dynamic, metadynamic, and static recrystallization.

Answer: Dr. Ahlblom—The only material we studied where delta ferrite is present, was Type 304 steel in the cast condition and, in this condition, recrystallization is much slower than for wrought material. However, this is mainly as a consequence of grain size differences rather than the presence of δ-ferrite.

Question: W. Dwyer[4]—Have you looked at dynamic recrystallization in the ferritic stainless steels? In particular, have you looked at a stabilized ferritic, something with high titanium? This would prevent any transformation. And, if not, do you have any feel for it?

Answer: Dr. Ahlblom—No! The problem with ferritic steels is that it is not very likely that they will recrystallize dynamically, because dynamic recovery is so rapid that the driving force never becomes sufficiently high for recrystallization during deformation.

Microstructural and Microchemical Studies in Weld Sensitized Austenitic Stainless Steels by P. Rao

Question: J. H. Steele, Jr.[5]—I have a question on sensitization and the relationship of the chromium depletion layer to the corrosion. If you make the premise that continuity of this depleted zone is necessary, it seems to me you have to look at it in terms of the spacing of the carbides and when continuity of this depleted zone exists. Is anybody doing any work in that specific area?

Answer: Dr. P. Rao—Yes. There are a number of models. One of our theoretical chemists, Dr. Mesmer, has been working on this to actually have models that really look at weld sensitization as opposed to thermal sensitization. There are some diffusion models to give you some idea of the critical spacing.

There is also another aspect of this to consider. If you look at very light sensitization, conditions that don't give rise to cracking, where you have very very small amounts of carbide formation, what you find is that you do not have a continuous average carbide distribution but rather some grain boundary segments that contain carbide while other grain boundary segments are completely free. So it's not only a question of the behavior between the individual carbides, but what fraction of the grain boundaries have any carbides in them at all. What you find is, if you look at something like an oxalic acid test and try to quantify it, you can get into a

[4] AC Spark Plug Div., GMC, Flint, Mich.
[5] Armco Corp., Middletown, Ohio.

situation where you get perhaps only 10 percent of grain boundaries having any carbides in them at all, although they may be moderately closely spaced, the other 90 percent of the grain boundaries are clear. There's a lack of continuity in this case, because only certain segments will be attached. You might get continuity along a single grain boundary, between two triple points—but then you go off to between other triple points and its completely clear. So you won't get attack in a modified Strauss test, for instance.

Question: R. Anderson[6]—Dr. Rao, in a presentation about a year ago, you had indicated that by longer times at sensitization temperatures that you could get a dampening out of this chromium depletion gradient. Could you comment on this in relation to other properties?

Answer: Dr. Rao—This has been observed in the alloy Armco Nitronic 50 or XM19 in which we see this phenomenon occurring quite readily. And what you observe and what has been measured is that with very long periods of time, you will still see the carbides present but you get a chromium replenishment, a healing effect.

In other words, the carbide is still present, but at long periods of time the chromium begins to build up again. So if you looked at a time-temperature sensitization curve, the diagram is skewed over. At very short times, there is no sensitization at a given temperature; at intermediate time, there is sensitization; and at long times, there is none.

And we have in fact observed this where we do see carbides, but then the chromium levels come back up again. And I refer you to the model of Stawstrom and Hillert that I think is the best explanation for why this occurs and it relates in fact to change in the chromium activity and the carbon activity as you begin to get carbide precipitation. In fact, you will get replenishment with long aging times at temperature.

Question: R. Anderson—Chromium carbide or other carbide?

Answer: Dr. Rao—No, it's still chromium carbide. And, in fact, Stawstrom and Hillert say that you still get carbides precipitating, but, in fact, the activity of the carbon and activity of the chromium is changing, and you keep the chromium level high at very long times.

Question: Dr. R. Simpson[7]—Obviously, the tendency to form the carbides is dependent on how fast you cool through the temperature range for sensitization. And the types of welds that I looked at are much heavier in section than the pipe welds. Therefore, it's a balance of heat input and the way in which the heat is conducted away, so welding parameters and

[6] Universal Cyclops Specialty Steel, Bridgeville, Pa.
[7] Westinghouse Electric Research & Development Center, Pittsburgh, Pa.

things like the thickness of the part being welded as well as the geometry make a big difference.

I'm interested, based on a question you asked me, do you ever find that you find chromium depletion in cases where you would not metallographically see carbides?

Answer: Dr. Rao—Generally, you can pick the carbides up metallographically. It depends upon what techniques you use. We often use oxalic acid.

We generally believe metallography is sufficient, although in some cases if you have a very small carbide fraction, let's say 10 or 20 percent of the grain boundaries containing carbides, it can be difficult to pick it up and you may need TEM in order to see it. But it is there and you can observe it optically, but it sometimes gets to be difficult.

Question: C. Matthews[8]—We use a lot of Type 304 stainless steel, and we find that with a given cooling rate that there's quite a difference in the susceptibility to sensitization between these different heats. And we've been unable to determine why this difference occurs. Do you have any information on that?

Answer: Dr. Rao—I won't answer that question, I'll leave that to the next speaker; that's an area in which he's been involved in working with this heat-to-heat variation. I have observed the same type of thing he's going to talk about. Sometimes pipes come in actually sensitized in the mill before we ever weld them. These pipes are then very severely sensitized by the subsequent welding process.

Correlation of Sensitization with Thermomechanical History of Type 304 Stainless Steel Pipe Joint by Y. G. Nakagawa, T. Kawamoto, M. Fukagawa, and Y. Saiga

Question: Dr. Solomon—I have one quick question. You mentioned the effect of 6 percent strain on continuous cooling sensitization. Did you look at lower levels of strain?

Answer: Dr. Y. Nakagawa—No, not yet, because that depends on the accuracy of the experiment, and in our set-up, 6 percent is the minimum strain with fair accuracy. But we have tried lower strain levels roughly estimated to be 4 and 3 percent, and we did observe the sensitization enhancement.

Comment: Dr. Solomon—I just want to make a quick comment. I have done similar experiments, and I find that in one heat that I looked at, there is very little effect on sensitization of straining (5 percent or less)

[8] Superior Tube Co., Norristown, Pa.

and at high strains there was a fairly large effect as you've shown here, but that if you went from 5 percent to even as high as 25 percent, it seemed to saturate. So I think there's a question of getting some more information at the very low strain levels. Also, there may be some heat-to-heat variability and interplay in these effects.

Question: D. Allen[9]—We've come across problems with probably smaller pipes than you are talking about. But, after you have solution treated them, there are often several operations that are known, certainly in Type 304, to accelerate or produce sensitization. Things like straightening and grinding, especially grinding of welds. Do you have any comments on this? And also, are the same effects in Types 304L and 316L?

Answer: Dr. Nakagawa—I agree with you. Our recent results for Type 304 indicate that those production and fabrication processes strongly influence sensitization of materials as well as initiation of cracking.

It seems to me that Types 316L and 304L are quite immune to these surface treatments. The best way to pick up the alternate material is to find material that is immune to any variability of heat treatments and fabricating the piping system, and these L-grade materials seem to have a great margin to them.

Microstructures Versus Properties of 29-4 Ferritic Stainless Steel by G. Aggen, H. E. Deverell, and T. J. Nichol

Question: Dr. Solomon—You made a comment about limiting the amount of copper. Have you ever done an experiment on heats containing higher amounts of copper? Specifically, do you know how the high copper might affect 475°C (885°F) embrittlement?

Answer: Dr. G. Aggen—We have not looked at the effects of copper on 475°C embrittlement. Your data, I believe, indicates copper accelerates the reaction?

Question: Dr. Solomon—There is some Climax Molybdenum work that dealt with a variety of different elements and their effects on 475°C (885°F) embrittlement. They didn't specifically do copper; they did do molybdenum, for instance.

Answer: Dr. Aggen—Which indicated that in some cases it (molybdenum) had no effect, and, in other cases, it accelerated embrittlement.

There are data in the literature indicating that cobalt and aluminum may slow 475°C (885°F) embrittlement, but even there, the data are inclusive. It may depend upon the level of alloying addition.

[9] General Electric Co., Wilmington, N. C.

Effect of Heat Treatment and Microstructure on the Mechanical and Corrosion Properties of a Precipitation Hardenable Stainless Steel by T. Kosa and A. DeBold

Question: B. Loescher[10]—I'd like to know if you have tested your material in the aged condition, say at 1125 or 1150°F, followed by a simulated service use at 750 or 800°F, and if so, did you find any adverse effect on notch toughness?

Answer: Dr. T. Kosa—For Custom 450 aged at 1150°F, exposure to temperatures of 700 and 800°F for times up to 3000 h decreases Charpy V-notch impact strength somewhat, but increases notch tensile strength and smooth tensile strength.

Question: Dr. Solomon—Why did you look at $MgCl_2$? That's an environment in which one might expect to see transgranular cracking in Type 304. Is there any specific reason why you chose that?

Answer: Dr. Kosa—We were trying to compare Custom 450 with Type 304, since the alloy was developed to have corrosion resistance similar to Type 304. (Type 304 was tested and was inferior to Custom 450 aged at 1150°F (894 K).)

Microstructure and Related Material Characteristics of Some Duplex Austenitic-Ferritic Alloys with Less Than 40 Percent Ferrite by G. C. Bodine, Jr., and C. H. Sump

Question: Dr. B. Wilde[11]—I noticed you didn't try any silicon variations, or at least you didn't discuss it on the board there. Is there any reason for this, say perhaps processing difficulties?

Answer: G. Bodine—You just introduced something interesting. As you and I know, we're doing work on some of the alloys that you have developed. Currently, we're doing work on duplex alloys ranging from 3.5Si to 4.5Si with essentially an 18-8 base. The stress corrosion cracking resistance on these materials is exceptional, but, first of all, we have found that these alloys can be processed from centrifugal castings by direct cold reductions. This is gratifying.

We haven't been able to crack either one of these alloys in $MgCl_2$ yet, and I understand that you have had some pretty good results in your testing. So as far as the silicon additives, this is current work. One thing—on one of the 3.5Si alloys, the ferrite is only around 4 or 5 percent; this might have an attraction for elevated temperature properties over and above the 4.5Si alloy.

[10] Dow Chemical Co., Midland, Mich.
[11] U. S. Steel Corp.. Research Center, Monroeville, Pa.

Question: Dr. Wilde—Are you doing any high-temperature water tests in the sensitized condition? Because this is the area where we have found these duplex steels to be outstanding?

Answer: G. Bodine—Yes—we have done some work previously at Battelle. But we didn't have, let's say, spectacular results, although we did have very encouraging results correlating with some of the other work.

Influence of Microstructure on the Mechanical Properties and Localized Corrosion of a Duplex Stainless Steel by H. D. Solomon and T. M. Devine

Question: Dr. G. Aggen[12]—I think there's some evidence that in the micro-duplex, there might be a galvanic effect too, which prevents stress corrosion.

I think Climax Molybdenum has done some work on ferritics welded with all austenitic filler. They can't crack that in $MgCl_2$.

The main question I wanted to ask you is how good is your evidence that you are seeing alpha prime above say about 550°C? Could that be some other phase such as gamma, for example?

Answer: Dr. Solomon—That is a very good point. Our evidence rests on the fact that while we observe the precipitate, we observe no extra diffraction spots, and we can light up the precipitate in dark field using a matrix alpha spot.

Now, when we go to 700°C, we also observe a very fine precipitation, but here we did observe extra spots. So I think at 700°C, you can get microstructures that look identical to those seen at 475°C, that is, a very very fine precipitation—but here we have extra diffraction spots and we believe that those may be due to a very fine sigma phase precipitate.

When you get austenite present, it's pretty easy to see it because you have an extra set of austenite spots coming out pretty clearly.

Closing Comments: Dr. F. B. Pickering—It would be invidious of me to comment specifically on the various papers presented in this session, particularly as they still have to be studied in their finalized textural form. However, there are several points that arise on listening to the general trend of the papers and of the discussions that ensued. The first is that perhaps we should be a little concerned at the ingenious alloy developments that have taken place over the years, which employed complex metallurgical phenomena, and moreover, often used several such phenomena conjointly to achieve quite outstanding combinations of properties. Many of these developments have posed almost insuperable problems of control, and so have not be exploited widely and indeed have

[12] Allegheny-Ludlum, Brackenridge, Pa.

often been abandoned without effective commercial exploitation. Much metallurgical effort has therefore been ineffectively used, although one must admit that these developments have often contributed greatly to our general metallurgical understanding. It seems however, that we need to show great care in pursuing developments that are so difficult to control, because in the present climate of economic stringency, developments that are believed to be academic and too difficult to control, lead to a loss of creditability in metallurgical research.

Secondly, there has, over the past few years, been a marked improvement in our appreciation of structure-property relationships, particularly in a quantitative sense. Much still remains to be done in this respect to further improve our understanding, but we must be sure that the knowledge we have already gained is applied to the optimization of steel properties, and particularly to ensure that the optimum properties are reliably produced. Consistency in producing the optimum properties is absolutely essential.

Thirdly, perhaps we should not try to reach a complete understanding of structure-property relationships before we branch out into even more productive avenues of research. We need now, I would suggest, to become microstructural engineers and to begin to develop microstructural profiles for particular property requirements but, especially, to show how these profiles may be achieved by variation and control of the processing conditions. It seems to me that it is essential for metallurgists to now devote even more effort to quantifying the relationships between processing parameters and microstructure so that we can predict the processing conditions by which a particular microstructural profile, and hence property combination, may be achieved. This should first be aimed at developing ideas or models that relate such effects at temperature, strain, strain rate, holding time, quality of stress and strain, cooling rate, transformation temperature, etc., to the microstructure that is developed. Such ideas are under development in high-strength low-alloy steels; why not in stainless and other types of steels?

Finally, I submit that we need to do much more work on the quantification of user properties with structure and processing. These are the *abilities* of steels, such as weldability, machinability, formability, corrodability, etc. The relationships between processing microstructure and these user abilities should be our prime objectives in order to ensure that at a time when raw materials and energy conservation is becoming so important, every last advantage is squeezed from the materials we used. This perhaps should be the ultimate aim of microstructural control, and aspects of the subject might well form the basis of future MiCon meetings.