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EXPERIENCE WITH NEUTRON IRRADIATED REACTOR PRESSURE VESSEL STEELS-A MÖSSBAUER STUDY

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The influence of neutron irradiation and post-irradiation heat treatment on the Mössbauer spectra of reactor pressure vessel steels is studied. Substantial changes in the materials are detected, but a final interpretation turned out to be impossible without performing further investigations.

1. Introduction

The deterioration of the mechanical properties of reactor pressure vessel (RPV) steels during their irradiation in a nuclear power plant is known as neutron embrittlement. The only possibility to reduce irradiation embrittlement and to increase the safety margin against brittle fracture of the RPV is thermal annealing. Recently a new kind of search for an efficient temperature-time regime for post-irradiation heat treatment using non-destructive test methods like positron annihilation and hardness and proof of the recovery of mechanical properties by destructive test methods was presented [1,2]. Although this approach is based on the annealing behaviour of irradiated specimens a detailed knowledge of the development of a fine-scale microstructure during irradiation was not essential for derivation of an efficient temperature-time regime. Any more detailed knowledge of microscopical mechanisms could be helpful in an understanding of the fact that a comparatively small (> 0.1 at.%) Cu content of RPV steels favours brittle fracture [3].

Recently the search for and discussion of microscopic mechanisms responsible for the observed materials behavior after neutron irradiation was continued by positron annihilation [4,5]. For the first time a possibility of explaining the positron annihilation data by irradiation induced carbide formation was proposed. The aim of our present Mössbauer (MB) investigations was

- to study the influence of neutron irradiation and post-irradiation heat treatment (450 °C/1 h) on the MB spectrum of RPV steels,
- to check the possibility of detecting irradiation-induced $M_{23}C_6$ precipitates proposed by positron annihilation [4,5] and
- to study the influence of Cu impurities on the hyperfine field in iron.

2. Experimental

Two types of RPV steels (Soviet type 15 Kh2MFA) were available, which were produced as 50 kg laboratory heats with the following heat treatment: 1000 °C/1 h/Ar with oil quenching followed by 700 °C/10 h/Ar with air cooling. In addition a binary Fe-0.31 wt.% Cu model alloy was available. The chemical compositions are given in table 1. Irradiation of the RPV steels was performed at a temperature of (265 ± 15) °C with fast neutrons ($E_n > 1$ MeV) at a neutron flux of 1.3×10^{15} n $\times$ m^{-2} xs^{-1} to a fluence of 2.5–2.8 $\times 10^{22}$ n $\times$ m^{-2}.

For the MB measurements foils of about 20/μm thickness were prepared from thicker specimens by mechanical grinding down to about 100 μm followed by a final chemical polishing in 94 ml H_2O_2 + 6 ml HF. The Mössbauer measurements were performed in transmission geometry and the samples were mounted with adhesive tape. The calibration of the velocity scale was done with a α-iron standard sample. The obtained spectra were fitted allowing for different sextets in a single spectrum. In the best fit the spectra were decomposed into 3 sextets.

3. Results and discussion

A typical MB spectrum of our RPV steel in the unirradiated state is shown in fig. 1. Two of the three sextets are clearly visible. The MB results of all measurements performed (unirradiated, irradiated as well as on irradiated + annealed specimens) are collected in table 2. The main component of the Mössbauer spectra is characterised by a magnetic hyperfine field value slightly higher than that of pure iron. This may be explained if the alloy components Cr, V, Mo are treated as dissolved in an α-iron matrix. The role of solute atoms of these elements are thought to increase the hyperfine field on iron [6,7,9,10], although there are reported contrary results too, especially for Cr [11]. In the case of increasing hyperfine fields cr atoms produce the largest effect and have the highest concentration in our alloy. The other two sextets of the spectra change their relative intensities in dependence on irradiation and post-irradiation annealing, respectively. From the positron annihilation measurements it was proposed, that the effect of irradiation is the development of precipitates of $M_{23}C_6$. This

Table 1
Chemical composition of RPV steels (designation taken from [4]) and reference materials

designation	composition [wt.-%]											
	C	Si	Mn	Ni	Cr	Mo	V	S	P	Cu	Co	N
C	0.145	0.12	0.28	0.07	2.35	0.70	0.23	0.028	0.018	0.14	0.010	0.017
E	0.145	0.18	0.36	0.07	2.60	0.67	0.30	0.030	0.018	0.34	0.010	0.018
FeCu	–	–	–	0.03	0.02	0.01	0.01	0.002	0.005	0.31	0.004	–

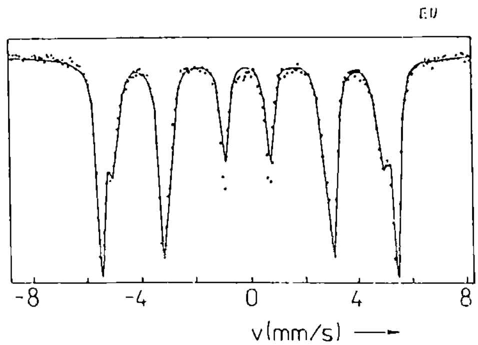

Fig. 1. Typical Mössbauer spectrum of irradiated RPV steel.

model does not explain the two additional magnetic sextets observed in the spectra with internal magnetic field around 300 kOe or smaller. According to [8] the Mössbauer spectra of manganese-chromium carbides of the types M_6C and $M_{23}C_6$ are characterised by a single absorption line at about -0.5 mm/s. The extensive search for irradiation-induced $M_{23}C_6$ precipitates was performed with a channel width of 0.05 mm/s up to a statistics of 1.6×10^6 total events. No

Table 2
Parameters of the fits of the Mössbauer spectra from unirradiated and irradiated RPV steels. H-magnetic hyperfine field in kOe (mean errors for the first two components $< 0.3\%$ and for the third component $< 1\%$); IS-isomer shift in mm/s; E_Q-quadrupole splitting in mm/s; Γ-FWHM in mm/s; area-relative intensity of the different sextets.

sample	H	IS	E_Q	Γ	area
C	333.05	−0.052	0.012	0.320	0.66
unirradiated	304.64	−0.070	0.010	0.361	0.29
	277.68	−0.090	0.035	0.380	0.05
C	332.67	−0.047	0.020	0.301	0.66
irradiated	307.82	−0.063	0.021	0.301	0.17
	295.85	−0.082	0.018	0.423	0.16
C	336.47	0.002	−0.002	0.274	0.66
irradiated	308.47	−0.004	−0.003	0.327	0.32
and annealed	277.68	−0.214	−0.023	0.300	0.02
E	337.86	−0.047	0.012	0.322	0.63
unirradiated	311.42	−0.061	0.010	0.358	0.27
	295.28	−0.078	0.007	0.399	0.11
E	336.94	−0.044	0.017	0.308	0.64
irradiated	314.42	−0.051	0.026	0.299	0.15
	302.01	−0.067	0.013	0.365	0.21
E	336.48	0.002	−0.002	0.283	0.62
irradiated	308.60	−0.004	−0.003	0.320	0.31
and annealed	281.60	−0.018	0.029	0.375	0.07

absorption line was detected in the spectra at $v = -0.5$ mm/s. From the suggestions given in [5] we expected their volume fraction to be in the range 0.08 to 2.5%. Such a low concentration is hardly detectable, but due to the preliminary character of the cited suggestion our measurements were justified as one of several possible experimental proofs. Indeed, the fit of the Mössbauer spectrum shows that a weak paramagnetic component at about -0.1 mm/s is present. When searching for carbides an explanation with M_7C_3 may be possible [8], but this is in contradiction to the former suggestions [4,5].

Another interesting difference between the samples of series C and E are the higher values of the magnetic hyperfine fields of all three components of the spectra for series E. The main difference between the series is the higher copper content of sample E. In order to study the effect of copper on the Mössbauer spectra a binary alloy with 0.31 wt.% Cu impurities in the Fe matrix was investigated. A homogeneous distribution of Cu atoms was achieved by 840 °C/2 h/Ar heat treatment followed by quenching in ice water. By subsequent heat treatment up to 700 °C a precipitation of the Cu particles was accomplished. This process was controlled by positron annihilation measurements which will be published elsewhere. The Mössbauer spectra of the two specimens with copper in solute and precipitated state show no difference, so that the copper content may not explain the behavior discussed above. Because copper impurities are thought to play an important role in radiation embrittlement of RPV steels the Mössbauer measurements may be a hint that not pure copper precipitates but the interplay of copper with other alloy components are responsible for this.

4. Conclusions

The present MB studies of different RPV steels show that changes in the materials due to neutron irradiation and post-irradiation heat treatment are well detected. However, the interpretation of these changes turned out to be very difficult due to the complex composition and structure of the RPV steels. The sextet with the biggest magnetic hyperfine field was related to an α-iron matrix which dissolves Cr and possibly V and Mo. The other two sextets, which interchange their relative contribution to the spectra after irradiation may be complex phases. The irradiation effect is to destroy one of them partially and promote the development of the other. From the study of a Fe-0.31 wt.% Cu model alloy it was concluded that Cu has no influence on the hyperfine field in iron, neither in well dissolved nor in precipitated state. The search for irradiation-induced $M_{23}C_6$ precipitates, suggested from positron annihilation [4,5], turned out to be not successful as expected.

Further comprehensive MB studies are necessary to get more insight into microscopic processes going on in the RPV steels, especially due to neutron irradiation and annealing.

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