NGL 19-001-024

~~Arf-08848~~
N70-10708
CR-106646

Hqtrs Code UST

COMPUTER DIFFERENTIATION OF MÖSSBAUER SPECTRA

by

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Paper is based on a thesis submitted by James M. Lewis in partial fulfillment of the degree of Master of Science to the faculty of Louisiana State University, Baton Rouge, Louisiana

ABSTRACT

Computer programs have been devised which permit more effective quantitative interpretation of Mossbauer 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^{o}F embrittlement in ferritic stainless steels was obtained.

INTRODUCTION

Mössbauer Effect Spectroscopy had its beginning in 1958 with the publication of "Kernresonanzfluoreszenz von Gammastrahlung in Ir^{191}" (1)* by Rudolph Mossbauer, a graduate student at the Max Planck Institute. Space does not permit an exhaustive explanation of this phenomenon. As briefly as possible will be given what the writers consider to be the most pertinent factors regarding the Mössbauer Effect.

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 (2).

The main factor which caused this situation is the relative size of the recoil energy to the width of the emitted γ-rays (3). Mössbauer found that the recoil energy can be eliminated by placing the atoms in a crystal lattice (1). Under certain conditions the γ-ray emission and absorption is recoilless. This recoilless process occurs whenever the energy of the recoil is insufficient to cause excitation of a vibrational mode of the crystal. Without energy loss due to recoil, resonant emission-

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*The numbers in parentheses pertain to references at the end of this paper.

absorption is readily observable. Now by modulating the γ-rays emitted by the source, a spectrum of energies around the absorption peak may be taken. When examining Mössbauer spectra, peak shifts and other effects become evident.

There are three different effects which are of interest; they are isomer shift, quadrupole splitting, and magnetic splitting. Isomer shift occurs whenever impurity elements are present in either the source or the absorber (3). The isomer shift of an isotope is a function of the change in electron density at the nucleus. Thus, when impurity elements are added to the source or the absorber the electron density is changed and a peak shift occurs.

Quadrupole splitting arises from the nuclear quadrupole moment. This moment is a result of a nonspherical charge distribution around the nucleus. The effect of the nonspherical charge distribution causes two of the nuclear energy levels to be resolved. This is evident because the single resonant peak becomes two resonant peaks. Quadrupole splitting depends primarily upon the d electrons whereas the isomer shift depends mainly upon the s electrons (3).

Magnetic splitting is caused by the magnetism of each atom's own electrons. This effect causes 6 of the 8 possible nuclear transitions to be resolved. This six peak pattern is characteristic of ferromagnetic and anti-ferromagnetic materials. The velocity spread between various pairs of peaks (center pair, middle pair, and outside pair) indicate the size of the internal magnetic fields (3).

Sometimes the outside pair of peaks do not show a common midpoint with the other pairs of peaks. This is due to the effect of quadrupole coupling. Most commercial ferromagnetic materials consisting of several phases will exhibit this difference of midpoint. Some oxides of iron also exhibit combined quadrupole and magnetic effects (4). These three effects, isomer shift, quadrupole splitting, and magnetic splitting, are the most useful properties for the application of Mössbauer Effect to metallurgical problems.

Uses of Mössbauer Effect

An excellent reference for all uses of Mössbauer spectroscopy is The Mössbauer Effect Data Index 1956-1965 (4). 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 (5) used Mössbauer spectroscopy to study precipitation in stainless steels and maraging steels. Extensive use was made of the hyperfine magnetic structure. 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 was later reported by others (6), the paramagnetic peak of the precipitated ($(CrFe)_{23}C_6$) was masked by the austenite peak.

A study of cementite was conducted by Ron et al (7) using the Mössbauer Effect. They found a six peak hyperfine structure of Fe_3C along with a paramagnetic component. The spectrum of carbide separated by HCl exhibited only the central paramagnetic peak which turned out to be a doublet. Although not stated in this reference, a central doublet should be expected from a paramagnetic Fe_3C. This should be the case because of non-symmetrical charge distributions causing quadrupole splitting. 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.

When austenitic stainless steels are held in a temperature range of 900°F to 1500°F an internal reaction occurs which leaves these steels vulnerable to intergranular corrosion. Strauss et al (8) suggested that there is a chromium depletion in the grain boundary areas due to carbide precipitation. More recently, Albritton (6) used Mössbauer spectroscopy to shed new light on this subject.

Albritton found that a highly stressed ferromagnetic phase, pseudomartensite, develops as carbides are precipitated in fully austenitic stainless steels. Thus, after sensitization has occured, 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 a second objective was also realized. Application of the techniques soon to be described resulted in additional information concerning 885° F embrittlement in ferritic stainless steels.

The phenomenon of 885° F embrittlement is perhaps the least understood of the solid state reactions known to occur in stainless steels. The Group II ferritic stainless steels are the most prone to suffer deleterious effects as a result of this reaction, but embrittlement of two phase, austenitic-ferritic materials has been reported (9,10). Changes occur in such physical properties as specific gravity, magnetic coercive force, and electrical resistivity (11). Hardness and tensile strength values increase while impact strength and ductility decrease (12). Corrosion resistance is also lowered (13). These alterations of material properties are accomplished either by sustained heating in the critical temperature range or by slow cooling through this range. All of these effects however can be quite readily removed by heating to 1100° F for a period of time followed by a rapid cool.

The embrittling temperature range is generally given as 700° F to 1000° F. At what temperature the maximum effect occurs, as shown by an increase in hardness, is dependent primarily on the chromium content. But, regardless of chromium content, the maximum rate of occurence supposedly happens at 885° F; hence the name. Tisinai and Samans (14) report that under certain conditions the maximum rate may occur as high as 930° F.

A complete explanation of this reaction has not yet been given. Ordering, the presence of minor phases not associated with the Fe-Cr system, and precipitation hardening have all been suggested as the principal mechanism. General acceptance has, however, been given only to the theory of precipitation hardening or aging.

Fisher et al (15) determined that a body-centered cubic phase, rich in chromium, precipitates from ferrite and is responsible for the embrittling effect. Moreover, it has been suggested by Heger (16) that this phase is of a transitory nature and, under conditions of true equilibrium, will eventually transform to the sigma phase.

Support for these findings has been given by Lena and Hawkes (17), Brown and Connoly (18) (who also note that this phase is nonmagnetic), and Tisinai and Samans (14). The last named authors believe the precipitate to be coherent with the matrix and never loses this coherency at any time. Further, they are not quite certain the precipitate is responsible for the hardening effect and they state that prior formation of chromium carbide reduces 885° F embrittlement.

Malone (19) has stated that the prior precipitation of chromium carbide and then aging at 885° F produces little or no change in impact strength but does increase tensile and yield strengths. From these data he concludes that the effects of 885° F embrittlement and sigma embrittlement are additive; all of which seems to indicate that the phase in question is not a transitory phase in the formation of sigma.

Williams and Paxton (20) are even more emphatic in their belief that the precipitate is of a non-transitory nature. They have suggested a phase diagram for the Fe-Cr system that includes a eutectoid and monotectoid in the sigma region of the diagram.

In summary then, it is generally agreed that a precipitate, rich in chromium and having a body-centered cubic structure with a lattice parameter only 0.2 percent larger than the matrix, forms when ferritic stainless steels are subjected to the temperature range of 700° F - 1000° F. In question is the relation of this precipitated phase to the sigma phase and whether sensitization reduce the susceptability of a material to 885° F embrittlement.

Experimental Equipment and Materials

The stainless steel foils used in this investigation were types 301, 347, 430 and 446. The 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 I.

TABLE I

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	

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 at 885° F ± 10° for times shown in Table II. 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 Fe^{57} 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"

TABLE II

Mechanical and Thermal History of Foils

Type	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

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 (2). 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

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

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

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

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, taken $I(\infty)$ 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 and 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 austentite 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

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

The difference is taken just as in INTC0M. However, if the difference is less than -0.001 in any channel between 80 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 80 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 80 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. Listings of these subroutines are given in the Appendix.

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 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

$$D = \frac{z_1 - z_2 + (1-F)(1-z_1)}{1 - I'_r(x_1)} \tag{4}$$

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,

$F = \frac{1-z_2}{1-z_1}$ = 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 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.

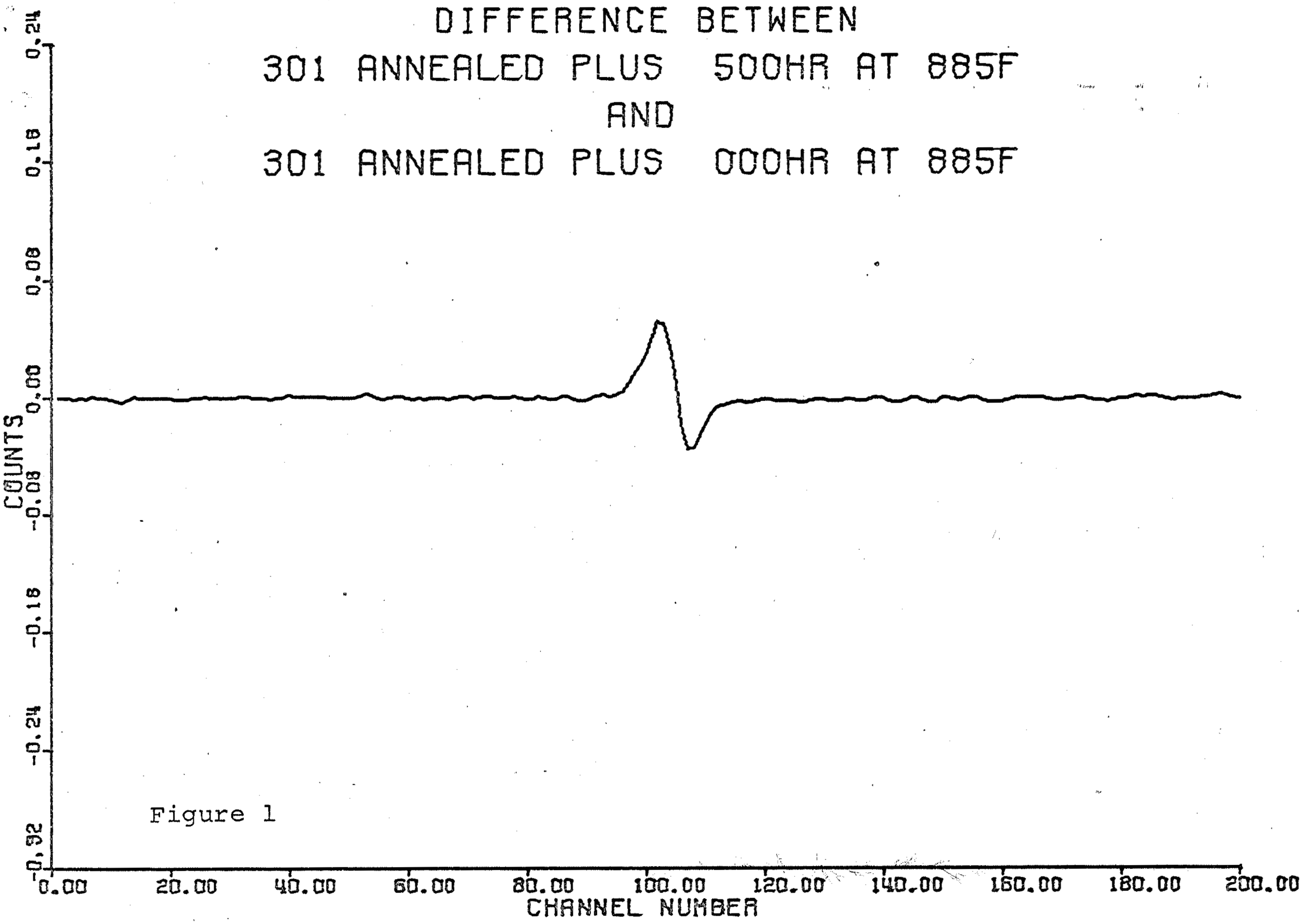

DIFFERENCE BETWEEN
301 ANNEALED PLUS 500HR AT 885F
AND
301 ANNEALED PLUS 000HR AT 885F
COUNTS
0.24
0.16
0.08
0.00
-0.08
-0.16
-0.24
-0.32
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 1

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. Malone (19) reports, however, that austenitic steels are not affected by 885° F embrittlement. This left only carbide precipitation as a possibility. As an aside, the ferromagnetic phase reported by Albritton (6) did not appear. This may be due to the longer aging times resulting in reversion of that phase back to austenite.

To check the carbide theory in the type 301 foils, a stablized grade was used. Type 347 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

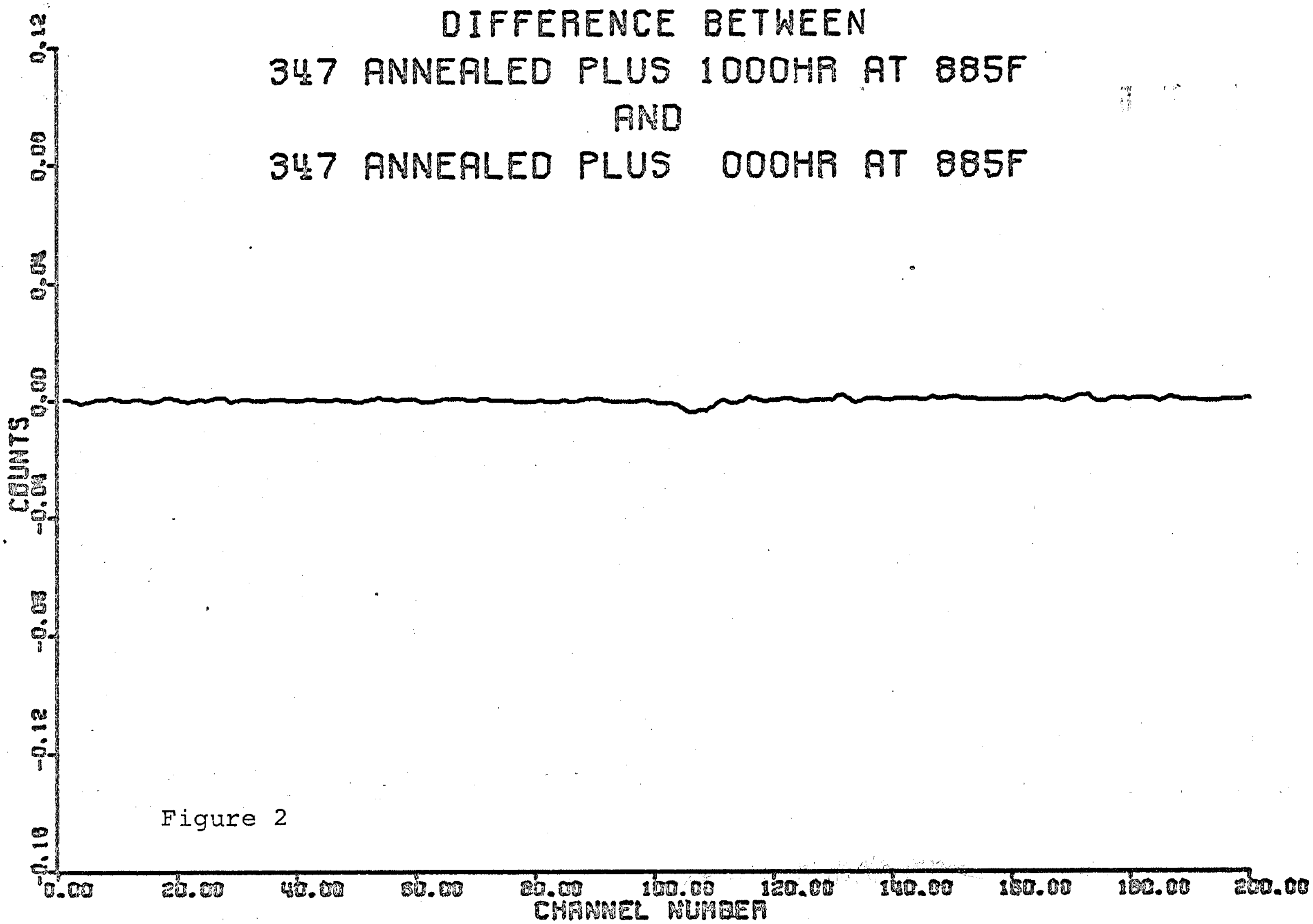

DIFFERENCE BETWEEN
347 ANNEALED PLUS 1000HR AT 885F
AND
347 ANNEALED PLUS 000HR AT 885F
COUNTS
0.12
0.08
0.04
0.00
-0.04
-0.08
-0.12
-0.16
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 2

value of 6.5 x 10^6 for I(∞). The results are shown in Figures 3,4, & 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 Fig. 6,7,8). Another possibility was that some of the pseudomartensite 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 equation 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-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 Fe^{57} 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 8½% for type 301 annealed

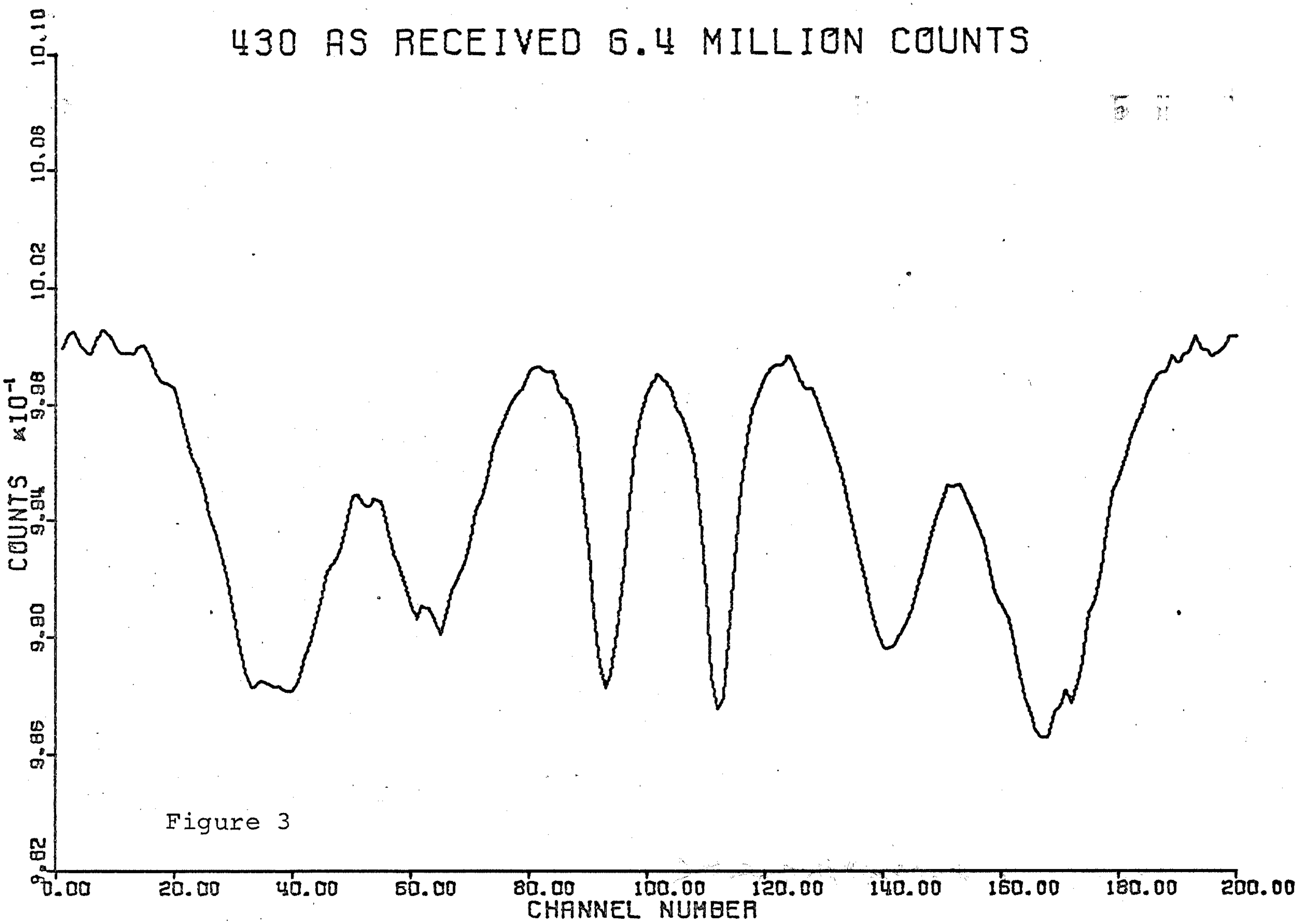

430 AS RECEIVED 6.4 MILLION COUNTS
COUNTS x10^-1
10.10
10.06
10.02
9.98
9.94
9.90
9.86
9.82
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 3

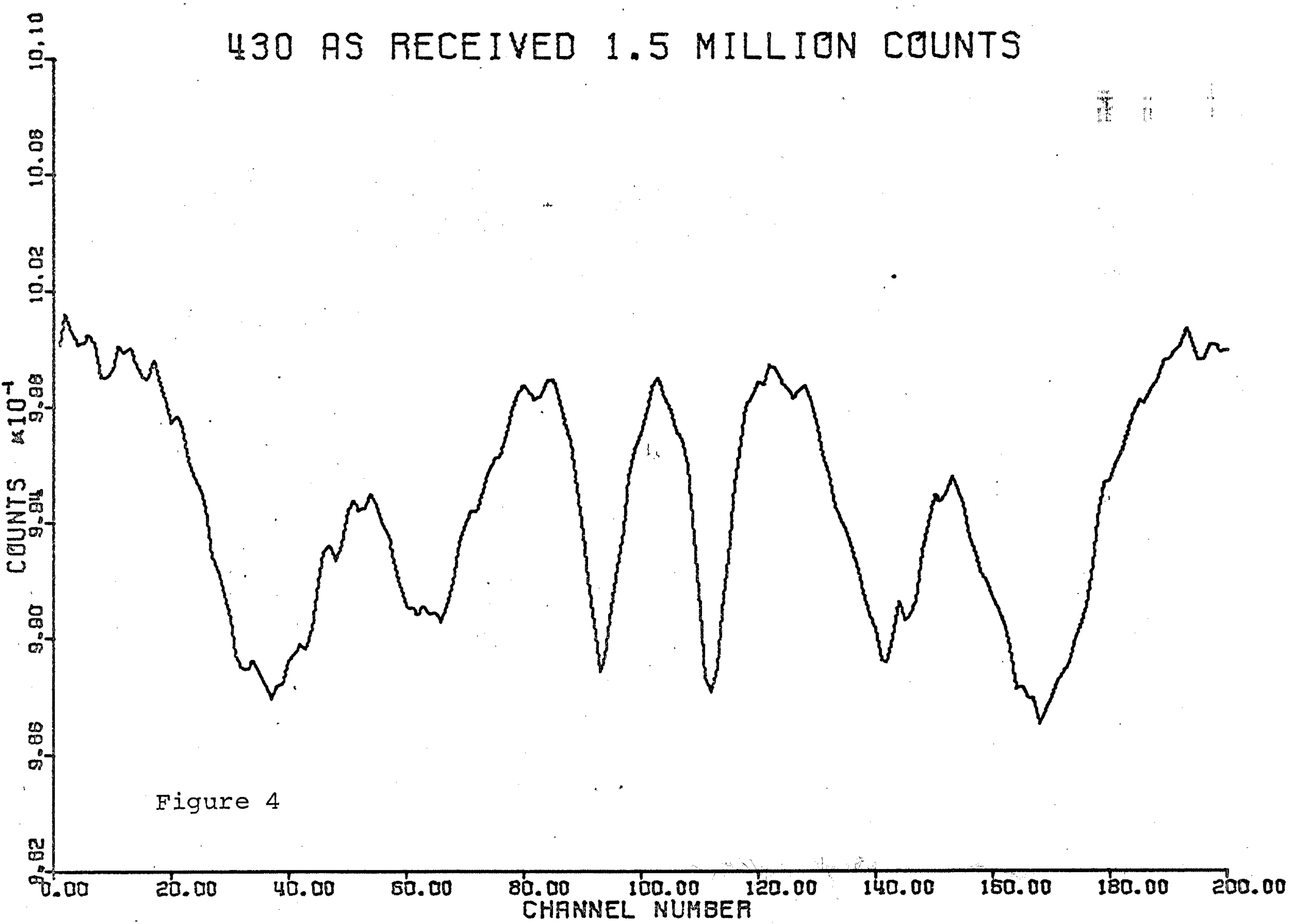

430 AS RECEIVED 1.5 MILLION COUNTS
COUNTS $\times 10^{-1}$
10.10
10.06
10.02
9.98
9.94
9.90
9.86
9.82
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 4

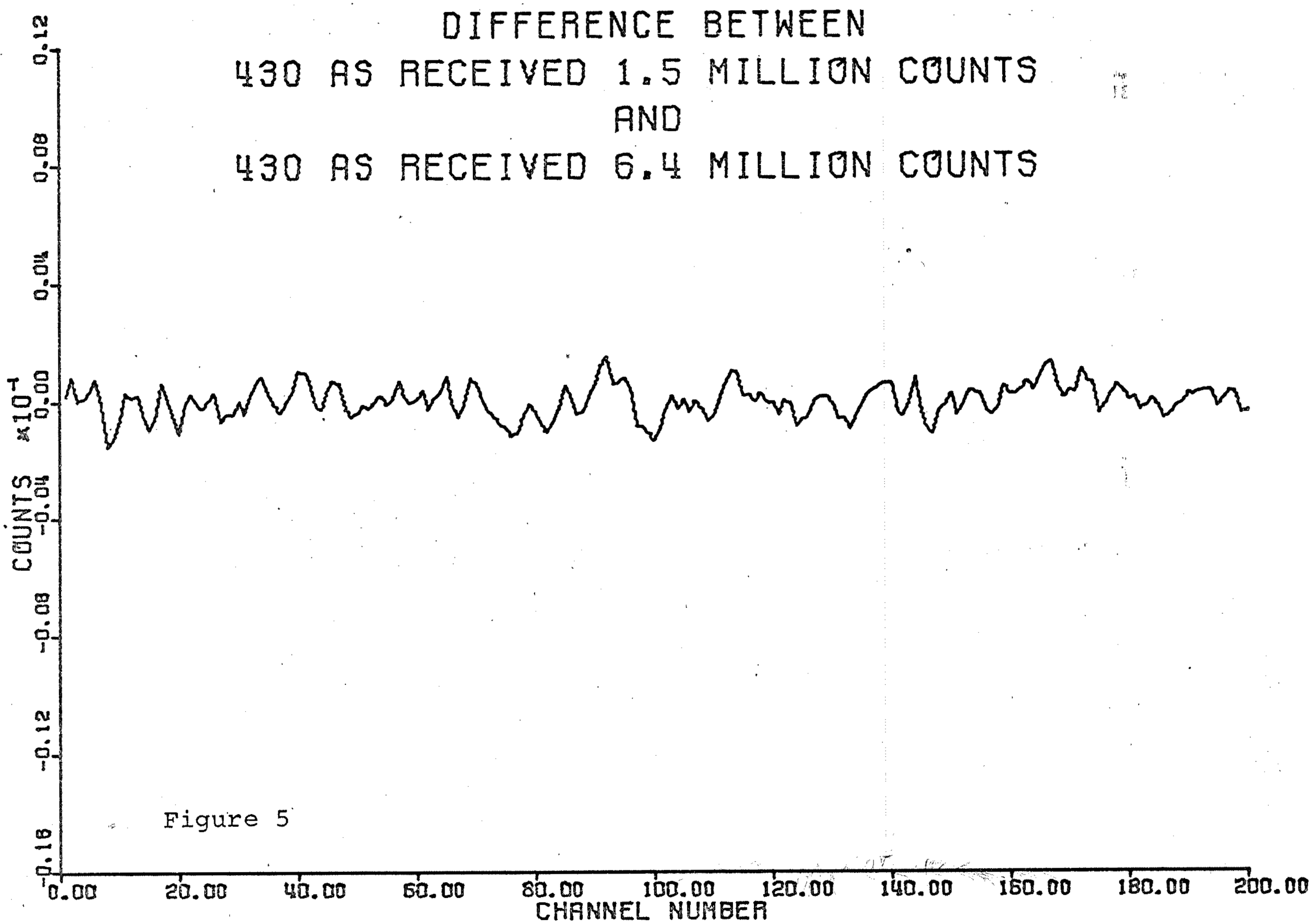

DIFFERENCE BETWEEN
430 AS RECEIVED 1.5 MILLION COUNTS
AND
430 AS RECEIVED 6.4 MILLION COUNTS
COUNTS ×10⁻¹
0.12
0.08
0.04
0.00
-0.04
-0.08
-0.12
-0.16
CHANNEL NUMBER
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00

Figure 5

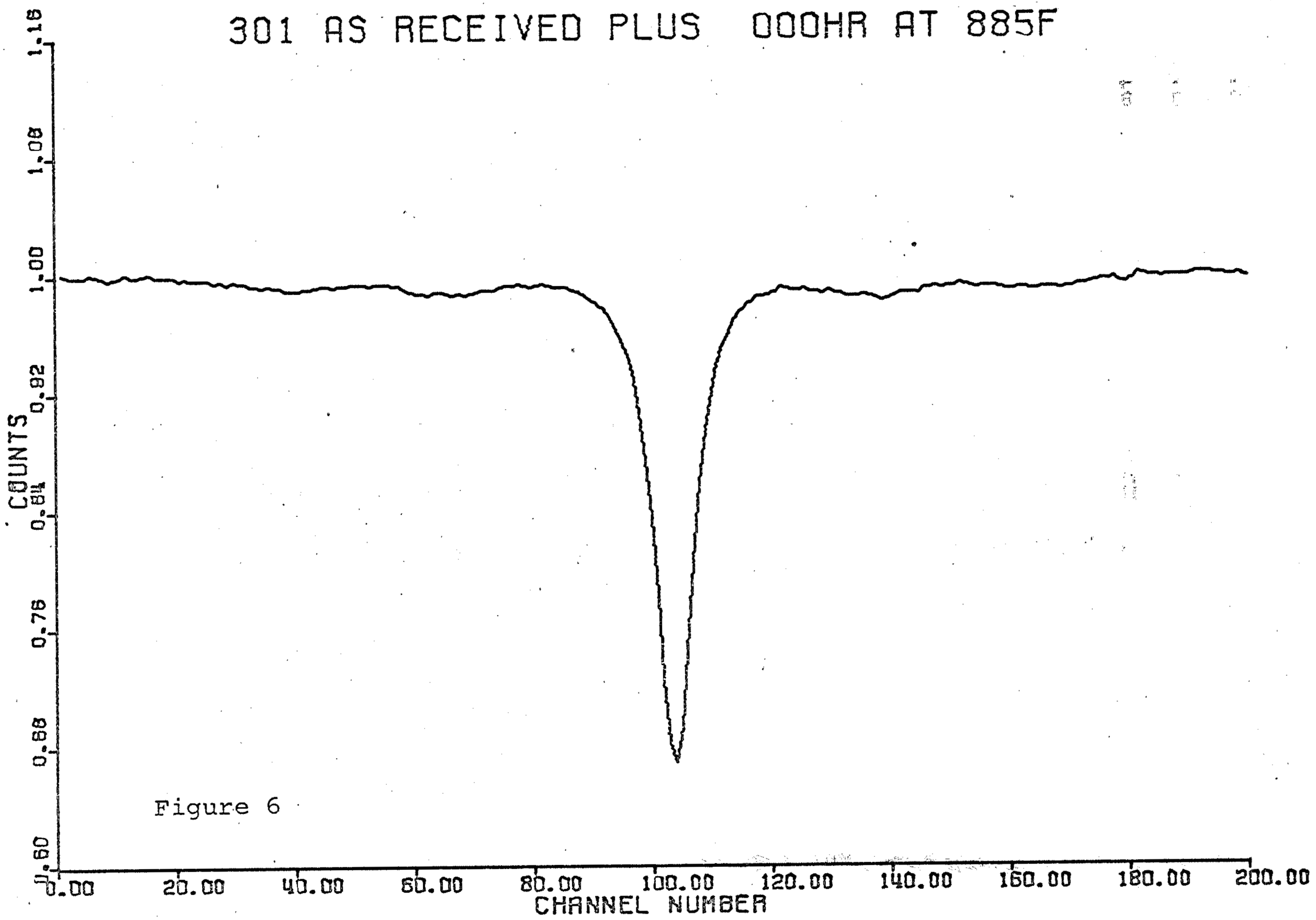

301 AS RECEIVED PLUS 000HR AT 885F
COUNTS
1.16
1.08
1.00
0.92
0.84
0.76
0.68
0.60
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 6

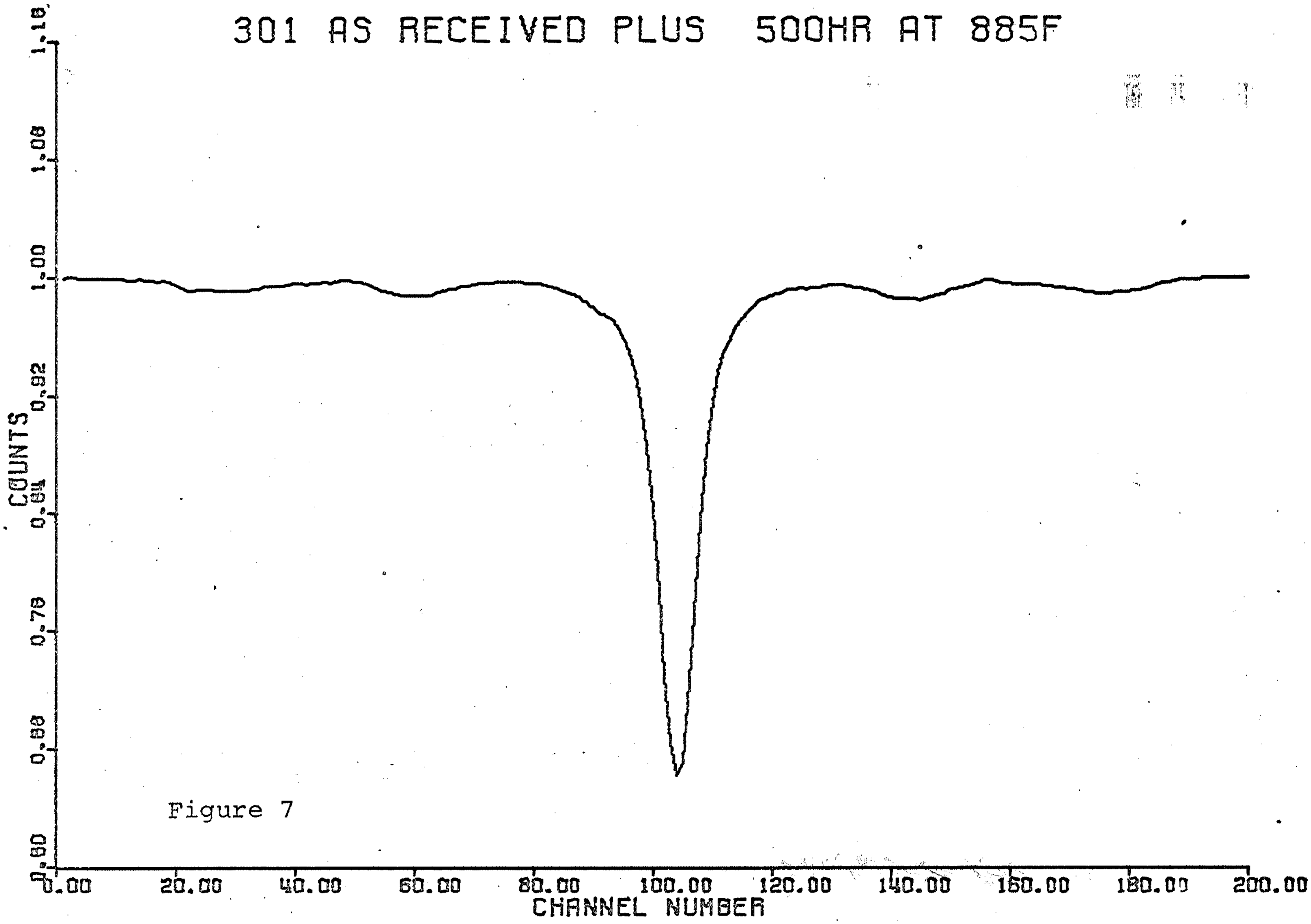

301 AS RECEIVED PLUS 500HR AT 885F
COUNTS
1.16
1.08
1.00
0.92
0.84
0.76
0.68
0.60
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 7

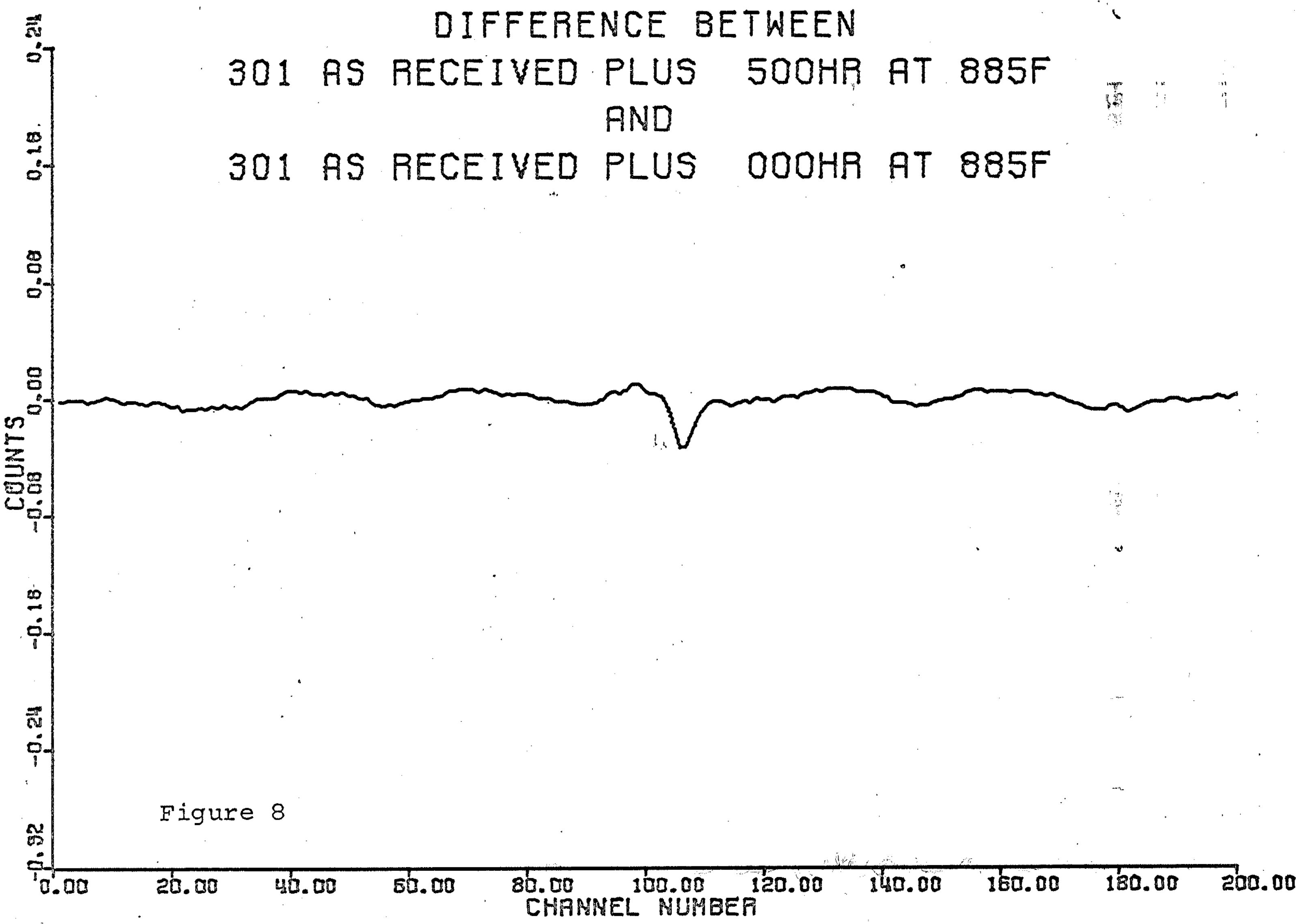

DIFFERENCE BETWEEN
301 AS RECEIVED PLUS 500HR AT 885F
AND
301 AS RECEIVED PLUS 000HR AT 885F
COUNTS
0.24
0.16
0.08
0.00
-0.08
-0.16
-0.24
-0.32
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 8

plus 250 hr. at 885° F and about 11½% for type 301 annealed plus 500 hr. at 885° F (see Fig. 9, 10, 11, 12).

The type 301 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 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 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

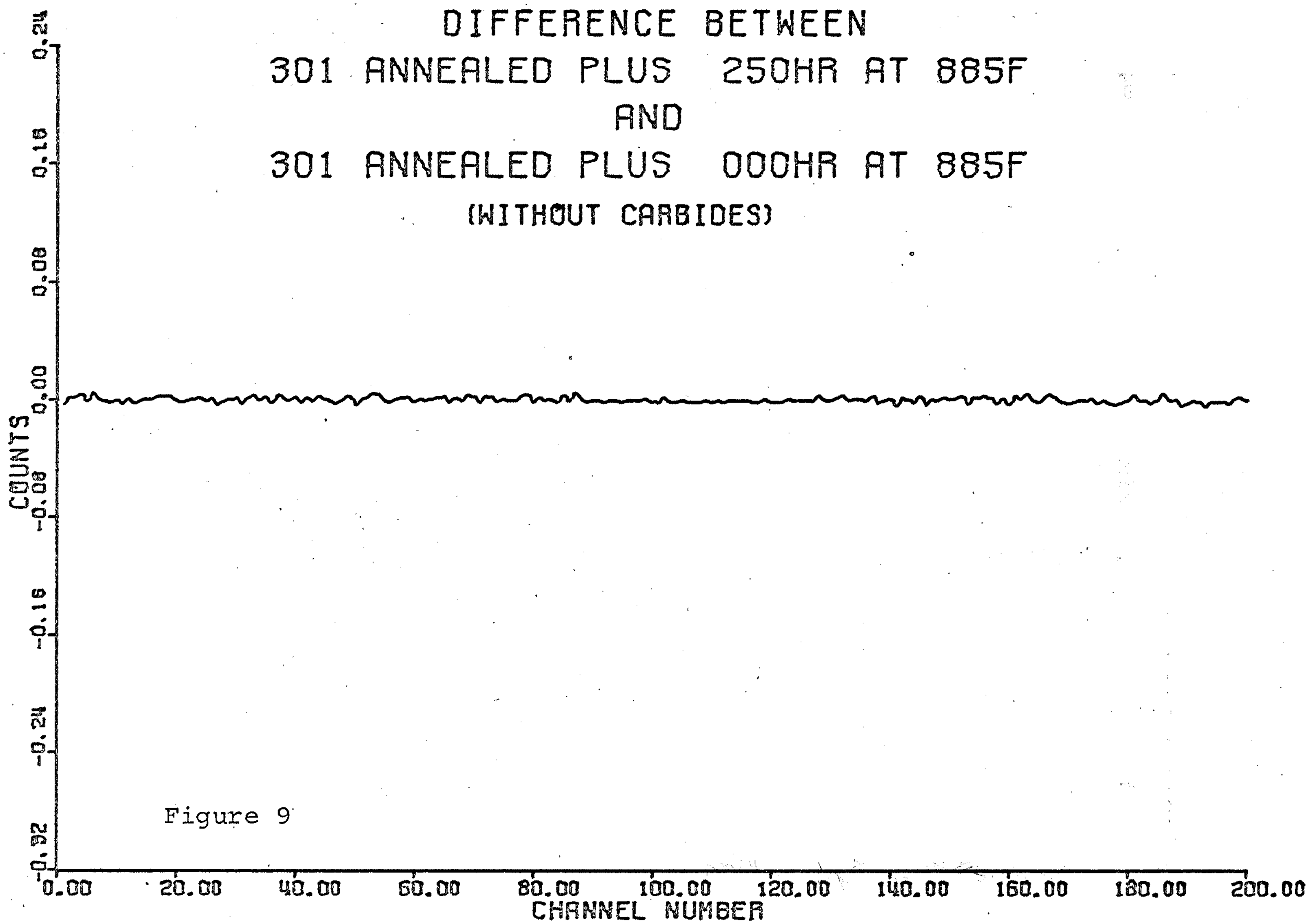

DIFFERENCE BETWEEN
301 ANNEALED PLUS 250HR AT 885F
AND
301 ANNEALED PLUS 000HR AT 885F
(WITHOUT CARBIDES)
COUNTS
0.24
0.16
0.08
0.00
-0.08
-0.16
-0.24
-0.32
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 9

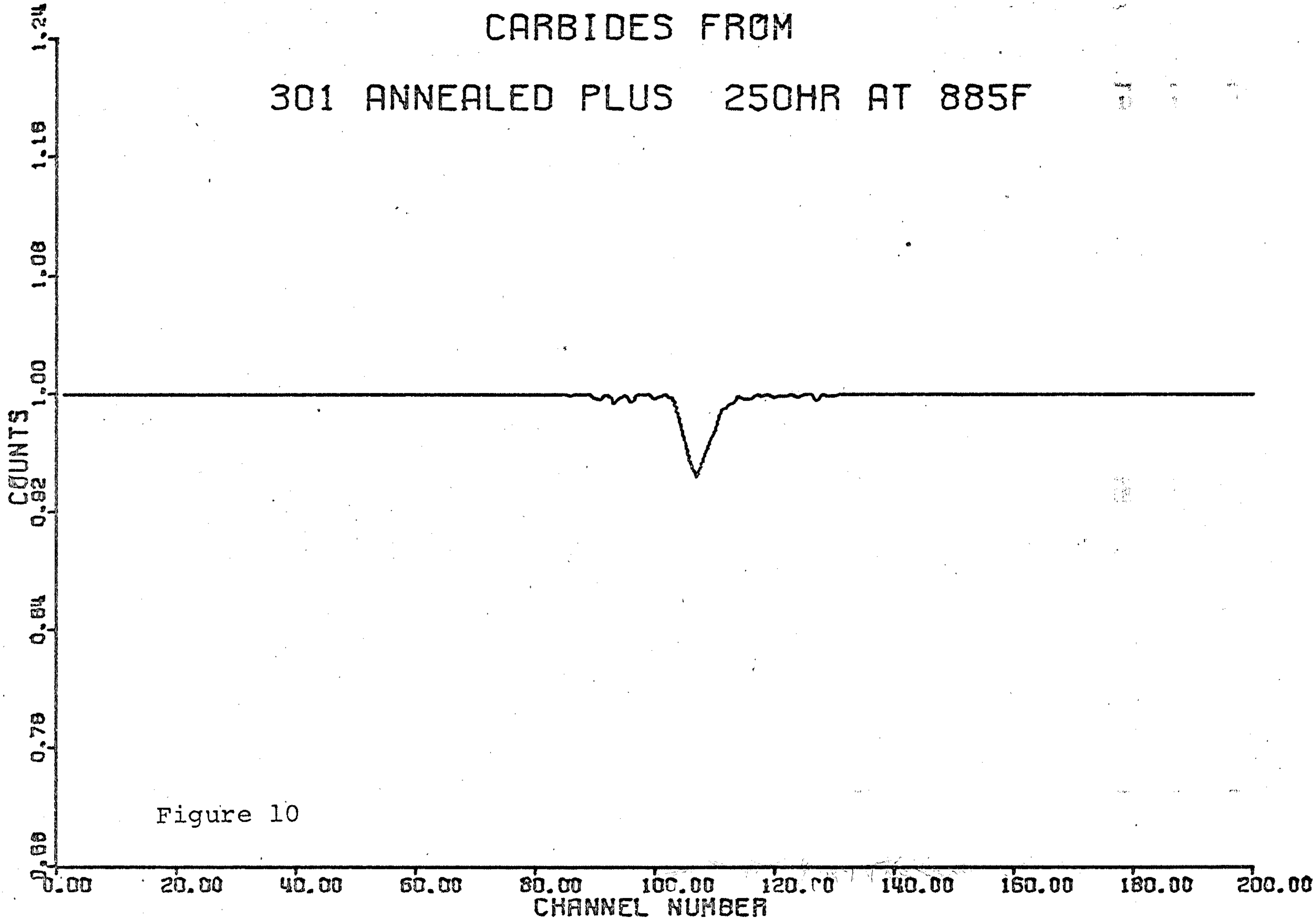
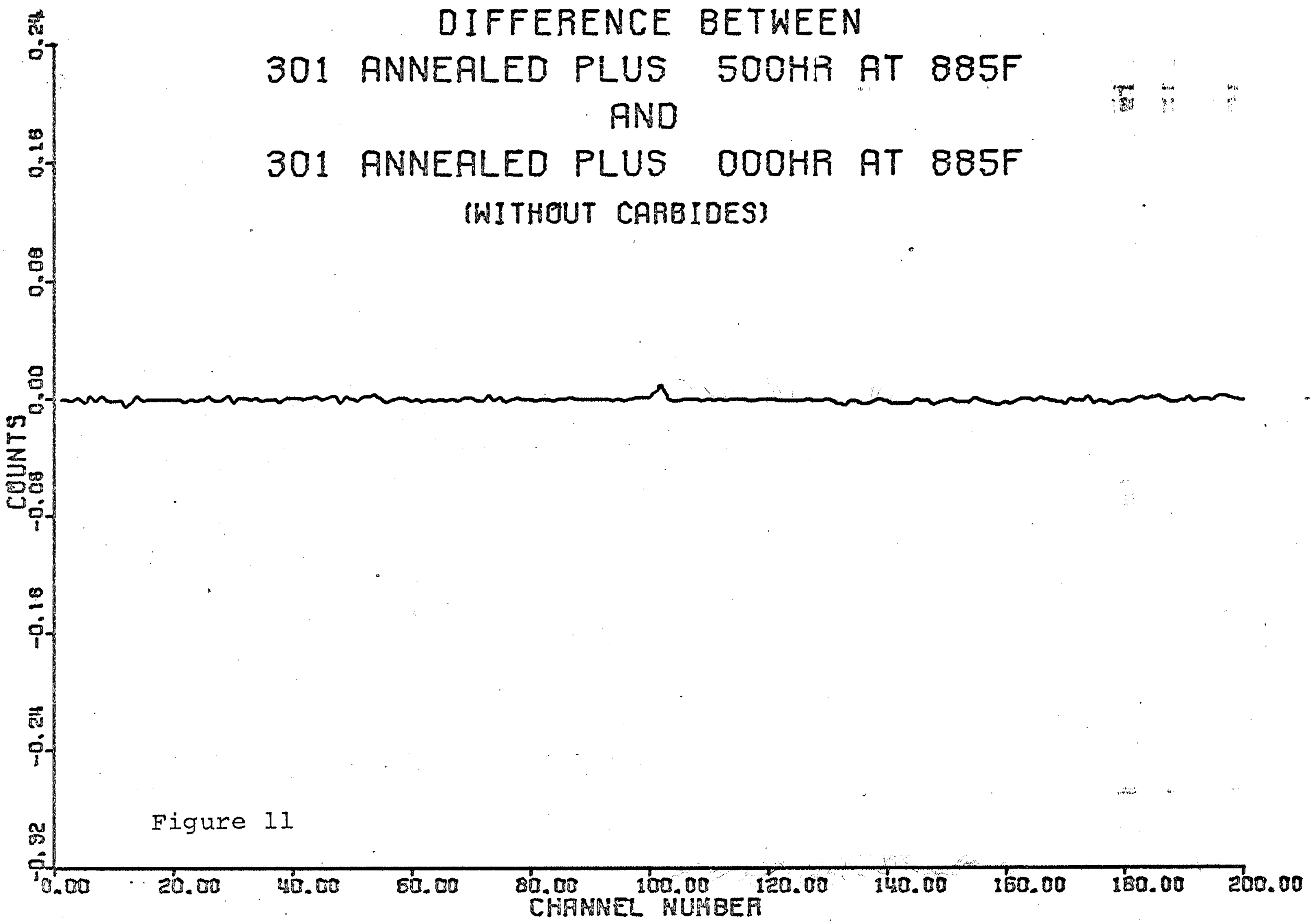
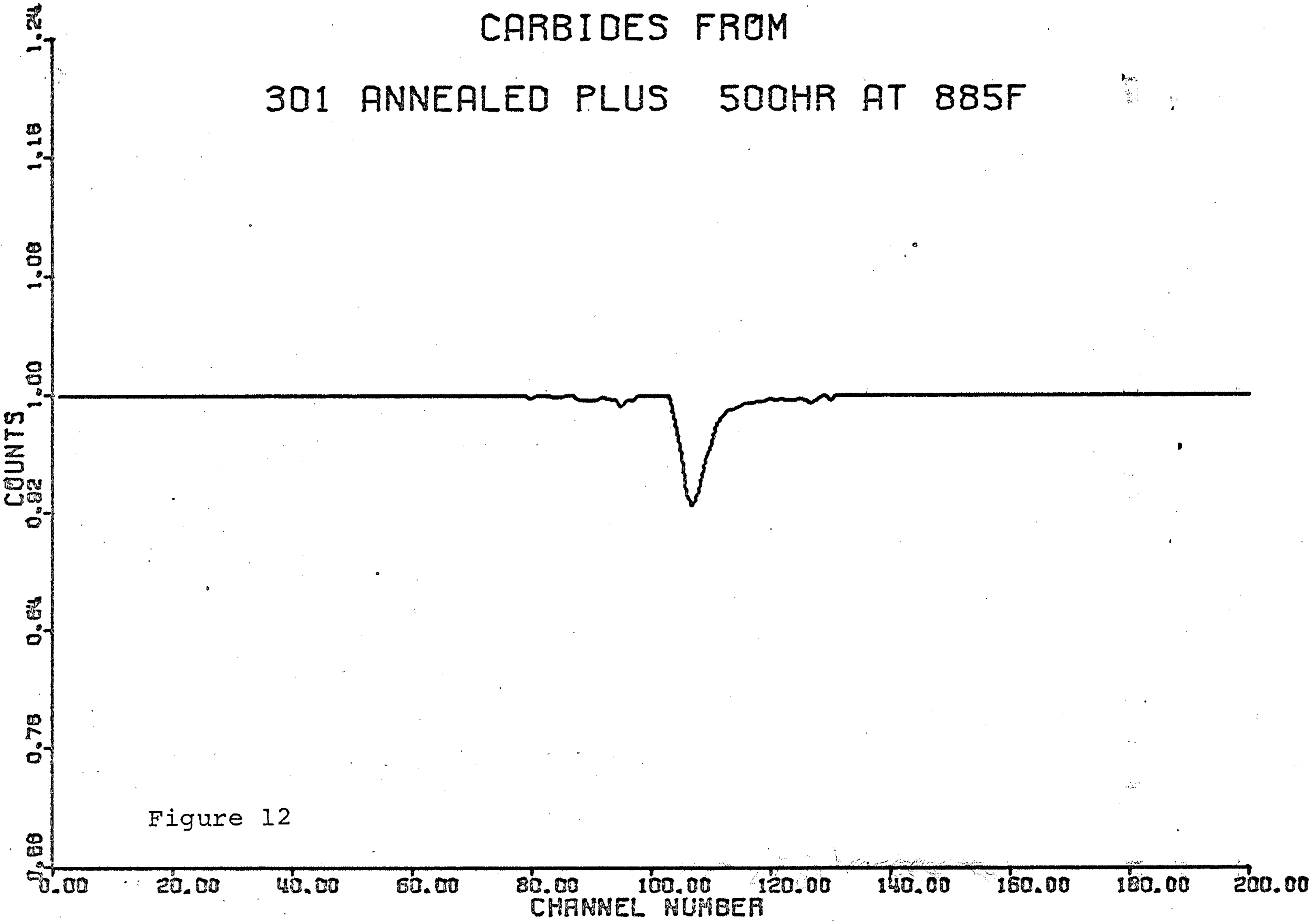

CARBIDES FROM
301 ANNEALED PLUS 250HR AT 885F
COUNTS
1.24
1.16
1.08
1.00
0.92
0.84
0.76
0.68
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 10



DIFFERENCE BETWEEN
301 ANNEALED PLUS 500HR AT 885F
AND
301 ANNEALED PLUS 000HR AT 885F
(WITHOUT CARBIDES)

Figure 11


CARBIDES FROM

301 ANNEALED PLUS 500HR AT 885F

Figure 12

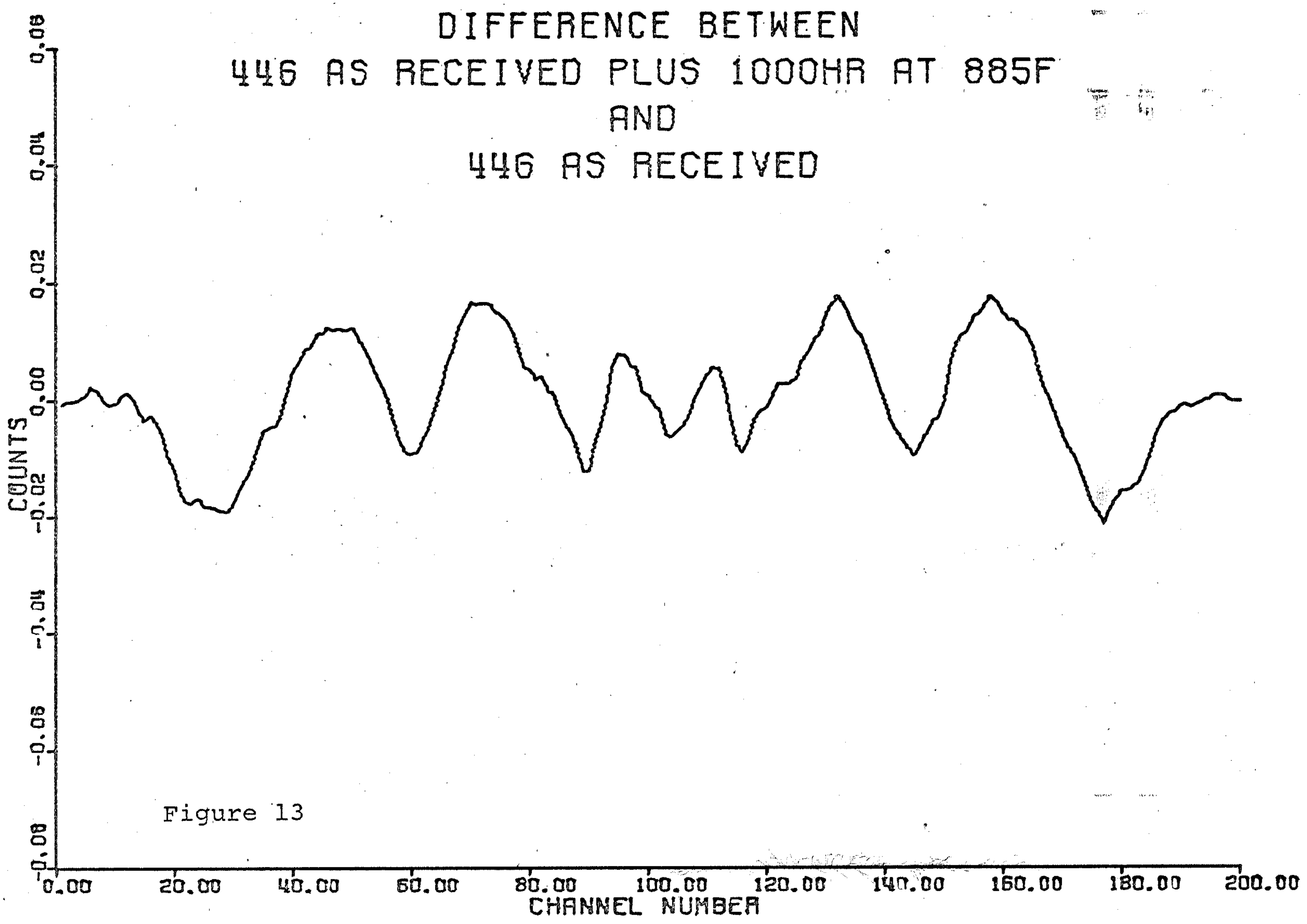

DIFFERENCE BETWEEN
446 AS RECEIVED PLUS 1000HR AT 885F
AND
446 AS RECEIVED
COUNTS
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
CHANNEL NUMBER

Figure 13

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 anti-parallel 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 (21). 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 (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 Mossbauer 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.

Acknowledgements

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

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APPENDIX

```
      SUBROUTINE BASE (S,N,B)
      DIMENSION S(205)
      Y=0.
      DO5I=1,N
      J=201-I
5     Y=Y+S(I)+S(J)
      A=2*N
      B=Y/A
      RETURN
      END
```

```
      SUBROUTINE NORM(S,B)
      DIMENSION S(205)
      DO6I=1,200
      C=S(I)/B
6     S(I)=C
      RETURN
      END
```

```
      SUBROUTINE INTCOM(S0,S4,DIFF,CARB)
      REAL*4 S0(202),S4(202),DIFF(202)
      REAL*4 CARB(202)
      DO21I=1,200
      DIFF(I)=S4(I)-S0(I)
21    CONTINUE
35    SUMD=0.
      SUM0=0.
      DO50I=1,200
      SUMD = SUMD+ DIFF(I)
      SUM0=SUM0+S0(I)
50    CONTINUE
      D=SUMD/(SUM0-200.)
      DO 51I=1,200
      Y=(S4(I)+D)/(1.+D)
      S4(I)=Y
      CARB(I)=(CARB(I)+D)/(1.+D)
      DIFF(I)=S4(I)-S0(I)
51    CONTINUE
      SUMD=0.
      DO 52I=1,200
      SUMD=SUMD+DIFF(I)
52    CONTINUE
      SU=ABS(SUMD)
      IF(SU.GT..005)GOTO35
      RETURN
      END
```

```
      SUBROUTINE CARBSP(S0,S4,DIFF,CARB)
      REAL*4 S0(202),S4(202),DIFF(202),CARB(202)
      L=20
      DO215J=1,L
      DO101I=80,130
      IF(DIFF(I).LT.-.001)GOTO100
      GOTO101
100   CARB(I)=DIFF(I)     + CARB(I)
      S4(I)=S4(I)+ABS(DIFF(I))
      DIFF(I)=0.
101   CONTINUE
      DO202I=1,200
202   DIFF(I)=S4(I)-S0(I)
      CALL INTCOM(S4,S0,DIFF,CARB)
215   CONTINUE
      SUM4=0.
      SUMC=0.
      DO105I=1,200
      SUM4=SUM4+1.-S4(I)
      SUMC=SUMC+1.-CARB(I)
105   CONTINUE
      PCT=(SUMC/(SUMC+SUM4))*100.
      WRITE(6,55)
      WRITE(6,57) PCT
57    FORMAT(1X,////////////10X,
     1'CARBIDE CONTENT IS',F10.3,'   PERCENT')
 55   FORMAT(1H1)
      RETURN
      END
```

```
      SUBROUTINE FERSEP(REF,COM,DIFF,F)
      REAL*4 REF(202),COM(202),DIFF(202),AUS(200)
      DO8I=1,200
      AUS(I)=1.
 8     CONTINUE
 6    CONTINUE
      Z1=1.
      DO1I=51,80
      IF(COM(I).LT.Z1)GOTO2
      GOTO1
  2   Z1=COM(I)
 1    CONTINUE
      Z2=1.
      DO3I=81,95
      IF(COM(I).LT.Z2)GOTO4
      GOTO3
 4    Z2=COM(I)
      I1=I
 3    CONTINUE
      D=(Z1-Z2+(1.-F)*(1.-Z1))/(1.-REF(I1))
      IF(ABS((1.-Z1)*F-(1.-Z2)).LT..0001)GOTO7
      DO20I=75,135
      COM(I)=COM(I)+   (1.-REF(I))*D
      AUS(I)=AUS(I)-(1.-REF(I))*D
 20   CONTINUE
      CALL BASE(COM,10,B)
      CALL NORM(COM,B)
      CALL BASE(AUS,10,B1)
      CALL NORM(AUS,B1)
      CALL INTCOM(REF,COM,DIFF,AUS)
      GOTO6
 7    CONTINUE
      SUMA=0.
      SUMM=0.
      DO10I=1,200
      SUMA=SUMA+1.-AUS(I)
      SUMM=SUMM+(1.-REF(I))
 10   CONTINUE
      PCT=SUMA/(SUMA+SUMM)     *100.
      WRITE(6,11)PCT,F
 11   FORMAT(1X,F10.5,18H PERCENT AUSTENITE ,'F=', F5.4)
      RETURN
      END
```