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ABSTRACT

A relatively new research tool has been brought to bear on a relatively old problem. start Mössbauer effect spectroscopy SS in conjunction with X-ray diffraction techniques were used to study the phenomenon of stainless steel sensitization SS.

A ferromagnetic phase, thought to be pseudomartensite, has been found to exist in sensitized Type 301 SS. Stresses generated in the matrix by morphology changes of the precipitated carbides is deemed responsible for the creation of this phase. No such phase was detected in the Type 304L SS.

It was confirmed that the precipitated carbides SS were of the complex type $(Cr,Fe)_{23}C_6$. Furthermore, it was established that these carbides are paramagnetic. In the presence of austenite, the Mössbauer peak for the carbides is overshadowed.

In single phase materials grain size SS has no effect on the Mössbauer spectrum. In multi-phase materials the peak locations are unaffected by grain size, but quantitative evaluations are influenced. end

INTRODUCTION

The problem of sensitization of austenitic stainless steels has commanded the attention and efforts of many investigators over the past forty years. The published results of these many studies are more than somewhat contradictory. Chromium impoverishment in areas immediately adjacent to grain boundaries in these steels is the most generally accepted theory to explain the sensitization of these metals. Such impoverishment supposedly results from the precipitation of $(Cr,Fe)_{23}C_6$ carbides, when the metal is subjected to temperatures within the range 900° to 1500° F. This impoverishment thus renders the material highly susceptible to intergranular corrosion in the presence of some corrosive media. Originally suggested by Strauss et al (1),[1] in 1930, data from many subsequent investigations have tended to confirm this explanation. There are many others, however, who have tended to disagree and have in turn proposed other mechanisms. A very brief review of the literature is, therefore, deemed necessary to present some of these conflicting arguments.

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[1] The numbers in parentheses pertain to references appended to this paper.

Survey of the Literature

Two independent studies have offered evidence which suggest that diffusion of atomic specie, due to carbide precipitation, is minimal. Carroll and Hopkinson (2), using an electron probe analyzer, found no evidence of chromium depletion in sensitized Type 310 steel in regions adjacent to grain boundaries. It was observed, however, that the chromium content of the carbides increased with increased sensitizing time yet still exhibited low corrosion resistance. Bruk and Nyrkovskaya (3) determined with isotopes that carbon concentration at grain boundaries even after heating 6 hours at 600° C was extremely small.

The question of the solution potential of carbides has received much attention. Houdremont and Tofante (4) have postulated that when Type 430 stainless steel becomes sensitized, precipitation of iron carbides from austenite at ferrite boundaries has occurred. Upon heating to 1450° F the iron carbide changes to a chromium carbide, probably $Cr_{23}C_6$, and immunity to intergranular attack is restored.

Kinzel and his co-workers (5) found the solution potential of the carbides to be not less than that of gold when in the form $Cr_{23}C_6$.

Carbides other than $Cr_{23}C_6$ exist according to Bendure et al (6), though the principal carbide to be found is $(Cr,Fe)_{23}C_6$. Their analyses indicate a ratio of 80 pct. chromium to 20 pct. iron is the most likely combination. Significant also was their suggestion that severe susceptibility can occur when only small amounts of carbides have precipitated. This led to the observation that the difference in resistance to intergranular corrosion between Type 302 and Type 304L cannot be explained on the basis of the amount of precipitate alone.

Of late, the hypothesis suggested by Payson (7) has been viewed with increasing interest. He concluded that the size and distribution of the precipitates were the most important factors to be considered as causing sensitization, regardless of the nature of the precipitates. Support for this idea has come from Kinzel (5), Mahla and Nielsen (8), Stickler and Vinckier (9).

From the results of a classic electron microscope study, Mahla and Nielsen (8) concluded that carbides form initially as two-dimensional dendrites or flakes. Continuing time at temperature results in changes in the shape and distribution of the particles. It was suggested that the changes followed the progression: small carbide flakes and dendrites → large dendrites → dendritic fragmentation → geometrical particles. No correlation was found to exist, however, between carbide form alone and rate of attack by HNO_3.

In a more recent study Stickler and Vinckier (9) observed that corrosive attack is caused by a potential difference between the carbides and the less noble matrix. Moreover, maximum etching occurs when specimens have been subjected to temperatures towards the upper limit of the sensitization range (1350° to 1500° F). Additionally, the morphology of the carbides is strongly temperature dependent. Sheet-type carbides, usually formed at lower temperatures, provide a continuous path for the electrochemical corroding process which can result in the complete disintegration of the material. Finally, the "regeneration stage" of a sensitized specimen, caused by holding for very long periods of time in the sensitization range, is reached when the sheet-type carbides separate into thick geometrical particles. This last observation is, of course, at odds with the chromium-depletion theory. That theory suggests that chromium will diffuse into the previously depleted areas restoring the chromium content to above the critical 12 pct. needed for protection.

The occurrence of phases other than austenite and carbides after sensitization has been reported. Substantiating somewhat the chromium-depletion theory, Aborn and Bain (10) found by magnetic measurements that ferrite precipitation followed carbide precipitation. Becket (11) states that ferrite precipitates first and is followed by carbide precipitation.

Not so says Dulis and Smith (12) who determined that ferrite is indeed present but that it forms during cooling from the sensitizing temperature range and not before. Alloy depletion i.e. lower chromium and carbon content in the areas adjacent to carbide particles is suggested as the reason for this reaction. Earlier work by Buehl et al (13) also indicated that ferrite forms during cooling but lattice strains around the precipitates was thought to be the reason for this occurrence.

The suggestion that lattice strains are the cause of susceptibility has been supported by Lula et al (14). They proposed that on rapid cooling a carbide or nitride is precipitated in the grain boundary causing excessive strain in the material. The stressed material then becomes the anode during corrosive attack.

From a study evaluating the influence of nickel on intergranular corrosion of 18 pct. chromium steels, Upp et al (15) found that all specimens, regardless of whether they were ferritic or austenitic, when water quenched from 1400° F, did not exhibit susceptibility to intergranular attack.

It has also been argued that some form of martensite may be the phase responsible for loss of corrosion resistance. That the M_s temperature is raised when carbide precipitation occurs, has been shown by (6) and (16) among others. Kramer and Baldwin (17) have noted though that the amount of martensite formed following sensitization cannot account for the brittleness found in austenitic steels. They found that the amount of martensite in sensitized Type 304 ELC was less than in annealed specimens of the same material when tensile tested under the same conditions.

Cold-working or deformation, it is acknowledged, does produce some transformation product of austenite. Furthermore, it has been shown by Buhr et al (18) that the phase is ferromagnetic. The suggestion is made that the ferromagnetic phase is composed of two constituents which are probably a complex carbide and α-iron. Private communications between the writer and several prominent investigators in this field (19) (20) (21) failed to disclose any references which indicate the carbides to be ferromagnetic.

It is acknowledged here that this literature survey is not complete and such was not intended. Unquestionably information pertinent to this study has been overlooked due to the considerable amount of published data. The desired purpose of this brief survey was to illustrate that a definite need for further research in this area exists. The present study was undertaken for this reason.

Scope of Present Investigation

In an effort to shed new light on this rather complex problem of sensitization, the writer and his co-workers undertook the present study armed with a relatively new research tool, Mössbauer effect spectroscopy. Supplemented by X-ray diffraction techniques, this new analytical tool has disclosed what may be some very significant information. Foils of Types 301 and 304L stainless steels have been studied in a wide range of heat-treated conditions. The results have been most gratifying. So much so that the investigation is continuing and foils of Types 310, 410 and 430 will next be considered. Additionally, work is being done on the sigma phase.

Comments on Mössbauer Effect Spectroscopy

A comprehensive review of the theory of the Mössbauer effect is unwarranted here. Interested readers are referred to a text by Wertheim (22). Applications of this technique, particularly where iron alloys are concerned, will however be cited.

Johnson et al (23) were among the first to study the Mössbauer effect in iron alloys. Their work demonstrated that the technique has the ability to distinguish between dissimilar magnetic atoms as in two iron sites Fe_3Al and Fe_3Si.

Two modifications of cementite were investigated by Niedzwiedz (24). The Mössbauer spectra revealed that both a ferromagnetic and a paramagnetic cementite exist.

Stainless steels have been investigated by Kocher (25) and by Marcus et al (26). Their findings will be discussed later in this paper.

In the above studies as in the present investigation, transmission techniques involving the use of foils or powders were employed. That the technique can be used for bulk samples, has now been demonstrated by Terrell et al (27). Very definitely a tremendous step forward has been taken towards the wider use of this powerful analytical tool. In the field of non-destructive testing numerous applications quickly come to mind.

Materials and Experimental Procedure

As mentioned earlier, foils of Types 301 and 304L stainless steels have been studied. These foils were approximately 0.001-inch in thickness and were received in the "fully-hard" condition. The chemistry and hardness values of these materials are given in Table I. The experimental procedures followed were essentially the same for each type of foil used and, therefore, a generalized outline should suffice.

TABLE I

Composition and Hardness of Foils

Type	C	Cr	Ni	Mn	Si	P	S	Mo	R_C(AR)*	R_C(A)**
301	0.10	16.81	7.55	1.04	0.44	0.027	0.014	0.27	45	25
304L	0.03	19.26	10.58	1.66	0.70	0.017	0.024	0.17	38	23

*As-received-value furnished by supplier

**Annealed-value furnished by supplier

First, X-ray diffraction patterns, using filtered chromium radiation, and Mössbauer spectra were obtained for the as-received material. Next, some 30 specimens of each type of foil were encapsulated in argon-purged, vycor tubing. These specimens were then subjected to the various following heat treatments:

1. Annealed at 1900° F for periods of 1, 2, 18½, and 48 hours followed by a water quench.
2. Annealed at 1900° F for 1 and 24 hour periods then allowed to furnace cool to ambient.
3. Annealed at 1900° F for 1 hour, water quenched and then sensitized for:
    - (a) ½ hour at 1200° F
    - (b) 3 hours at 1200° F
    - (c) 15 hours at 1200° F
    - (d) 24 hours at 1200° F
    - (e) 1 hour at 1350° F
    - (f) 2 hours at 1350° F
    - (g) 3 hours at 1350° F
    - (h) 4 hours at 1350° F
    - (i) 10 hours at 1350° F
    - (j) 24 hours at 1350° F
4. As-received and heated to 1550° F for 6 and 12 days.
5. Annealed at 1900° F for 48 hours, water quenched, reheated to 1350° F for 24 hours and, by changing furnaces, the temperature quickly increased to 1550° F and held at this temperature for 8 days.

Mössbauer analysis, X-ray diffraction procedures, and in some instances, metallographic examinations were carried out on each group of specimens.

Results and Discussion

The Mössbauer spectra and X-ray diffraction patterns for the as-received Type 301 foil both revealed the presence of a phase other than austenite. Two very broad peaks located at $2\theta = 68.6^\circ$ and 155.0° on the diffraction pattern clearly indicated the presence of a highly stressed phase. Thielsch (28) refers to this phase as pseudomartensite and that it is structurally similar to α-ferrite. Parr and Hanson (29) state that Type 301 is readily hardened by cold-working. Kocher (25) did not find the above to be true and reported no magnetic splitting on the Mössbauer spectrum. The writer and his co-workers did find that magnetic splitting occurred and this indicated the presence of a ferromagnetic phase.

After annealing at 1900° F for 1 hour, followed by a water quench, the peaks on both the X-ray diffraction pattern and Mössbauer spectrum, attributed to the ferromagnetic phase, disappeared. Only those peaks characteristic of austenite remained. As is shown in Table I the hardness decreased from $R_c 45$ to $R_c 25$.

The specimens which were annealed for 2, 18½ and 48 hours and then quenched were next studied. As was expected, the intensity of the peaks recorded on the diffraction charts decreased due to an increase in grain size. The Mössbauer spectra were virtually unchanged. This does not imply that Mössbauer spectroscopy is unaffected by grain size. As will later be shown, when the material contains more than one phase, quantitative results are affected by grain size.

Consider now the specimens which had been annealed, quenched, and re-heated to 1200° F. After ½ hour, and 3 hours, the Mössbauer spectra did not indicate the presence of a ferromagnetic phase. However, after 15 hours at 1200° F, a ferromagnetic phase was detected. The spectra for the specimens held for 24 hours at 1200° F showed the amount of the ferromagnetic phase had increased.

For the specimens held at 1350° F for varying times, the X-ray diffraction patterns showed that only austenite was being detected in the specimens held for 1, 2, 3, and 4 hours. After 10 hours the existence of a second phase was clearly evident. As was the case for the specimens held for 24 hours at 1200° F, the amount of the second phase increased with increased time at temperature. Significantly, the locations of the peaks, indicative of the second phase, were at the same Bragg angle as were the second phase peaks in the as-received material. The presence of the second phase was revealed by Mössbauer spectroscopy in the specimen held for 4 hours at 1350° F. Furthermore, the spectrum indicated that this second phase was ferromagnetic.

There is no question that carbides precipitated in the specimens held for only short periods of time at 1200° and 1350° F. Metallographic examinations confirmed their presence.

There is a ready explanation as to why X-ray diffraction did not indicate their existence. To obtain diffraction patterns for these carbides, it is generally agreed that to produce the necessary intensities, the carbides must be extracted from the matrix and concentrated.

The question now poses itself, why weren't their presence noted on the Mössbauer spectra? Either the carbides are paramagnetic and the peak is masked by the austenite peak or the carbides initially contain no iron atoms. The literature strongly insists that the carbides are of a complex nature [$(Cr,Fe)_{23}C_6$] (6)(8). Thus, to confirm this, carbides were extracted from sensitized Type 309 stainless steel by the methanol-bromine method and subjected to Mössbauer analysis. The spectrum indicated the material to be paramagnetic and the peak to be slightly shifted from the location of the austenite peak. Marcus et al (26) have shown that the presence of a paramagnetic Cr-rich precipitate can be determined by Mössbauer spectroscopy. Furthermore, the residues were analyzed with a Guinier powder camera and the results showed the material was indeed a complex carbide of the $(Cr,Fe)_{23}C_6$ type.

It is much more difficult to explain the appearance of a ferromagnetic phase after longer holding times in the sensitizing temperature range. It is here suggested that the phase is pseudomartensite which is created by stresses generated in the matrix immediately surrounding the carbides as the morphology of the carbides changes with time. Justification for this suggestion is based on the fact that the Mössbauer spectra of the sensitized specimens held for the longer periods of time were identical, except for quantity, to those obtained on the as-received material. Additional support is given by the X-ray diffraction patterns. Moreover, it is generally known that prolonged heating [40 to 50 days] (30) in the sensitizing temperature range will restore immunity to intergranular attack. It is believed by the writer that the prolonged heating is in effect a stress-relieving operation. As has been shown by Mahla and Nielsen (8) and, Stickler and Vinckier (9) the morphology of the carbides continues to change with time at temperature. The shapes assumed tend toward the geometric configuration with the lowest surface-volume ratio. When this happens the formation of pseudomartensite ceases, stresses are relieved and a reversion of the pseudomartensite to austenite occurs. Unfortunately, the above statements do not account for the fact that severe susceptibility can occur when only small amounts of carbides have precipitated as has been noted by Bendure et al (6).

The Mössbauer spectra for the specimens allowed to furnace cool were identical to those spectra obtained for the specimens which had been annealed, quenched and re-heated to 1350°F for 4 hours. Metallographic examination revealed the microstructures to be essentially the same in both cases. Mahla and Nielsen (8) found that entering the sensitizing range from above results in less severe sensitization than when entering from below. It was observed by Stickler and Vinckier (9) that maximum etching occurs when the material is subjected to temperatures towards the upper limit of the sensitization range (1350° to 1500°F). In checking the cooling rate of the furnace, it was found that the cooling rate was an exponential function and 3 hours were required to cool from 1500° to 900°F. There is no question that the specimens were at the higher temperatures for shorter periods of time than at the lower temperatures. The significance of these results is not clearly understood.

It was noted earlier that when the material is multi-phase, grain size can affect Mössbauer spectra. The furnace cooled specimens, annealed for 1 hour at 1900°F, exhibited an ASTM #7 grain size, whereas an ASTM #2 grain size was found in the specimens annealed for 24 hours and then furnace cooled. The Mössbauer spectra for the specimens with the smaller grain size showed these specimens contained the larger amount of the ferromagnetic phase.

For the as-received specimens held for 6 and 12 days at 1550° F, Mössbauer and X-ray spectroscopy revealed only austenite to be present. This seems to suggest that, for thin sections of this material, 1550° F is above the sensitizing range and the pseudomartensite found in the as-received condition reverted to austenite. On the other hand the specimens annealed for 48 hours at 1900° F, quenched, re-heated to 1350° F and held for 24 hours, and then the temperature quickly raised to 1550° F and held for 8 days produced results in direct contrast to the above. For these specimens, not only was the ferromagnetic phase still present, but was present in a much greater amount than the samples held at 1350° F for 24 hours. This anomalous behavior cannot be explained at this time and subsequent study is planned to try to find an explanation.

Turning now to the results obtained on the Type 304L foils, it was found that only austenite was detected in all the specimens tested. Even the as-received, fully-hard specimens revealed no ferromagnetic phase, though distortion of the austenite peaks was observed. It is suspected that the material was not received in the "fully-hard" condition. Some degree of cold-working had been carried out, but not enough to form significant quantitites of pseudomartensite. It is known (29) that when the carbon content is lowered to reduce susceptibility to sensitization a reduction in the susceptibility to work-hardening also occurs.

It was not unexpected that only austenite was found in the remaining specimens. In the absence of carbide precipitation, no pseudomartensite will form. Emphasis is thus added to the suggestion that one of the principal factors causing sensitization is the occurrence of a stress-created ferromagnetic phase resulting from carbide precipitation.

Conclusions

In summary then, it may be concluded that:

1. Mössbauer spectroscopy will be found most useful in the study of the sensitization phenomenon as well as other reactions in stainless steels.
2. It is suggested that sensitization can be for the most part attributed to the appearance of a highly stressed ferromagnetic phase caused by morphology changes in precipitated carbides.
3. The precipitated carbides are of a complex nature and are paramagnetic.
4. Grain size assumes importance in Mössbauer spectroscopy only in multi-phase materials, and then only as to the amount of the phases present.

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