IMPURITY CONTENT OF REDUCED-ACTIVATION FERRITIC STEELS AND THE EFFECT ON THE REDUCED-ACTIVATION CHARACTERISTICS—R. L. Klueh (Oak Ridge National Laboratory), E. T. Cheng (TSI Research, Inc.), M. L. Grossbeck, and E. E. Bloom (Oak Ridge National Laboratory)

OBJECTIVE

This work was conducted to obtain concentrations of important impurity elements in reduced-activation ferritic steels, to estimate the lowest concentrations of the impurities that could be achieved with present technology, and concentrations that could be achieved in the future with innovative processing techniques.

SUMMARY

Three heats of reduced-activation martensitic steel were analyzed by inductively coupled plasma mass spectrometry for low-level impurities that compromise the reduced-activation characteristics: a 5-ton heat of modified F82H for which an effort was made during production to reduce detrimental impurities, a 1-ton heat of JLF-1, and an 18-kg heat of ORNL 9Cr-2WVTa. Specimens from commercial heats of modified 9Cr-1Mo and Sandvik HT9 were also analyzed. The objective was to determine the difference in the impurity levels in the F82H and steels for which less effort was used to insure purity. Silver, molybdenum, and niobium were found to be the tramp impurities of most importance. The modified F82H had the lowest levels, but in some cases the levels were not much different from the other heats. The impurity levels in the F82H produced with present technology did not achieve the limits for low activation for either shallow land burial or recycling. The results indicate the progress that has been made and what still must be done before the reduced-activation criteria can be achieved.

PROGRESS AND STATUS

Introduction

Development of low- or reduced-activation materials for fusion has focused on the issue of radioactive waste disposal [1] or recycling [2] of materials from fusion power plant components after they have reached the end of their service lifetime. The objective has been to eliminate or minimize those elements from an alloy that would produce long-lived radioactive isotopes during irradiation in a fusion neutron spectrum. Emphasis in the development process has generally centered on eliminating Nb, Cu, Ni, Mo, and N, widely used alloying elements, with niobium usually receiving the most attention, because of the very low levels (<1 wppm) that niobium cannot exceed if the steel is to meet low-activation criteria.

Besides the elements listed above, Butterworth and co-workers [2-4] have pointed out that there are various other elements that must be restricted to extremely low levels. Such elements could appear in the materials as tramp impurities and include Ag, Ho, Bi, Co, Sm, Lu, Dy, Gd, and Cd. Murphy and Butterworth [4] calculated the maximum amount of these elements allowed for recycling based on the assumption that "the concentrations of impurity elements were restricted to levels that would allow attainment of a surface γ dose rate not exceeding the "hands-on" dose rate limit of 25 μSvh^{-1} at a 100 y cooling time for material subjected to a first wall neutron fluence of 12 $MWym^{-2}$. This limit was suggested as a "target value" [4].

Since the Murphy and Butterworth work [4], an updated library of activation cross sections, FENDL/A-2.0, was developed as part of the Fusion Nuclear Data Library (FENDL) under the coordination of the International Atomic Energy Agency [5,6]. These new cross sections were used previously to calculate the concentration limits of natural elements in low-activation fusion materials [7], and they will be used in this paper to compare the values obtained by analysis of

selected steels. It needs to be emphasized that these criteria have no "official" status relative to what might be required in the future (when fusion power plants are built or when they are decommissioned) for recycling or shallow land burial (should that be allowed at that time).

Activation calculations to determine the decay characteristics of radioactive products produced during irradiation of a material in a fusion environment have often ignored many of the tramp impurities listed above. In this paper, several of these elements have been determined in selected steels by analytical techniques to establish a base concentration for activation calculations and also to give an indication of what elements may need to be considered when processes are developed for maximizing reduced-activation characteristics for potential structural materials. A similar procedure was used previously to explore impurities in V-Cr-Ti alloys [8].

Murphy and Butterworth [4] chose to apply the criterion to each element individually and disregard additive effects. However, they pointed out that additive effects could be important for real materials. Under those conditions, the concentration of an individual element must be less than the limit for that element, and the amount allowed for the material to meet the guidelines for shallow land burial or recycle will depend on all the non-reduced-activation elements present. For n restricted elements, shallow land burial will be allowed if the waste disposal rating (WDR) is

$$WDR=\sum_{i=1}^{n}\frac{c_i}{c_{imax}}\leq 1 \qquad (1)$$

where c_i is the concentration of the *ith* element present in the alloy and c_{imax} is the maximum allowable concentration for that element as determined by the guideline for shallow land burial. A similar materials recycling rating (MRR) can be defined, where c_{imax} is the concentration of the *ith* element and c_{imax} is the maximum allowable concentration of that element according to guidelines for recycling.

Experimental Procedure

A sample from a heat of ferritic/martensitic reduced-activation steel was analyzed by inductively coupled plasma mass spectrometry (ICPMS). The steel specimen was taken from a 5-ton heat of modified F82H (IEA Mod F82H) , a nominal Fe-7.5Cr-2W-0.2V-0.02Ta-0.1C steel (all compositions are in weight percent) that was purchased by the Japan Atomic Energy Research Institute, Tokai, Japan, from NKK Corporation, Kawasaki, Japan, for use in a collaborative test program by investigators in the U.S., Japan, and the European Union coordinated by the International Energy Agency (IEA) to establish the feasibility of using ferritic steels for fusion. During the production of this heat, an effort was made to minimize niobium in the steel, but no special effort was made to reduce any of the other elements that are not specified (i.e., Ag, Cd, Co, etc).

To determine the variation in impurities in current fusion-program steels (reduced-activation and commercial steels), several other steels were analyzed by ICPMS. These included specimens taken from: (1) a 1-ton heat of JLF-1, a nominal Fe-9Cr-2W-0.2V-0.09Ta-0.02N-0.1C reduced-activation steel (also used in the IEA collaboration) produced in Japan by Nippon Steel Corporation; (2), an experimental 18-kg heat of the ORNL 9Cr-2WVTa, a nominal Fe-9Cr-2W-0.25V-0.07Ta-0.01C steel produced by Combustion Engineering, Chattanooga, TN, (3) a commercial heat of modified 9Cr-1Mo, a nominal 9Cr-1Mo-0.2V-0.07Nb-0.06N-0.1C steel; and (4) a commercial heat of Sandvik HT9, a nominal 12Cr-1Mo-0.3V-0.5W-0.5Ni-0.2C steel.

The metal samples for the ICPMS were dissolved in a mixture of HNO_3, HF, and H_2O_2. A reagent blank was prepared with the sample. A semiquantitative scan was conducted of the samples, and the spectra were examined for elements of interest and any other elements that were present. Before analyzing the sample, the instrument was checked for mass calibration and resolution. All elements reported were obtained by quantitative analysis using a blank, 10 ppb and 60 ppb standard for all the elements in a calibration curve. A calibration verification combined of an EPA QC standard and a multi-element SPEX standard was analyzed to validate the calibration standards. All elements in the verification standard were within 10% of the calibration standards. A ten-fold dilution was made on the dissolved sample that was analyzed, and the reagent blank was subtracted and calculated with an appropriate dilution factor applied. A portion of the diluted sample was spiked with 20 ppb of all elements reported. Spike recoveries were within 10%, which is the accuracy reported for the technique. Two readings were made and the precision for the elements for the first specimen are given in Table 1.

Table 1. Precision for elements analyzed by inductively coupled plasma mass spectrometry (wppb)

Element	Concentration	Element	Concentration	Element	Concentration
Li	0.01	Cd	0.23	Ta	0.3
Zr	0.67	Co	0.43	Er	1.5
Cr	0.11	Fe	0.65	Tb	0.2
Al	0.4	Ir	0.6	Ho	0.4
Ni	1.2	Nb	0.7	Y	2.0
Ag	0.4	Mo	1.2	Hf	0.14
B	1.8	Pd	0.04	W	0.5
Bi	0.03	Sn	0.5	Eu	0.14

Results

The following elemental impurities that must be limited for reduced-activation consideration were determined by ICPMS: Ag, Bi, Cd, Co, Dy, Er, Eu, Ho, Ir, Mo, Nb, Ni, Os Tb, and U. Results for two specimens of the IEA Mod F82H are given in Table 2. Also shown in the table are results for the JLF-1, ORNL 9Cr-2WVTa, Modified 9Cr-1Mo, and HT9 steels.

Discussion

Table 2 indicates that with the exception of two elements, cobalt and nickel, the concentrations of the individual impurity elements in the IEA F82H steel are lower or as low as in any of the other five steels. Nickel and cobalt are lowest in the JLF-1. These results provide an indication of what may be possible for reduced-activation steels. They can also serve as the starting point for determining how these steels can be processed to the purity levels required. That is, a detailed analysis of the materials processing techniques used for these heats could indicate reasons for the differences and how the impurities might be further reduced.

For the IEA Mod F82H heat produced by NKK Corporation, high purity iron ingots were produced using a converter, after which only ingots containing below 0.5 ppm Nb were selected for the heat [9]. Clean materials were also selected for the other alloying additions, and

Table 2. Chemical composition of deleterious impurity elements in reduced activation of ferritic steels determined by inductively coupled plasma mass spectrometry (wppm)

Element	IEA Mod F82H		JLF-1	ORNL 9Cr-2WVTa	Modified 9Cr-1Mo	HT9
Ag	<0.05	<0.1	0.21	0.16	0.23	1.3
Bi	<0.2	<0.05	<0.1	<0.05	<0.1	<0.1
Cd	<0.4	<0.05	<0.05	<0.05	3.3	5.1
Co	28	16	7.6	34	58	393
Ir	<0.02	<0.05	<0.05	<0.05	<0.05	<0.05
Mo	21	19	20	70	**	**
Nb	3.3	2.4	4.3	4	**	23
Ni		474	13	402	1251**	5692**
Os		<0.05	<0.05	<0.02	<0.02	<0.05
Pd		<0.05	<0.05	0.18	0.27	0.4
Dy		<0.05	<0.05	<0.05	<0.05	<0.05
Er		<0.05	<0.05	<0.05	<0.05	<0.05
Eu	<0.02	<0.05	<0.05	<0.05	<0.05	<0.05
Ho	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tb	<0.02		<0.05		<0.05	<0.05
U	<0.003	<0.05	<0.05	0.6	0.12	<0.05

** Element is part of the specified composition

vacuum-induction melting (VIM) was used. This choice of materials resulted in this steel having the lowest silver and niobium content for the steels in Table 2. Despite the chosen process to reduce niobium content, the concentration for the IEA F82H was only slightly lower than for JLF-1 and 9Cr-2WVTa. The exact procedure used for choosing the melt stock for the JLF-1 is not known, but VIM was used for melting. The ORNL 9Cr-2WVTa was a small 18-kg experimental heat of steel made using off-the-shelf melt stock that was air melted and then electro-slag remelted. Molybdenum was slightly lower in the IEA Mod F82H and the JLF-1 steel than the 9Cr-2WVTa, but only by a factor of 3. The Sandvik HT9 and modified 9Cr-1Mo steels were large commercial heats, probably made with scrap. The niobium concentration was an order of magnitude higher in the HT9 than for the reduced-activation steels (niobium is part of the specified composition of modified 9Cr-1Mo steel).

Table 3. Limits of deleterious impurity elements for shallow land burial and recycle compared to the concentration of these elements in present and future reduced-activation steels (wppm)[a]

Element	Waste Disposal Limit[b]	Materials Recycle Limit[b]	IEA F82H	Present	Future
Ni	15-38%	87-470 (1.6-4.3%)[c]	474	13	0.1
Mo	31-37	3.6-20 (4.1-23)	20	5	1
Ag	1.2-2.7	0.012-0.026 (0.017-0.036)	<0.1	<0.05	<0.005
Bi	22-109	0.017-0.41 (0.48-3.2)	<0.2	<0.05	<0.01
Cd	0.14-1.7%	2.1-24 (2.9-29)	<0.4	<0.05	<0.05
Co	19%-No Limit	2.3-14 (0.53-18%)	28	8	<0.02
Ir	22-29	0.21-0.27 (0.37-0.48)	<0.05	2	0.05
Nb	2.4-3.5	0.055-0.08 (0.055-0.08)	3	0.5	<0.02
Os	560-3100	5.2-29 (9.3-52)	<0.05	<0.05	<0.02
Pd	110-1700	0.17-2.5 (0.23-3.5)	<0.05	<0.05	<0.05
Dy	4.6-140	0.095-2.0 (0.11-2.8)	<0.05	<0.05	<0.05
Er	28-285	0.73-6.5 (0.82-7.3)	<0.05	<0.05	<0.05
Eu	1.3-1.4%	0.016-0.0054 (2.4-1.3)	<0.05	<0.02	0.01
Ho	0.7-1.2	0.017-0.028 (0.019-0.032)	<0.05	<0.05	0.01
Tb	1.9-5	0.0046-0.012 (0.0099-0.026)	<0.02	<0.02	<0.001
Al	660-3900	13-79 (13-79)	140	30	0.5
Cu	73%-No Limit	160-No Limit (20%-No Limit)	10	10	<5

[a] Cooling time for waste disposal and hands-on materials recycling 100 y after 20 MW y/m^2 exposure.
[b] The low number of the two is for first wall alone; the high number is for the blanket average.
[c] Concentration limits given in parentheses are for cooling time of 300 y.

As pointed out, the IEA Mod F82H had the highest nickel and cobalt content of the reduced-activation steels. These elements go together; that is, most of the cobalt probably comes from the nickel. Even electrolytic nickel (described as 99.95% Ni+Co), which is also known as "pure nickel," contains 0.3-0.5% cobalt. The data in Table 3 indicate a correlation between the cobalt and nickel in the steels. Nickel (0.5%) is added to the HT9, and this steel also has the highest cobalt (0.04%) content. Of interest is the low level of cobalt in the JLF-1 and the relatively high level in the IEA Mod F82H and 9Cr-2WVTa.

Since no nickel was added to any of these steels, tracing the origin of the nickel should indicate part of the solution to reducing cobalt in future heats, should that be necessary.
These results provide a "starting point" for discussing the present status of reduced-activation ferritic/martensitic steels and the steps required to reach the goal of a steel that meets the criteria for shallow land burial and/or recycling. In Table 3, the Waste Disposal Limit (WDL) and Materials Recycle Limit (MRL) are calculated using FENDL/A-2.0 [5,6] for the elements that need to be restricted for a fusion system after four years of operation at 5 MW/m^2, an integrated wall loading of 20 MW y/m^2. In the range of values given for the WDL and MRL, the low number is for the first wall alone, and the high number is for the blanket average. Values are for a cooling time of 100 y, except for the MRL values in parentheses, which are for a 300 y cooling period. The WDL and MRL values are the c_{imax} of Eq. (1) used to calculate WDR and MRR, which are given in Table 3.

The fourth column of Table 3 gives the concentration of restricted impurity elements for the IEA Mod F82H (the highest of the two values in Table 2 was chosen). A WDR value of 2.2-1.5 was calculated with Eq. (1) for the low and high WDL values, indicating that more of the restricted elements need to be removed before the steel will meet reduced-activation criteria for shallow land burial. Calculated WDR and MRR values are given in Table 4.

Table 4. Waste disposal rating (WDR) and materials recycle rating (MRR) for reduced-activation ferritic/martensitic steels[a]

Rating	IEA Mod F82H	Present	Future
WDR (100 y)	2.1-1.2	0.51-0.28	0.09-0.04
MRR (100 y)	120.2-60.6	33.1-16.8	4.6-3.3
MRR (300 y)	82.2-45.5	21.1-10.7	2.9-1.25

[a] WDR<1 and MRR<1 to meet criteria for shallow land burial and recycling, respectively.

In the column labeled "Present," concentrations are given that are the lowest values that have been measured in different steels (e.g., the low values measured for IEA Mod F82H, the Ni and Co in JLF-1, Os in ORNL 9Cr-2WVTa, etc.). These values should be achievable at present with a relatively modest effort by analyzing the techniques used to achieve the low levels in the different steels. The WDR calculated for these values are 0.53-0.32 (Table 4), thus meeting the criteria for shallow land burial.

The final column in Table 3 labeled "Future" gives estimated concentration values that should be possible to achieve in the near future with the proper choice of techniques to produce "pure" melt stock. These estimated values were arrived at by chemically analyzing "high purity" Fe, Cr, W, and V obtained from commercial vendors and other sources. The materials analyzed included a piece of iron purified by "selective prepurification and oxidation zone melting" [10]. This material contained <0.2 ppm Nb, the lowest value of this element in any of the iron

analyzed. The lowest value in commercial high purity iron was 1.2 ppm. WDR values for the "Future" concentrations are 0.09-0.04 (Table 4).

Despite the low WDR values for the "Future" reduced-activation steel, the steel would not meet the criteria for recycling because the MRR is 4.6-3.3 after a 100 y cooling period. For a 300 y cooling period, the MRR drops to 2.9-1.25, still above the value required for "hands-on" recycling. This applies to the 20 MW y/m^2 integrated first wall neutron exposure. It could be hands-on recycled after 100 years if the neutron exposure was reduced to 6 MW y/m^2 or after a 300 y cooling period if the exposure was reduced to 16 MW y/m^2.

These results lead to a similar conclusion for the reduced-activation ferritic/martensitic steels to that reached previously for V-Ti-Cr alloys [8]. Namely, it should be possible to produce steels that will meet the present-day criteria for shallow land burial of the nuclear waste, but this will probably not be achieved without some effort and expense. Much more work and probably considerable more expense will be required to reach the levels required for materials recycling based on a "hands-on" dose-rate limit of 25 μSvh^{-1} at a 100 y cooling time. Even a 300 y cooling time would not allow these criteria to be reached easily for a 20 MW y/m^2 neutron exposure. Indeed, it would probably take considerable effort and expense just to determine if those criteria for recycling could ever be met for the compositions in question.

Another problem for recycling an Fe-Cr-W-V-Ta steel appears when the WDL and MRL values are examined for the major alloying elements (Table 5). Although none of these elements will

Table 5. Estimated Concentration of Typical Elements in Reduced-Activation Steel (wt %)[a]

Element	Waste Disposal Limit	Materials Recycle Limit[b]	IEA F82H	Present	Future
C	No Limit	No Limit	0.1	--	--
Si	No Limit	No Limit	0.1	--	--
Mn	No Limit	No Limit	0.2	--	--
P	No Limit	No Limit	0.008	0.002	0.001
S	No Limit	No Limit	0.002	0.001	0.001
Cr	No Limit	No Limit	7.5	--	--
W	41-No Limit	0.11-0.37 (1.8-19)	2	--	--
V	No Limit	No Limit	0.2	--	--
B	No Limit	No Limit	0.002	--	--
N	0.18-0.36	No Limit	0.006	0.006	0.001
Ti	No Limit	0.14-1.4 (9.3-No Limit)	0.001	0.001	0.0005
Ta	No Limit	0.026-1.0 (2.2-7.8)	0.05	0.05	0.05

[a] Cooling time for waste disposal and hands-on materials recycling 100 y after a 20 MW y/m^2 exposure.
[b] Concentration limits given in parentheses are for cooling time of 300 y.

affect the WDL values calculated from the impurity concentrations (Table 4), there will be an effect of tungsten and tantalum on the MRL. Obviously, if a reduced-activation steel is ever to be recycled under the criteria used for the present calculations—those proposed by Murphy and Butterworth [4]—then they would essentially have to be free of tungsten. Tantalum would probably also need to be restricted, depending on the levels of other restricted elements. This means that new steels need to be developed for the recycling option.

Conclusions

Chemical analysis of potential reduced-activation ferritic steels produced by present technology were analyzed to provide an indication of the level of tramp impurity elements that compromise the reduced-activation characteristics of the steel. The results for the steels indicate that progress has been made in reducing the level of detrimental impurities for two large heats of reduced-activation steel. Silver, niobium, and molybdenum proved to be the most important of the restricted elements, and the steels that have been made up to now do not meet the criteria for low-activation for shallow land burial of nuclear waste made up of these steels after an integrated wall loading of 20 MW y/m^2 after a 100 y cooling off period. However, it appears that reduced-activation steels could be produced with these detrimental impurity elements at levels low enough to meet the present criteria for shallow land burial. If instead of shallow land burial, it is desired to recycle the steel, with a "hands-on" dose rate limit of 25 μSvh^{-1} after a 100 y cooling time, then it appears that considerable research and expense will be required to develop processes that will allow the production of steel that will meet these criteria.

There has probably never been a requirement for a structural material to be processed to have specified impurity levels as low as those required to meet the reduced-activation criteria. Even though the materials will not be needed for some time, it would appear that an effort should be mounted to determine the means to achieve the desired purity levels, especially if recycling is to be pursued. Such an effort should enlist support from industrial materials processors to examine techniques used in the past to produce high-purity materials and determine ways that these techniques might be combined with the latest technology for future application. The effort should not be delayed if reduced-activation materials are to be available when fusion power production is ready to begin operation.

REFERENCES

1. R. W. Conn, E. E. Bloom, J. W. Davis, R. E. Gold, R. Little, K. R. Schultz, D. L. Smith, and F. W. Wiffen, Panel Report on Low Activation Materials for Fusion Applications, UCLA Report PPG-728, (University of California at Los Angeles, 1983).
2. G. J. Butterworth, and L. Giancarli, J. Nucl. Mater. 155-157 (1988) 575.
3. G. J. Butterworth, J. Nucl. Mater. 179-181 (1991) 135.
4. D. Murphy and G. J. Butterworth, J. Nucl. Mater. 191-194 (1992) 1444.
5. A. B. Pashcenko, H. Wienke, and D. W. Muir, Proceedings of the International Conference on Nuclear Data for Science and Technology, 1997, Trieste, Italy; E. T. Cheng, A. B. Pashchenko, and J. Kopecky, Fusion Technol. 30 (1996) 1182.
6. J. Kopecky et al., FENDL/A.2, UKAEA Report, 1996.
7. E. T. Cheng, J. Nucl. Mater., 258-263 (1998) 1767.
8. M. L. Grossbeck, R. L. Klueh, E. T. Cheng, J. R. Peterson, M. R. Woolery, and E. E. Bloom, J. Nucl. Mater., Analysis of V-Cr-Ti Alloys in Terms of Activation of Impurities, J. Nucl. Mater., 258-253 (1998) 1778.
9. M. Tamura, Private Communication, February 18, 1999.
10. B. F. Oliver and E. W. Troy, Mémoires Scientifiques Rev. Métallurg., LXV (1968) 39.