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Solubility of uranium at very low concentration in RAFM steel

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Abstract

In this work we present the results to develop standards of reduced activation ferritic–martensitic (RAFM) alloys for the quantitative determination of uranium in these materials. The results show that a very low efficiency can be obtained during alloying of uranium due to the segregation to the slags. The solubility of U can be increased by adding small quantities of Sn but the use of U intermetallics as raw materials do not provide any improvement. The detection limit of U in RAFM alloys using particle induced X-ray emission is also reported.

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1. Introduction

The development of reduced activation ferritic–martensitic (RAFM) steels depends on our ability to maintain as low as possible the concentration of elements that are easily activated by thermal neutrons. The development and characterisation of candidate structural materials for thermonuclear fusion power reactors (TFPRs) are actually an important international research task. Low activation and radiation swelling resistance are key properties for these materials. Candidate materials are SiC_f/SiC composites, vanadium alloys and ferritic–martensitic alloys. Of the three candidates, RAFM alloys are recognised as the most advanced materials as they are in the stage of qualification and optimisation [1,2]. Chromium, high chromium alloys and commercial austenitic AISI-316 stainless steel are considered as attractive structural materials for the TFPR, because of its mechanical properties, weldability and corrosion resistance [3]. However, the high Ni, Mo and Co contents in these alloys cause such problems as long-life activation [4,5]. Therefore a lot of research devoted to the adjustment of alloying elements is being carried out. In this way many researchers studied the substitution of these elements by Mn and N, which lead to the development of 24.5Mn–13.5Cr stainless steel [6,7]. Also chromium and chromium alloys have been recently studied by other authors [8,9].

Regardless of the final chemical composition of the alloy selected, there will be a need of adequate standards for analysing small concentrations of elements that are easily activated by neutrons. The standards allow the quantitative determination of the concentration of those elements in the metallic alloys.

In this work we present the results obtained in order to fabricate standards of RAFM alloys with low U levels of several ppm. We have alloyed U with the F82H base composition. Initially we used metallic U, however the low solubility in these alloys is very reduced as this metal tends to segregate to the slags so that a very low efficiency was obtained. Then small quantities of Sn were added to the alloy increasing the U uptake and finally U intermetallics were used to include U in the alloy. Also the detection limits for U in these alloys using the particle induced X-ray emission (PIXE) are reported.

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Table 1
Composition of the alloys used in this work

Alloy	Composition	U added (wt%)
A	Base + 0.5 g U	0.5
B	Base + 0.1 g U + 0.02 g Sn	0.1
C	Base + 1 g U_3Si	0.96
D	Base + 1.14 g U_6Mn	1

Base: 7.65Cr–1.7W–0.8V, Fe balance.

Table 2
U concentration, efficiency for U uptake and U detection limit (d.l.) by PIXE in the alloys studied in this work

Alloy	U (ppm)	Efficiency (%)	PIXE (d.l.) (ppm)
A	56	1.12	4
B	47	4.7	5
C	64	0.66	6
D	b.d.l.[a]	–	–

[a] Below detection limit.

2. Experimental

Reduced activation ferritic–martensitic alloys were prepared in silica–zirconia crucibles by melting in an induction furnace under argon atmosphere and were centrifugally casted into 30 × 15 mm (∅ × h) cylindrical 100 g ingots. The base chemical composition of the alloys is 7.65 wt% Cr, 0.8 wt% V, 1.7 wt% W, Fe balance. A soaking treatment at 1200 °C during 1 h was given to the alloys before analysis. Metallic U was added to the alloys in several ways: one alloy was prepared by adding 0.5 g U; the second was supplied with 0.1 g U and 0.02 g Sn, and two more alloys were prepared by adding 1 g U_3Si and 1.14 g U_6Mn intermetallics. Table 1 presents a summary of the experimental RAFM alloys used in this work.

The U uptake efficiency was calculated by the ratio $U_{measured}/U_{added}$ and the detection limits were determined by threefold count rate in an interval of 1.2 times the FWHM of the ULα peak.

PIXE measurements were performed at the Instituto Tecnológico Nuclear with the 3.1 MV Van de Graff accelerator using 2.2 MeV protons. The X-rays were collected by a Si (Li) detector with 145 eV resolution. To reduce strongly the contribution of FeKα lines to the spectra, a filter composed of 330 μm Al and 1 mm Pearspec was positioned in front of the detector. The deconvolution of the spectra using the AXIL computer code [10] allows the calculation of the percentages of U in the samples and the detection limits determined using the DATTPIXE program [11].

3. Results and discussion

Table 2 presents the values of the U concentration in each experimental alloy obtained by the PIXE analysis together with the U uptake efficiency, and the values calculated for the detection limit using the PIXE analysis.

Alloy A has a concentration of 56 ppm U well below that expected of about 0.5%. The PIXE spectra obtained on this sample are shown in Fig. 1 and reveal the presence of U both in the alloy and the slag produced during the casting process. An analysis of the slag in this alloy indicates that the U concentration is about 0.1% showing that almost all the metallic U added to the alloy has segregated to the slag. The main problem we have to deal with during the preparation of the alloys is the high reactivity of U. The low efficiency obtained is due to the fact that U tends to react with residual oxygen and oxides forming the ceramic crucible. The segregation to the slags happened during melting.

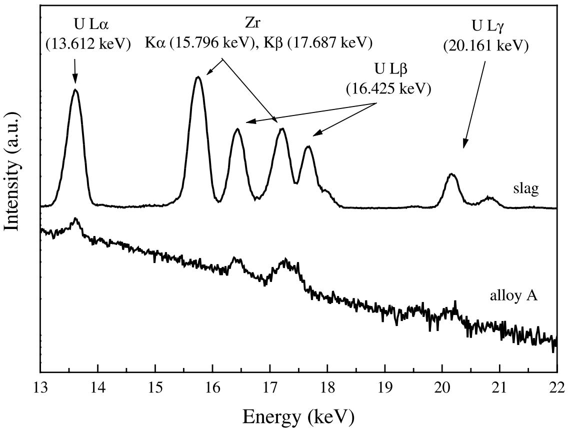

Fig. 1. PIXE intensity (logarithmic scale) of the main uranium peaks in alloy A and in the slag formed during the fabrication of this alloy.

In order to increase the U solubility in the alloy a small quantity of Sn was added, and the results show an increase in the efficiency (4.2 times larger than in alloy A). Another route we investigated to avoid the segregation of U to the slags was the addition of U already alloyed in the form of intermetallics. The results in Table 2 show that the efficiency values are even worse than those obtained with metallic U additions. In fact for alloy D only 2 ppm U were measured, this value is below the detection limit of U by PIXE analysis.

It must be pointed out that, during the melting process of alloy C and D, the U intermetallics quickly reacted with the crucible walls avoiding its incorporation to the alloy and forming insoluble slags. In order to obtain good standards with low U levels, extreme care must be taken during the melting process. Direct contact of U with ceramic crucibles must be avoided, in order to produce less amounts of slags. Melting of larger quantities of material reduces the surface-to-volume ratio and will probably increase the efficiency.

4. Concluding remarks

In this work we present the results obtained to fabricate standards of reduced activation ferritic–martensitic alloys with low U levels in the ppm range. The main pitfall in the development of standards is the low solubility of U in RAFM alloys and the high reactivity of U that tends to segregate to the slags so that a very low efficiency was obtained for the U uptake. The solubility of U can be increased four times by adding small quantities of Sn (0.02 wt%). The use of U intermetallics as raw materials, U_3Si and U_6Mn, does not provide any improvement. Special care must be taken during casting to avoid direct contact between U and the ceramic crucibles. The detection limits for U in RAFM alloys using the PIXE can be stabilised at about 5 ppm.

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