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WANL-TME-672

MASTER

GADOLINIUM-STAINLESS STEEL DEVELOPMENT

PART I

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J. A. Begley

February 3, 1964

Astronuclear Laboratory
Westinghouse Electric Corporation

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19

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GADOLINIUM-STAINLESS STEEL DEVELOPMENT

PART I

INFORMATION CATEGORY

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TABLE OF CONTENTS

	<u>Page</u>
I Abstract	iii
II Introduction	1
III Background Information	1
IV Development Effort	2
V Evaluation Procedure	3
VI Results	4
VII Discussion	5
VIII Summary	7
IX Bibliography	8

LIST OF FIGURES

		<u>Page</u>
1	Flat Tensile Specimen Design - TS1 TS1N	9
2	Flat Tensile Specimen Design - TS2 TS2N	10
3	Location of Chemistry Specimens and Gadolinium Contents at Indicated Locations	11
4	Metallography of AISI 304 + 1 w/o Gadolinium	12
5	Tensile Strength, .2% Yield Strength Versus Test Temperature	13
6	Percent Elongation Versus Test Temperature	14
7	Notched/Unnotched Ultimate Strength Versus Test Temperature	15

ABSTRACT

Processing procedures were developed by Carpenter Steel Company for the production of large ingots of AISI 304 + 1 w/o Gadolinium. The material was evaluated at WANL for use in neutron-absorbing cluster plates. Tensile properties, both notched and plain, were determined over the temperature range -328°F to 900°F . Over this temperature range the material met the design requirements for strength and ductility. Metallographic results showed the Gd-bearing phase to be finely dispersed throughout the structure. Chemical analysis confirmed the homogeneous distribution of Gd. Radiation damage is not expected at the environmental flux level of cluster plates for a 20-minute NERVA hot test.

INTRODUCTION

Analysis of the neutron flux conditions in the dome end of the NERVA Reactor indicated flux peaking. Therefore, a neutron-absorbing cluster plate material was sought to reduce this peaking. AISI 304 stainless steel + 1 w/o gadolinium was chosen as the optimum material. Gadolinium possesses the required nuclear characteristics and AISI 304 stainless steel meets the following requirements for the matrix:

1. -160 °F to 1000 °F temperature capability.
2. Resistance to radiation damage at environmental flux level of cluster plates.
3. Compatibility with hydrogen.

The presence of a small amount of Gd was not expected to materially affect the properties of the AISI 304 stainless steel matrix. This report covers the development by Carpenter Steel Company of an AISI 304 + 1 w/o Gd alloy and its evaluation at WANL for use as cluster plates. The development effort was closely followed by WANL and for this reason a brief history is included in the report.

BACKGROUND INFORMATION

Previous work has been done with Gd-AISI 304 stainless alloys. Kato and Copeland¹ investigated the Gd-AISI 304 pseudo-binary phase diagram. Small ingots (20-75 grams) of stainless steel with up to 10 w/o Gd have been arc melted. In general, homogeneous workable products have been obtained.² However, there has been no previous reported effort on melting and fabrication of relatively large ingots of gadolinium-bearing stainless steels.

Of the companies contacted, only Carpenter Steel and Universal Cyclops Steel possessed suitable facilities and were interested in producing the quantities of material required.

Carpenter Steel had experience with misch metal additions to steel melts. Data on a Type 347 stainless steel indicated its mechanical properties were virtually unchanged by a 0.5% Gd addition. Also the corrosion resistance of the steel was not seriously impaired. However, chemical homogeneity was poor. It was thought that the use of vacuum melting would yield an acceptable product. Using the data of Carpenter Steel, WANL and Carpenter personnel agreed upon the technical requirements for a material specification for future purchases.

Both Carpenter and Universal agreed to submit small heats of Gd-stainless steel to WANL for preliminary evaluation. The following section relates the history of development of melting and fabrication techniques for AISI 304 + 1 w/o Gd.

DEVELOPMENT EFFORT

Universal Cyclops' first vacuum-melted ingot proved to be "hot short" and, thus, fractured during forging. Although a remelt of this ingot was successfully processed to strip, the gadolinium yield was poor for the material contained only 0.13 w/o Gd. Universal Cyclops then lost interest in continuing and was dropped as a possible supplier.

Preliminary processing of three 17 lb. heats by Carpenter indicated success and a WANL order for 1000 lbs. of material per PDS 30057 was accepted. However, Carpenter's first large melt (greater than 1000 lbs.) was low in gadolinium content. A remelt of a small portion of this ingot indicated gadolinium was absorbed by the refractory crucible. The major portion of the ingot was then arc melted in a copper crucible but it exhibited prohibitive inhomogeneity and could not be processed further. Homogeneity of the parent ingot, which had been vacuum-induction melted, was not determined. Concurrently, three small ingots (17 lbs.), prepared by vacuum-induction melting, were processed to strip and met all requirements of PDS 30057. This material was forwarded to WANL for evaluation.

The next effort was a 500 lb. ingot prepared by vacuum induction melting. It exhibited serious hot tearing during forging and was not processed to strip. Its failure was attributed to a size effect. Materials with marginal workability often become more difficult

to fabricate as the cast ingot size increases. A smaller 60 lb. ingot was then melted. This smaller ingot could not be melted in vacuum, and, as a result, the chemical homogeneity was poor. Following a review of all previous experiments, it was decided to induction melt a 7-1/2" square ingot (300 lb.) in vacuum and to adjust the composition to obtain 5 - 10% ferrite in the austenitic matrix. With this procedure it was hoped that:

1. The detrimental large ingot size effect would be avoided.
2. Vacuum induction melting would yield a homogeneous product.
3. The presence of free ferrite would improve the workability of the ingot.

This ingot was successfully forged and exhibited good homogeneity. Nuclear requirements prevented acceptance of this material as the Gd content was slightly below specification. Another heat using the above procedure was then processed to strip. A proprietary method of Gd addition improved the yield of gadolinium and this heat met all specification requirements. Forty pounds of 3/16" hot rolled strip, annealed at 1900 °F for ten minutes and air cooled, was submitted to WANL for evaluation.

EVALUATION PROCEDURE

Chemical homogeneity was determined from samples across the width of the supplied strip. Samples were approximately 1 gram of drillings (1/4" drill) through the strip. The accuracy of gadolinium determinations was calculated to be $\pm 0.01\%$ at the 1.0% level. All analyses were performed by the Westinghouse Atomic Power Division.

Tensile tests, both notched and plain, were performed at WANL over the temperature range -328 °F to 900 °F. Specimens from both the longitudinal and transverse directions of the strip were tested. Figures 1 and 2 show the tensile specimen designs. Plain tensile tests were carried out at a crosshead speed of 0.05 in/min to yield, followed by 0.10 in/min to failure. Notched specimens were tested at a constant crosshead speed of 0.05 in/min. Elongation of the plain specimens was measured between scribe marks on a 1" gage length. All notched specimens had a stress concentration factor (K_t) of 3.5 as determined from Peterson's charts.³

RESULTS

Figure 3 shows the locations of chemistry samples and their respective Gd contents from the last 300 lb. ingot. As shown, the homogeneity is good. The area of chemistry samples in the plane of the strip (perpendicular to the primary component of neutron flux) is 31.5 mm^2 . Homogeneity of this sample size is acceptable from a nuclear standpoint.⁴ The matrix chemistry conformed to the limits of AISI 304. Analyses from the initial small heats were similar but not as complete and are not shown.

Metallographic results are shown in Figure 4. As the solubility of Gd in the matrix is negligible, Gd is present only in the second phase which is believed to be an Fe-Gd compound. Photomicrographs in Figure 4 show the second phase to be finely dispersed. Rolling has caused layering to some extent in the longitudinal view, as expected. However, the individual particles of the Fe-Gd compound are not significantly elongated as illustrated in Figure 4d. Severe elongation would be detrimental to mechanical properties in the transverse direction.

Figure 5 presents the range of tensile and .2% yield strengths for longitudinal and transverse specimens over the temperature range -328°F to 900°F . Two specimens from each direction were tested. Longitudinal and transverse strengths are nearly equivalent. There was no systematic difference in results between the two directions. Elongation values, shown in Figure 6, were also nearly the same with the exception of those at -328°F . Excepting this point, transverse ductilities were slightly lower than longitudinal. This is due to the layering and slight elongation of the second phase. The author is unable to explain the anomalous difference in ductilities at -328°F .

Notched tensile properties of the material were determined to investigate a possible embrittling effect of the dispersed phase. No embrittling effect was found. Both the longitudinal and transverse specimens exhibited favorable notched/unnotched ratios at room temperature and above, as shown in Figure 7. Again there was no systematic difference in results between the two directions. At -328°F the notch ratio falls below unity for both the longitudinal and transverse specimens. This is due to a strain-induced martensite reaction in the stainless steel matrix. Plastic flow reduces the stability of the austenite and induces a

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martensite transformation at cryogenic temperatures. All specimens became magnetic after testing at -328°F , indicating the presence of a transformation. Also, metallographic examination of these specimens under dark-field illumination indicated transformation products concentrated along slip lines. The martensite embrittles the matrix and lowers the notched properties. Gunther and Reed⁵ report the strain-induced martensite transformation as the cause of an unfavorable (below unity) notch ratio in annealed AISI 304 sheet at -328°F . Thus it is seen that the presence of the Fe-Gd compound in the stainless matrix does not significantly embrittle AISI 304 + 1 w/o Gd.

DISCUSSION

Homogeneity

Although the Gd is present as an Fe-Gd compound, the distribution of Gd throughout the structure is quite homogeneous. Figure 4 shows the second phase to be finely dispersed without large agglomerations. Chemical analyses showed a range of Gd content of 0.89 to 0.97% for a total of 13 samples taken at two different locations across the strip. On the basis of these results the material is considered acceptable for use in cluster plates from the standpoint of chemical homogeneity.

Mechanical Properties

Results of the mechanical property evaluation show the material to be comparable with annealed AISI 304. The presence of a second phase has little effect on the properties of the matrix. The material meets the design requirement of a 10,000 psi yield strength from -160°F to 1000°F . Tensile results were obtained at 900°F rather than 1000°F to permit direct comparison with preliminary evaluation data. At the time of testing it was not certain that material was available for additional testing at 1000°F due to material requirements for NRX-A3. Since cluster plates are not expected to see temperatures much greater than 500°F

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it was thought that testing at 1000 °F might be delayed to a later date. At present, material is available and tensile results at 1000 °F will be obtained in the near future. However, by extrapolation, which is thought valid, strength properties at 1000 °F are considered acceptable. AISI 304 + 1 w/o Gd also possessed good ductility at all test temperatures. Notch sensitivity at -328 °F is due to a strain-induced martensite transformation in the matrix. It is not a significant problem since plastic flow at cryogenic temperatures is required to produce the embrittling martensite phase. Furthermore, the yield strength increases as the temperature decreases, thus reducing the tendency for plastic flow. At -160 °F, it is doubtful if a transformation is thermodynamically probable. The mechanical properties of the material permit its use in cluster plates over the design temperature range of -160 °F to 1000 °F.

Radiation Damage

A fast neutron flux on the order of 7.2×10^{17} nvt is expected in the vicinity of cluster plates for a 20-minute hot test. As indicated in a previous report⁶ such a flux should not produce any appreciable damage to austenitic stainless steels. Thus, the matrix of AISI 304 + 1 w/o Gd is compatible with the flux environment of cluster plates. Another possible source of radiation damage is the absorption of thermal neutrons by the gadolinium in the structure. With the calculated 2.4×10^{17} nvt thermal neutron flux a Gd burnup of less than 5% is expected. Little data is available on radiation effects on AISI 304 + 1 w/o Gd. However, a meaningful comparison may be drawn between boronated and gadolinium bearing stainless steels. Both boron and gadolinium (at 1 w/o) are present in the stainless matrices as compounds. At comparable burnup levels, gadolinium bearing stainless should exhibit less radiation damage than boronated stainless since Gd captures neutrons by a (n, γ) reaction as opposed to the (n, α) reaction with B. Data in another report indicates the acceptability of boronated stainless (.93 w/o B¹⁰) for application as cluster plates at a 5% burnup level⁷. AISI 304 + 1 w/o Gd at the same burnup level should exhibit less damage and is, therefore, thought to be acceptable for use as cluster plates.

SUMMARY

1. A brief history of fabrication has been given illustrating the tendency toward hot shortness of large ingots and the necessity of vacuum induction melting to achieve a homogeneous distribution of Gd.
2. Gd was found to be present in the structure in the form of an evenly dispersed second phase. This phase is believed to be an Fe-Gd compound. Chemical analyses and metallographic results indicate good homogeneity.
3. The presence of approximately 1 w/o Gd in the structure had no significant effect on the mechanical properties of the AISI 304 matrix. Evaluation of the mechanical properties of this material showed it to meet the design requirements of cluster plates for the required service range of -160° to 1000° F.
4. AISI 304 + 1 w/o Gd should not sustain prohibitive radiation damage at the flux level of cluster plates.
5. The chemical homogeneity, mechanical properties and resistance to radiation damage of this material render it suitable for use as cluster plate material.

BIBLIOGRAPHY

1. Kato and Copeland, Proc. Sec. Conf. Rare Earth Research, September, 132, (1961).
2. Ray and Kato, "Alloys Containing Lanthanons As One Constituent", Neutron Absorber Materials for Reactor Control", N. R. Div. Reactor Dev., USAEC, (1962).
3. R. E. Peterson, Stress Concentration Design Factors, John Wiley & Sons, New York (1953).
4. D. C. McCutchan - WANL Reactor Analysis - personal communication.
5. Gunther and Reed, Trans. ASM, Vol. 55, 399 (1962).
6. WANL-TME-567, Evaluation of Three Candidate Cluster Plate Materials, October, 1963.
7. IBID, pg. 29.

PLAIN SPECIMEN TS - 1

NOTCHED SPECIMEN TS - 1N

TOLERANCES

.X $\pm .1$
.XX $\pm .01$
.XXX $\pm .001$

RADIUS TANGENT WITH TEST
SECTION, NO UNDER CUT
PERMITTED

.125 THICKNESS

✓32

F A O

Figure 1 - Flat Tensile Specimen Design

PLAIN SPECIMEN TS - 2

NOTCHED SPECIMEN TS - 2N

TOLERANCES

.X	$\begin{smallmatrix} + \\ -. \end{smallmatrix}$	.1
.XX	$\begin{smallmatrix} + \\ -. \end{smallmatrix}$	.01
.XXX	$\begin{smallmatrix} + \\ -. \end{smallmatrix}$	.001

RADIUS TANGENT WITH TEST
SECTION, NO UNDER CUT
PERMITTED

+ .000
.125 - .001 THICKNESS

32

F A O

Figure 2 - Flat Tensile Specimen Design

% GD	
A ₁	.955
B ₁	.967
C ₁	.910
D ₁	.917
E ₁	.912
F ₁	.907
G ₁	.913
H ₁	.923

% GD	
A ₂	.890
B ₂	.914
C ₂	.886
D ₂	.927
E ₂	.912

596190A

NOTE: BOTH 3" AND 5" STRIP FABRICATED FROM SAME BILLET

Figure 3 - Location of Chemistry Specimens and Gadolinium Contents
at Indicated Locations

LONGITUDINAL VIEW
(A) 100X

SURFACE VIEW
(B) 100X

TRANSVERSE VIEW
(C) 100X

**Gd BEARING
PHASE**

LONGITUDINAL VIEW
(D) 400X

Figure 4 - Metallography of AISI 304 + 1 w/o Gadolinium

Figure 5 - Tensile Strength, .2% Yield Strength Versus
 Test Temperature

Figure 6 - Percent Elongation Versus Test Temperature

Figure 7 - Notched/Unnotched Ultimate Strength Versus
Test Temperature