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Journal of Nuclear Materials 255 (1998) 67–71

journal of nuclear materials

Letter to the Editors

Study on the precipitates in Zircaloy-4 by Mössbauer spectroscopy

Wei Xiao, Chunlai Ma [*]

Department of Material Science and Engineering, Tsinghua University, Beijing, 100084, People's Republic of China

Received 19 May 1997; accepted 7 February 1998

Abstract

Mössbauer spectroscopy of ^{57}Fe was used to study the content and structure of precipitates in different thermal-treated Zircaloy-4 specimens. The spectra of Zircaloy-4 have two sets of peaks. One of them can be ascribed to precipitates of intermetallic compound $Zr(Cr,Fe)_2$. The structure of the specimen is changed by thermal treatment. The area of the Mössbauer peak is also changed. Content of $Zr(Cr,Fe)_2$ in a water quenched sample is the same as that in an as-received (50% cold worked) sample. The content of alloying element-iron in matrix between precipitates is not an important factor which has an influence on corrosion resistance of Zircaloy-4. © 1998 Elsevier Science B.V. All rights reserved.

PACS: 61.18.Fs, Mössbauer spectra structural analysis; 61.66.Dk, Alloys

1. Introduction

Due to low neutron-capture cross-section, high mechanical strength, high thermal conductivity and good corrosion resistance in water and steam, Zircaloy-4 (Zr, .5 Sn, 0.2 Fe, 0.1 Cr wt%) is widely used as fuel cladding tubes in pressurized water reactors (PWR). Zircaloy-4 comprises an α-Zr matrix with Sn in solid solution and intermetallic precipitates containing major alloying elements Fe, Cr. Only about 10% of these alloying elements have been reported to remain in the matrix [1]. These intermetallic precipitates are about 0.1–1.0 μm in diameter, depending on the fabrication conditions. The structure, composition, average size and morphology of the second phase precipitates are closely related to the corrosion behavior of Zircaloy-4 [1–8]. Under neutron, electron and ion irradiations, amorphization occurs in the precipitates in Zircaloy [9–17]. Irradiation also has an influence on the corrosion behavior [5,12,18,19]. The properties of these intermetallics have been studied for over two decades by using electron microscopy techniques, but the determination of volume fractions of different phases using electron microscopy has proven to be difficult.

It is well known that Mössbauer spectroscopy using ^{57}Fe has the advantage of providing information of the averaged characteristics of all Fe species being sampled over a relatively large specimen volume, independent of the degree of dispersion and the size of the precipitates. In particular, it is capable of studying much smaller (nanoscopic) objects, such as individual atoms, their aggregates and embryos of precipitates. Mössbauer spectra can provide detailed information about the chemical form of iron atoms in the alloys to help us better understand the structure and composition of the intermetallics. The local character of iron species can be inferred from measured s-electron densities, electric field gradients and hyperfine magnetic fields at ^{57}Fe nuclei. By measuring the Lamb–Mössbauer factors, different types of intermetallics can be identified. The technique may also provide the unique possibility of determining the concentration fraction of various precipitated phases, as a function of fabrication regime, heat treatment and irradiation [20]. In this paper, we report structure, content and distribution of intermetallics in Zircaloy-4 specimens subjected to different

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[*] Corresponding author. Fax: +86-10 6277 1160; e-mail: mcl-dms@mail.tsinghua.edu.cn.

PII S0022-3115(98)00032-4

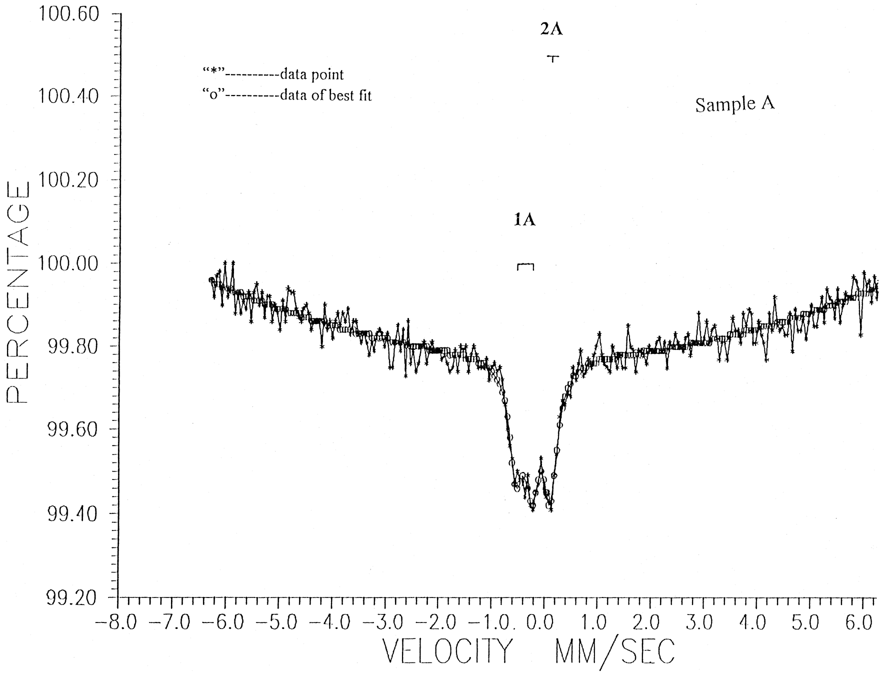

Fig. 1. Mössbauer spectra of as-received sample (Sample A).

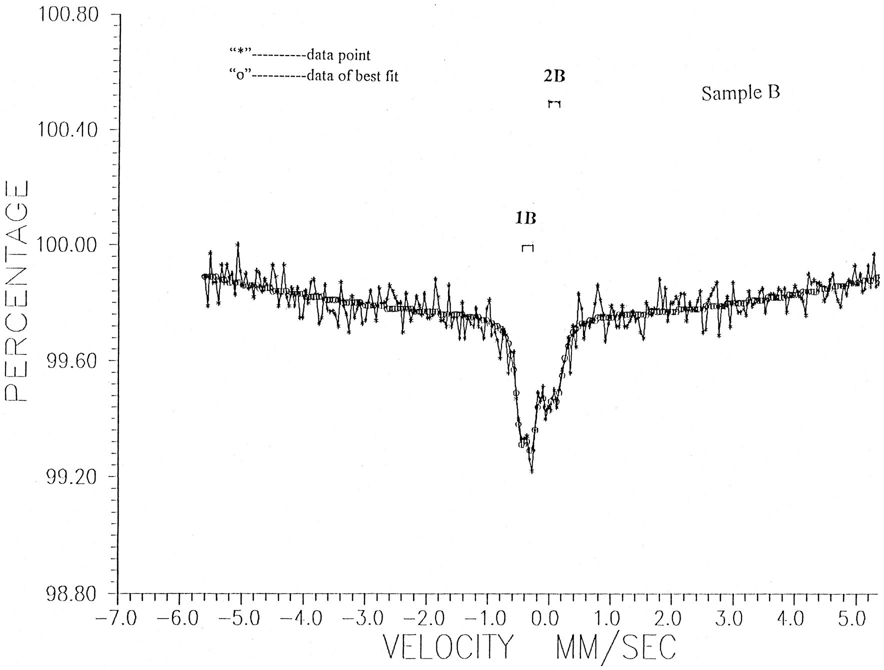

Fig. 2. Mössbauer spectra of water quenched sample (Sample B).

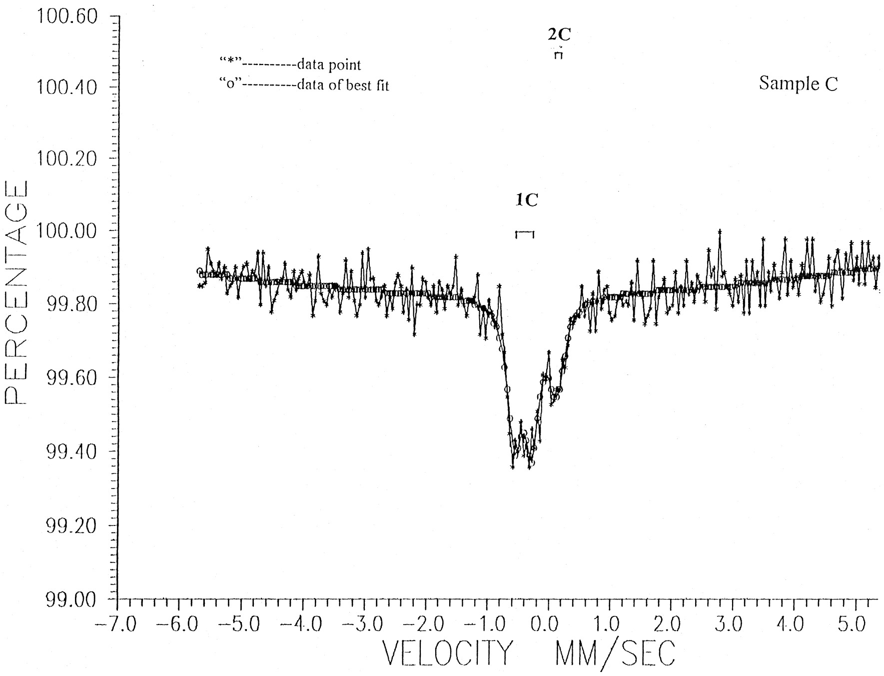

Fig. 3. Mössbauer spectra of annealed sample (Sample C).

thermal treatments by using the ^{57}Fe Mössbauer spectroscopy.

2. Experimental technique

Sheet specimens of as-received Zircaloy-4 (50% cold work) were sliced into small plates $1 \times 15 \times 15$ mm^3 in size (Sample A). Some of the Sample A were heated at 1373 K for 20 min and then water quenched (Sample B). Some of the Sample B were annealed at 1053 K for 72 h (Sample C). Foil specimens of 150 μm in thickness were prepared from the samples A, B, C by chemical polishing.

All Mössbauer spectra were taken by AME-50 with γ-ray transmission geometry, using an Amersham source of ^{57}Co diffused in a single-crystal rhodium platelet. Both the source and the absorbers were kept at room temperature. The activity of the source was in the range of 7–8 mCi. Because of the low content of Fe (0.2 wt%) in Zircaloy-4, low natural abundance of ^{57}Fe (2.2%), complexity of absorption patterns, and the small resonant absorption effect ($< 0.5\%$), 10 days were required to get a high-quality Mössbauer spectrum for each Zircaloy-4 specimen.

3. Experimental results

Figs. 1–3 show Mössbauer spectra for the three types of Zircaloy-4 specimens at room temperature. They consist of two sets of peaks; the location of the peak of single line is indicated by a symbol 'T'. The place of two Lorenzian peaks of quadrupole-split doublets of absorption lines are indicated by symbol Π. Major doublet peaks, i.e., the first spectra denoted by 1A, 1B and 1C, can be ascribed to intermetallic compound Zr(Cr,Fe)$_2$. The spectra have been

Table 1
Parameters of the first spectrum of ^{57}Fe Mössbauer spectra in Zircaloy-4 compared with published data [20]. IS is the isomer shift with respect to ^{57}Fe in metallic α-Fe, QS is the electric quadrupole splitting, GA is the half width at half maximum

	IS (mm/s)	QS (mm/s)	GA (mm/s)	Relative spectral area (%)
Sample A	−0.204	0.303	0.159	63.2
Sample B	−0.219	0.170	0.110	63.2
Sample C	−0.265	0.284	0.143	75.7
Zr(Cr,Fe)$_2$ C14 [20]	−0.20	0.26	0.115	30–60
Zr(Cr,Fe)$_2$ C15 [20]	−0.21	0.13	0.11	35–70

Table 2
The parameters of the second spectra of Zircaloy-4

	IS (mm/s)	QS (mm/s)	GA (mm/s)	Relative spectral area (%)
Sample A	0.286	0.000	0.154	36.8
Sample B	0.208	0.170	0.106	36.8
Sample C	0.278	0.097	0.130	24.3

analyzed by least-squares fitting. The fitting parameters which determined the first quadrupole doublets for the Samples A, B, C are listed in Table 1. The experimental error in the present work is estimated to be ±0.05 mm/s. By comparing the results with the published data [20], the parameter of the quadrupole splitting shows that the structure type of the intermetallic compounds in the Sample B (QS = 0.170) is face-centered cubic structure (C15). The intermetallic compounds in the Samples A and C are of a hexagonal closed packed structure (C14). Relative spectral area of the Samples A and B is 63.2%, while in the Sample C it is 75.7%. After water quenching and annealing, the second set of spectra which is originally of a single line (Sample A) splits as shown in Figs. 2 and 3. The parameters for the second spectra are listed in Table 2.

4. Discussion

In Mössbauer spectroscopy, the chemical information about iron-bearing phase is mainly derived from the isomer shift (IS) and the quadrupole splitting (QS) of the Mössbauer line. The IS is proportional to the s-electron density at an iron nucleus, which increases with the oxidation state of the iron and the covalence of the bonds. As a rule, as the Fe atom is compressed into smaller volumes, the IS becomes more negative, indicating a larger electron density at the nucleus. The QS is determined by the tensor of the electric field gradient at the iron nucleus, which reflect both the symmetry and covalence of the electron shells, and the symmetry of the crystal sites occupied by the iron atom. The measured IS and QS values (Table 1) are little different from the data in Ref. [20] and can be correlated with the values known for the relevant intermetallic compounds. The IS of the Sample A is about −0.2 mm/s. QS is about 0.3 mm/s. These values are very close to those of $Zr(Cr,Fe)_2$ C14 [20]. 63.2% of the total ^{57}Fe resonance comes from these precipitates. After water quenching, IS is about −0.22 mm/s. QS is 0.17 mm/s. They are close to the values of $Zr(Cr,Fe)_2$ C15. There are still 63.2% Fe atoms in these precipitates. In the water quenched sample most alloying element-iron still stays in intermetallic, not in solution. The values of IS and QS of the first spectra of Sample C are also close to $Zr(Cr,Fe)_2$ C14. These precipitates contain 75.7% of total Fe. After annealing, C15 $Zr(Cr,Fe)_2$ transforms to C14. And more Fe atoms come into $Zr(Cr,Fe)_2$ C14. The first spectra of the Samples A, B and C can be ascribed to intermetallic $Zr(Cr,Fe)_2$ precipitates which contain 60–70% of total Fe atoms of Zircaloy-4. After annealing for 72 h, more Fe atoms diffuse into $Zr(Cr,Fe)_2$. The second spectra may be due to other iron-bearing precipitates in Zircaloy-4. After water quenching and annealing, the spectra of this precipitate show splitting (Table 2). The other iron-bearing phase than the $Zr(Cr,Fe)_2$ may have evolved during the quenching and annealing treatment.

After water quenching, the present experiment shows that there are no more Fe atoms coming into the matrix of Zircaloy-4. Uniform corrosion resistance in static steam at 673 K is improved with an increasing cumulative annealing parameter (ΣA) [8]. It shows that the content of alloying element-iron in Zircaloy-4 matrix may not be an important factor influencing the corrosion resistance of Zircaloy-4.

5. Conclusion

Mössbauer spectra have shown that most atoms of alloying element Fe are in precipitates of intermetallics in Zircaloy-4, in particular, in the intermetallics of $Zr(Cr,Fe)_2$. The structure of $Zr(Cr,Fe)_2$ in the water quenched sample is C15. After annealing, the amount of intermetallics of C14 $Zr(Cr,Fe)_2$ in Zircaloy-4 increases. Other iron-bearing intermetallics may evolve by different thermal treatment.

The content of alloying element-iron in matrix of Zircaloy-4 is not an important factor which has an influence on corrosion resistance of the Zircaloy.

Acknowledgements

Special thanks are due to Professor Naifei Gao for his expert technical assistance in Mössbauer experiments and data treatment of Mossbauer spectra. The authors also thank Professor Jianzhang Liu (Northwest Institute for Nonferrous Metal Research) for providing as-received samples in this work. The support of this research by grants from National Nuclear Science Foundation of China is gratefully acknowledged.

References

[1] D. Charquet, J. Nucl. Mater. 211 (1994) 259.

[2] R.M. Kruger, R.B. Adamson, S.S. Brenner, J. Nucl. Mater. 189 (1992) 193.

[3] B. Wadman, H.-O. Andren, A.-L. Nystrom, P. Rudling, H. Pettersson, J. Nucl. Mater. 200 (1993) 207.

[4] Y. Ito, T. Furuya, J. Nucl. Sci. Technol. 32 (11) (1995) 1118.

[5] Y.H. Jeong, K.S. Rheem, H.M. Chung, in: C.M. Eucken, A.M. Garde (Eds.), Proc. 9th Int. Symp. on Zirconium in the Nuclear Industry, ASTM-STP 1132, ASTM, Philadelphia, 1991, p. 683.

[6] H.G. Weidinger, H. Ruhmann, G. Cheliotis, M. Maguire, T.-L. Yau, in: C.M. Eucken, A.M. Garde (Eds.), Proc. 9th Int. Symp. on Zirconium in the Nuclear Industry, ASTM-STP 1132, ASTM, Philadelphia, 1991, p. 499.

[7] D. Pecheur, F. Lefebrve, A.T. Motta, C. Lemaignan, D. Charquet, in: A.M. Garde, E.R. Bradley (Eds.), Proc. 10th Int. Symp. on Zirconium in the Nuclear Industry, ASTM-STP 1245, ASTM, Philadelphia, 1994, p. 687.

[8] H. Anada, K.-i. Nomoto, Y. Shida, in: A.M. Garde, E.R. Bradley (Eds.), Proc. 10th Int. Symp. on Zirconium in the Nuclear Industry, ASTM-STP 1245, ASTM, Philadelphia, 1994, p. 307.

[9] Y. Etoh, S. Shimada, J. Nucl. Mater. 200 (1993) 59.

[10] M. Griffiths, R.W. Gilbert, G.J.C. Carpenter, J. Nucl. Mater. 150 (1987) 53.

[11] D. Pecheur, F. Lefebvre, A.T. Motta, C. Lemaignan, D. Charquet, J. Nucl. Mater. 205 (1993) 445.

[12] Y.S. Lee, K.Y. Huang, C.Y. Huang, J. Nucl. Mater. 205 (1993) 476.

[13] L.M. Howe, D. Phillips, A.T. Motta, P.R. Okamoto, Surf. Coatings Technol. 66 (1994) 411.

[14] A.T. Motta, D.R. Olander, Acta Metal Mater. 38 (11) (1990) 2175.

[15] A.T. Motta, F. Lefebvre, C. Lemaignan in: C.M. Eucken, A.M. Garde (Eds.), Proc. 9th Int. Symp. on Zirconium in the Nuclear Industry, ASTM-STP 1132, ASTM, Philadelphia, 1991, p. 718.

[16] D. Pecheur, A.T. Motta, C. Lemaignan, J. Nucl. Mater. 195 (1992) 211.

[17] F. Lefebvre, C. Lemaignan, J. Nucl. Mater. 171 (1990) 223.

[18] Y. Etoh, S. Shimada, K. Kikuchi, K. Kawai, J. Nucl. Sci. Technol. 29 (12) (1992) 45.

[19] Y. Etoh, J. Nucl. Sci. Technol. 29 (6) (1992) 589.

[20] J.A. Sawicki, J. Nucl. Mater. 228 (1996) 238.