

Computer Differentiation of Mössbauer Spectra

Computer programs are devised which permit more effective quantitative interpretation of Mössbauer Effect spectra and additional information is obtained concerning 885° F embrittlement in ferritic stainless steels

BY O. W. ALBRITTON AND J. M. LEWIS

ABSTRACT. Computer programs have been devised which permit more effective quantitative interpretation of Mössbauer Effect spectra. Peaks representing the predominant phase in stainless steels have heretofore overshadowed peaks representative of minor phases. The computer techniques developed during this study allows one to differentiate between these data utilizing an iterative, integration, comparison procedure.

Additional information concerned with 885° F embrittlement in ferritic stainless steels was obtained.

Introduction

The Mössbauer Effect is a resonant emission-absorption process. Radiation emitted from a nucleus is absorbed and re-emitted by another nucleus of the same isotope. The principle is deceptively simple; however, until recent years observations of nuclear resonant emission-absorption have been limited. Today, extensive use is made of Mössbauer spectroscopy in many fields. An excellent reference for all uses of Mössbauer spectroscopy is *The Mössbauer Effect Data Index 1958-1965*.¹ Our purposes here may best be served by restricting our discussion of uses to examples which were instrumental in prompting the present investigation.

Marcus et al.² used Mössbauer spectroscopy to study precipitation in stainless steels and maraging steels. Since austenite exhibits a paramagnetic peak, pointwise integration was tried to determine the percent retained austenite in a martensite matrix. No precipitates were reported in

the two phase alloys. As has been later reported³, the paramagnetic peak of the precipitated $(CrFe)_{23}C_6$ was masked by the austenite peak. The next case to be cited illustrates the need for a new method for analyzing the raw data obtained by Mössbauer spectroscopy. The example to be discussed is the sensitization of stainless steel.

Albritton³ found that a highly stressed ferromagnetic phase, pseudomartensite, develops as carbides are precipitated in fully austenitic stainless steels. Thus, after sensitization has occurred, what had been a single phase alloy now had become a three phase alloy. The presence of two of these phases was clearly evident from the Mössbauer spectra. Both the characteristic and familiar paramagnetic peak of austenite and the newly determined ferromagnetic peaks of the pseudomartensite could be noted. Absent, however, was any evidence of a peak or peaks denoting the presence of the carbides.

By using a very laborious chemical extractive technique and irradiating the residues, the paramagnetic Mössbauer peak for the carbides was made evident. Its position on the Mössbauer spectrum was completely masked by the much larger and broader paramagnetic peak of austenite. Clearly, if some means could be devised to more effectively "sift" the raw data obtained by Mössbauer Effect spectroscopy, new strength would be added to an already powerful research tool. Such was the principal objective of this investigation.

In carrying out the principal objective of the investigation, additional information concerning 885° F embrittlement in ferritic stainless steels was obtained.

Experimental Equipment and Materials

The stainless steel foils used in this investigation were Types 301, 347, 430 and 446. Types 301 and 430 were received in the as-rolled condition whereas the Types 347 and 446 were obtained in the annealed condition. Selected samples of Types 301 and 430 were annealed by recommended procedures for later use. Composition of the foils are shown in Table 1.

A velocity sweep-type Mössbauer spectrometer was used employing a source of Co^{57} in a copper matrix. The data obtained were stored in a 400 channel analyzer from which a read-out could be made by a digital printer. The raw data so obtained were then analyzed by an IBM system 360 computer and a Calcomp 563 plotter.

Experimental Procedure

All of the foils studied were sealed in Vycor tubing with an argon atmosphere. This was accomplished by evacuating the tubing and then filling the tube with argon. Such was done several times to insure that all extraneous gases were removed. The tubing was then sealed leaving the foil in an argon atmosphere.

Once encapsulated, the specimens were placed in a furnace maintained

O. W. ALBRITTON is Professor of Materials, Dept. of Engineering Mechanics, and J. M. LEWIS is a Graduate Student, Louisiana State University, Baton Rouge, La.

Paper based in part on thesis submitted by J. M. Lewis in partial fulfillment for degree of Master of Science to faculty of Louisiana State University—manuscript for paper received by WELDING JOURNAL on March 9, 1970.

Table 1—Composition of Foils, %

Type	C	Cr	Ni	Mn	Si	P	S	Mo	N	Ta+Cb
301	0.10	16.81	7.55	1.04	0.44	0.027	0.014	0.27	—	—
347	0.059	18.05	9.53	1.74	0.64	0.019	0.016	0.16	—	0.74
430	0.10	16.05	—	—	—	0.015	0.012	—	—	—
446	0.10	24.74	0.27	0.69	0.33	0.014	0.012	—	.11	—

at 885° F ± 10° for times shown in Table 2. After aging, Mössbauer spectra were obtained for all foils. These data were then transferred to IBM cards for analytical interpretation.

Computer Programs

In order to compare Mössbauer spectra, the effects of various errors must be eliminated. Some of these errors are variations in counting times, differences in foil thicknesses, and variations of background radiation. Certain conditions were assumed to exist so as to facilitate removal of these errors.

It was assumed that the natural percent occurrence of Fe⁵⁷ remained constant throughout a particular heat of steel. As a result of this assumption, it would be expected that the total absorption or integrated intensity of two Mössbauer spectra would be the same if the spectra had been accumulated for the same length of time. However, since it is very difficult to obtain "equal" accumulation time, the effect of different counting times must be removed or reduced to a low level.

One method suggested for accomplishing this is normalizing the spectra.⁴ If $I(\infty)$ is the intensity or counting rate in a channel in which there is no resonant absorption and $I(v)$ is the intensity in the channel corresponding to the velocity v , then normalization is accomplished by taking $I(v) = I(v)/I(\infty)$. However, certain equipment errors might occur which would change the amount of background radiation (some of the X-rays may be detected). When comparing two spectra, this error may be removed by forcing the integrated intensities of both normalized spectra to be the same. This may be accomplished by using one spectrum as a reference data set and by changing the comparison data set (second spectrum) according to the form:

$$I''(x) = \frac{I'(x) + D}{1 + D} \quad (1)$$

where x = channel number; D = constant.

The constant, D , is derived using a simple rectangular integration of absorbed intensity. If the integrated intensities of the reference data set and the comparison data set are the same, then D is zero. If the integrated intensities are not the same then D is given by:

$$D = \frac{\sum_{x=1}^{200} (I_r'(x) - I_c'(x))}{200 - \sum_{x=1}^{200} I_r'(x)} \quad (2)$$

Table 2—Mechanical and Thermal History of Foils

Type stainless steel	Condition received	Annealing treatment	Hours at 885° F
301	As-rolled	1 hr @ 1950° F WQ	0
			250
			500
301	As-rolled	None	0
			250
			500
347	Annealed	None	0
			250
			500
			750
			1000
446	Annealed	None	0
			250
			500
			750
			1000

where $I_r'(x)$ = intensity of reference spectrum in channel x ; $I_c'(x)$ = intensity of comparison spectrum in channel x .

When both the reference spectrum and comparison spectrum are on an equal basis, a point by point difference may be computed to observe changes which have occurred.

It was also believed that all line broadening effects would be approximately equal, since the temperatures of the source and absorber remained essentially constant. The spectra were taken in an air-conditioned building. Thus, the Doppler broadening due to temperature remained constant for all foils. Moreover, all the foils of a particular type should have the same approximate grain size. Thus, grain size would not cause a line broadening effect. The reason for line broadening would be due to phases which appear after aging.

In order to normalize Mössbauer spectra a value of $I(\infty)$ must be calculated. The ten channels on each end of the spectra represent approximately zero resonant absorption. Therefore, $I(\infty)$ is taken as the average of the first ten and last ten channels. The subroutine which does this is called BASE. Another subroutine NØRM, takes $I(\infty)$ from BASE and calculates the normalized intensities.

To complete a basic analysis, a subroutine designated as INTCØM takes a reference data set and a comparison data set and performs an integration and comparison. The value of D , eq (2), is calculated and the comparison data set is modified. Then a point by point difference is computed to indicate changes between the reference data set and the comparison data set. The reference data set, comparison data set and difference are

plotted using the Calcomp 563 plotter. If further analysis is indicated by the difference plot, two more subroutines may be used. These subroutines are named CARBSP and FERSEP. CARBSP may be used to separate the effect of carbides in austenitic steels while FERSEP may be used to separate austenite from pseudomartensite and carbides.

CARBSP is used only on austenitic materials with no ferromagnetic components and with no large degree of quadrupole splitting. The reason that these requirements are made is that the integration only extends from channel 81 to channel 130. The value of D for this integration is obtained by replacing the summation limits with 81 and 130. D then becomes:

$$D = \frac{\sum_{x=81}^{130} (I_r'(x) - I_c'(x))}{50 - \sum_{x=81}^{130} I_r'(x)} \quad (3)$$

The difference is taken just as in INTCØM. However, if the difference is less than -0.001 in any channel between 81 and 130, then the absolute value of the difference is added to the comparison spectrum in the corresponding channel. A record is kept of these additions. Then the comparison spectrum is integrated and compared again to see if any of the difference falls below -0.001 in any channel between 81 and 130. If the difference does fall below -0.001 then the whole procedure is repeated until the difference has no values less than -0.001 between channels 81 and 130. The record of the values added to the comparison spectrum is called CARB because it represents the effect of paramagnetic carbides in the austenitic matrix. When the comparison data is changed in INTCØM, CARB is changed using the same constant, D . This is done to keep the right size relationship between the comparison data and CARB.

One more subroutine was used in this preliminary study. FERSEP was used to separate austenite from other ferromagnetic and paramagnetic phases. Specifically, it uses the relative intensities of the hyperfine structure of pseudomartensite to pick the proper percentage of austenite to be removed. In this subroutine, as well as with CARBSP, the reference data set must be pure austenite.

In order to remove the austenite peak, an iteration procedure was used. The reference peak, which is 100% austenite, was scaled down so that when the austenite peak was subtracted from the comparison spectrum, the proper intensity ratio of the

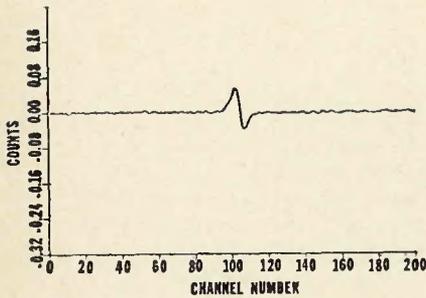


Fig. 1—Difference between Type 301 annealed plus 500 hr at 885° F (aged) and Type 301 annealed plus 0 hr at 885° F (not aged)

second and third most positive peaks was obtained. To scale down the austenite peak, a modified value for D was needed. This value is given by:

$$D = \frac{z_1 - z_2 + (1 - F)(1 - z_1)}{1 - I_r'(x_1)} \quad (4)$$

where z_1 = minimum value of second most positive peak; z_2 = minimum value of third most positive peak; x_1 = channel in which z_2 occurs; F =

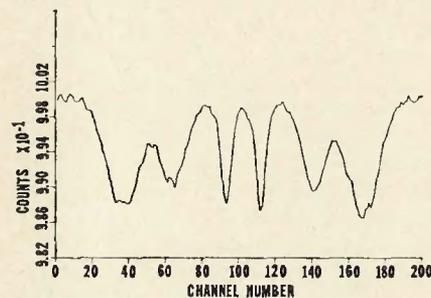


Fig. 3—Type 430 as-received—6.4 million counts.

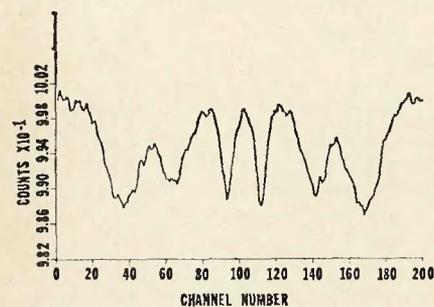


Fig. 4—Type 430 as-received—1.5 million counts

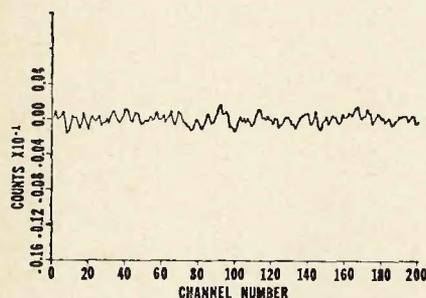


Fig. 5—Difference between Type 340 as-received (1.5 million counts) and Type 430 as-received (6.4 million counts)

$$\frac{1 - z_2}{1 - z_1} = \text{peak height ratio.}$$

As a check on integration procedures, a double precision program was run using trapezoidal integration. The results agreed with the results of rectangular single precision integration down to the sixth decimal place. This was far more accurate than the plotter.

Results and Discussion

The Type 301 stainless steel annealed foils exhibited a non-symmetrical difference, when the aged foils were compared with the annealed foil which had not been aged as is shown in Fig. 1. The area which lies below zero represents more absorption in the aged steel.

This type of difference was caused by a shift in the austenite peak. Such a shift could have been caused by several factors. The most probable reason was carbide precipitation. Formation of σ phase was another possibility. The σ phase has been known to form in heavily cold worked samples after aging for 4 years at 885° F but such is ruled out in the present case because of the annealed condition and short aging time. A third possibility was 885° F embrittlement. Malone⁵ reports, however, that single phase austenitic steels are not significantly affected by 885° F embrittlement. This left only carbide precipitation as a possibility.

To check the carbide theory in the Type 301 foils, a stabilized grade was used. Type 347 stainless steel exhibited absolutely no change as is shown by Fig. 2. This also helps prove the validity of the computer procedure. One might suggest that a difference in counting times could have masked any change in the Type 347. An extreme case was used to show that the program eliminated the effect of counting time (except for statistical scatter). A specimen of Type 430 foil in the as-rolled condition was used and two spectra of the same foil were taken. One of the spectra had a value of 1.5×10^6 counts for $I(\infty)$ while the other had a value of 6.5×10^6 for $I(\infty)$. The results are shown in Figs. 3-5. The difference is essentially zero except for scatter.

The Type 301 as-rolled foils indicated some complex reaction. First of all, some paramagnetic phase appeared which could be carbides, σ , or the 885° F phase. Secondly, there was an increase in the hyperfine field indicating chromium depletion from the matrix. (see Figs. 6-8). Another possibility was that some of the pseu-

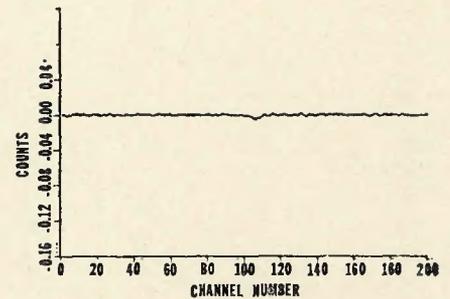


Fig. 2—Difference between Type 347 annealed plus 1000 hr at 885° F (aged) and Type 347 annealed plus 0 hr at 885° F (not aged)

domartensite reverted back to austenite. This, however, could not explain the increase in the hyperfine field. At the present time this situation is similar to 2 equations with 3 (or more) unknowns. The difference produced by using annealed Type 301 as a reference has almost no meaning. However, the modified difference procedure called FERSEP can separate the austenite content in the as-

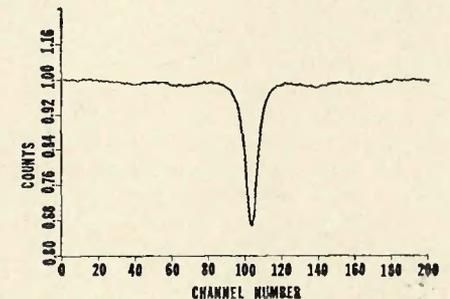


Fig. 6—Type 301 as-received plus 0 hr at 885° F (not aged)

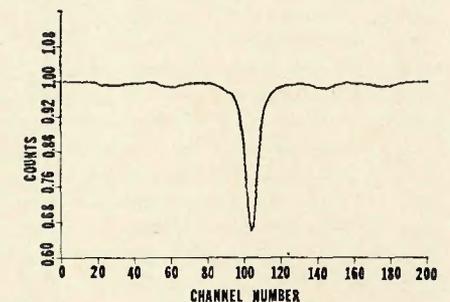


Fig. 7—Type 301 as-received plus 500 hr at 885° F (aged)

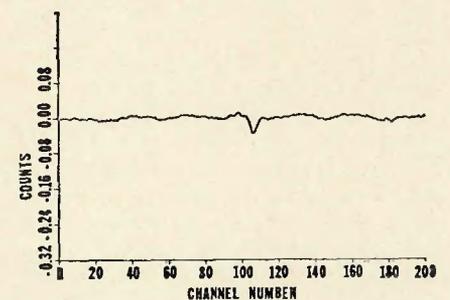


Fig. 8—Difference between Type 301 as-received plus 500 hr at 885° F (aged) and Type 301 as-received plus 0 hr at 885° F (not aged)

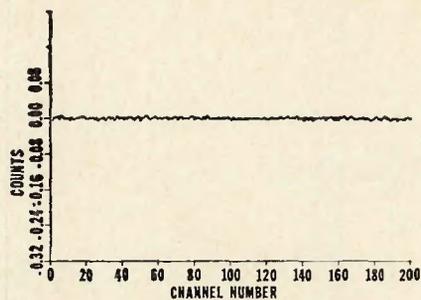


Fig. 9—Difference between Type 301 annealed plus 250 hr at 885° F (aged) and Type 301 annealed plus 0 hr at 885° F (without carbides)

rolled steels.

The more advanced programs take the difference and separate the phases. The Type 301 annealed foils were used with the program CARBSP and the effects of the carbide precipitation were separated. The separated phase was integrated to find the percent Fe⁵⁷ in that phase. The peaks which were separated represent the actual phase present and the effect of this phase on the rest of the matrix. It must be remembered that the Mössbauer spectrum of carbides plus austenite is not necessarily the spectrum of carbides plus the spectrum of austenite. The carbides (plus their effect on the parent matrix) represent about 8¹/₂% for Type 301 annealed plus 250 hr at 885° F and about 11¹/₂% for Type 301 annealed plus 500 hr at 885° F (see Figs. 9–12).

The Type 301 stainless steel as-rolled foils were analyzed using FERSEP. Annealed Type 301 was used as a basis to remove the center peak due to paramagnetic austenite. The results show that the austenite peaks of the as-rolled alloys have been shifted slightly due to the presence of the pseudomartensite. This presents a complex problem. The reference peak must be shifted to compensate for the effect of the pseudomartensite. Thus far, this has not been successfully done. However, the percentage austenite in the as-rolled steels was calculated without using a reference peak shift and the values obtained are close to the accepted value of 70% austenite in "fully hard" Type 301. Several values of peak height ratio were used. Within limits, the peak height ratio, *F*, did not make a significant difference.

The Type 446 stainless steel foils constitute a more interesting case. The difference yields a seven peak pattern rather than just a six peak pattern as can be observed in Fig. 13. The aging temperature and time at temperature do not indicate that σ could form. Carbides are also ruled out because ferritic grades are highly resistant to sensitization in this temperature

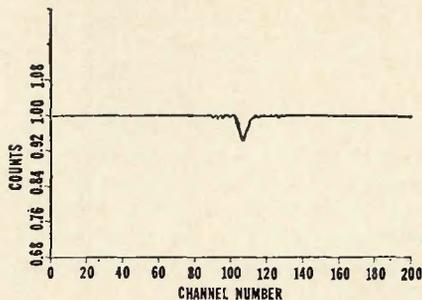


Fig. 10—Carbides from Type 301 annealed plus 250 hr at 885° F

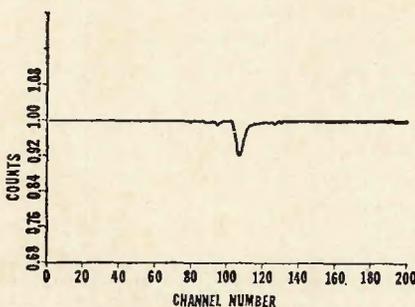


Fig. 12—Carbides from Type 301 annealed plus 500 hr at 885° F

range. The paramagnetic peak close to channel 100 must be due to 885° F embrittlement. The isomer shift of this peak is more negative than the peak for pure austenite. The isomer shift of the 885° F phase is also more negative than the isomer shift of the ferrite matrix. This indicates that the 885° F phase has a greater electron density than the ferrite matrix. The six peaks of the hyperfine structure also shift out from the center after aging at 885° F. This suggests that the matrix has lost some Cr. (Cr enters the matrix with its magnetic moment antiparallel to the magnetic moment of the iron and reduces the internal magnetic field.) Also, the precipitate accompanying 885° F embrittlement is reported to contain 80% Cr and 20% Fe by Johnson et al.⁶ They also note that upon reaching a chromium content of 80%, the alloys cannot exhibit a ferromagnetic structure since the Curie temperature drops to 0° K. Reported also is the fact that the change in hyperfine field is directly proportional to the chromium content

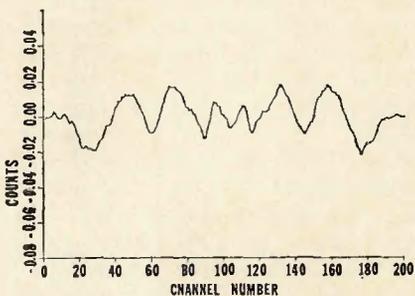


Fig. 13—Difference between Type 446 as-received plus 1000 hr at 885° F and Type 446 as-received

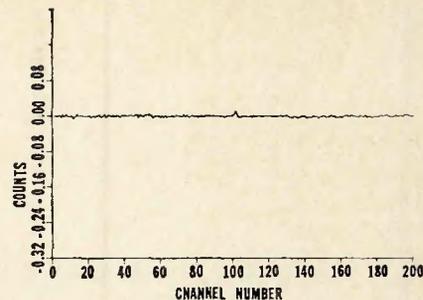


Fig. 11—Difference between Type 301 annealed plus 500 hr at 885° F and Type 301 annealed plus 0 hr at 885° F (without carbides)

(in a/o). However, the constant of proportionality which relates Cr content and velocity separation of peaks has not yet been found.

Conclusions

The difference procedure is a valid method of analysis which reveals the effects of solid state reactions which before could not be observed. The procedure followed for carbide separation does converge for the cases studied and yields reasonable percentages for paramagnetic phases (other than austenite) and the affected area of the parent matrix. The pseudomartensite separation procedure works well and yields answers within a few percent. This procedure could be used for determining the percent cold-work of austenitic sheet up to a limiting thickness for Mössbauer spectroscopy.

The 885° F phase was confirmed as paramagnetic and containing approximately 80% Cr. Also, the depletion of Cr from the matrix was found to be uniform.

Acknowledgments

Financial aid for this study was provided by the National Aeronautics and Space Administration under the NASA Sustaining Grant No. 19-001-024.

References

1. Muir, A. H., Ando, K. J., and Coogan, H. M., Mössbauer Effect Data Index 1958-1965, Interscience Publishers, New York, 1966.
2. Marcus, H., Schwartz, L. H., and Fine, M. E., "A Study of Precipitation in Stainless and Maraging Steels Using the Mössbauer Effect", ASM Trans. 1966, Vol. 59, p. 498.
3. Albritton, O. W., "A Study of Sensitization in Types 301 and 304L Stainless Steels Using Mössbauer Spectroscopy", NASA Report Cr-1077, June 1968.
4. Frauenfelder, H., "The Mössbauer Effect", W. A. Benjamin, New York, 1962, Chap. I.
5. Malone, M. O., "Sigma and 885° F Embrittlement of Chromium-Nickel Stainless Steel Weld Metals", WELDING JOURNAL, 46 (6), Research Suppl., 241-s to 253-s, (1967).
6. Johnson, C. E., Ridout, M. S., and Cranshaw, T. E., "Mössbauer Effect in Iron Alloys", Proc. Phys. Soc., 1963, Vol. 81, p. 1070-1090.