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Letter to the Editors

Impurity concentrations of niobium and molybdenum in the Japanese steel F82H-mod by activation analysis

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Abstract

An activation experiment with 19.5 MeV α-particles was made in order to check the niobium and molybdenum impurity concentrations of the Japanese steel F82H-mod. The γ-spectroscopic analysis yielded a concentration of (2.5 ± 1.0) wt. ppm niobium and of (46 ± 17) wt. ppm molybdenum. These values are in good agreement with the manufacturer's data being 1 wt. ppm niobium and 30 wt. ppm molybdenum. © 1997 Elsevier Science B.V.

1. Introduction

Within the fusion technology program the development of low activation steels for first wall and blanket components has become a major activity towards an environmentally attractive fusion power reactor. A joint effort in fusion neutron activation calculations and material development has led to a number of candidate low activation steels, such as 7–10% Cr W V Ta alloys. The calculations have shown that their long-term activation is decisively influenced especially by the residual concentration of the element niobium which by the nuclear reaction ^{93}Nb(n,γ)^{94}Nb yields to ^{94}Nb with a half-life of 20300 a. Whereas the European reduced activation ferritic–martensitic alloy Optifer [1] has been produced by double vacuum melting on electrolyte iron basis, however, without a special control of impurities, the Japanese reference alloy F82H-mod has been manufactured from pure ingot materials and has thus a very low niobium content of nominally 1 ppm [2]. Since first analytical results in the frame of a coordinated European program on characterizing this steel indicated differences in the measured niobium content of more than one order of magnitude, an activation experiment was made with 19.5 MeV α-particles at the Isochronic Cyclotron of the Forschungszentrum Karlsruhe. The α-induced nuclear reactions with niobium and molybdenum lead to radionuclides with higher specific activity due to their short half-lives.

2. Activation analysis technique

The measurement of very small concentrations of a given element by the activation analysis technique is a well known procedure and is described elsewhere. If the nuclear cross-section of the reaction to be used is given and the γ-peak to be measured is well isolated, the procedure turns out to be standard. In the case of a niobium concentration in the ppm range besides a high number of dominant elements the analysis conditions are much more unfavorable and have to be discussed in detail.

2.1. Nuclear processes

The measurement of the niobium concentration in an iron-based alloy can be done under α-particle irradiation by the nuclear process ^{93}Nb(α,n)^{96}Tc, because niobium has only one stable isotope. If the alloy has a molybdenum content, too, the ^{96}Tc will additionally be produced by reactions of the type ^{nat}Mo(α,pxn)^{96}Tc. On the other hand

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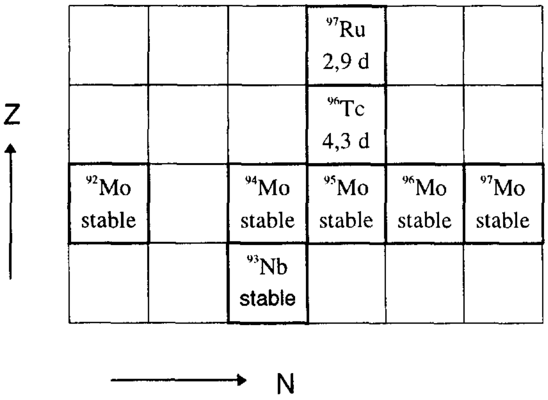

Fig. 1. Overview of the relevant part of the nuclide chart for the niobium and molybdenum reactions [4].

$^{\mathrm{nat}}$Mo leads to ^{97}Ru by the reactions of type (α,xn). ^{97}Ru, however, can fortunately not be reached by ^{93}Nb under α-irradiation. This can be seen in Fig. 1, which shows an overview of the relevant part of the nuclide map. Since the γ-energies are 778.2 keV and 216 keV for ^{96}Tc and ^{97}Ru [3], respectively, ^{97}Ru is measurable separately. This means the interference with ^{96}Tc can be unfolded and the niobium concentration can be measured unmistakably. Furthermore, the half-lives of ^{96}Tc and ^{97}Ru, which are 4.3 d and 2.9 d, respectively, are short enough to give a proper response. It has been also checked that no other nuclide, appearing in the F82H-mod alloy, does interfere with the same γ-energy.

For the impurity concentration calculations the corresponding nuclear excitation functions are necessary. In the cases of ^{93}Nb(α,n)^{96}Tc and $^{\mathrm{nat}}$Mo(α,xn)^{97}Ru, the excitation functions in the relevant energy domain are not well known or even missing [5]. For this reason, for both elements, reference measurements of the excitation functions with high purity $^{\mathrm{nat}}$Nb and $^{\mathrm{nat}}$Mo foils under identical experimental conditions have been generated.

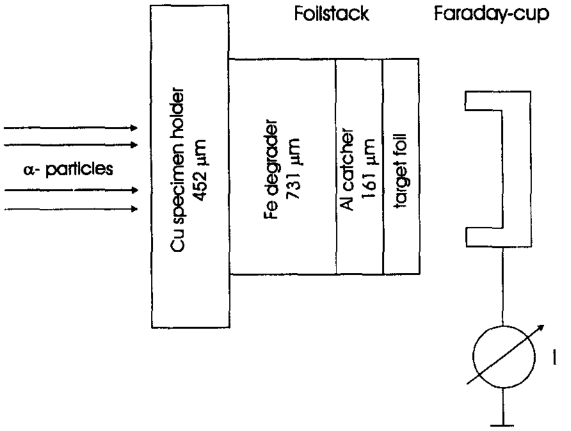

Fig. 2. Sketch of the experimental setup.

Table 1
Irradiation parameters

Target foil	Thickness (µm)	Density (g/cm^3)	E_{irrad} (MeV)	E_{exit} (MeV)
Nb	41	8.57	19.5	≈ 14
Mo	43	10.22	19.5	≈ 12
F82H-mod	43	8.05	19.5	≈ 14

2.2. Experimental setup

The activation experiments have been provided with the 104 MeV α-particle producing Isochron Cyclotron of the Forschungszentrum Karlsruhe. The experimental setup is sketched in Fig. 2.

The 104 MeV α-particles pass through the copper-made specimen holder, the iron degrader and the aluminum catcher before they hit the target foil. The Al catcher foil is used to prevent recoil nuclei from the iron degrader foil to be implanted into the target foil.

The Cu/Fe/Al material degrades the primary energy of the α-particles down to the irradiation energy of 19.5 MeV. This has been calculated with the computer code PRAL (Projected Range ALgorithm) [6]. Depending on the target foil thickness and the target material density, the exit energy of the α-particles is between about 12 MeV and 14 MeV. The irradiation parameters are given in Table 1. The beam current was measured by collection of the transmitted α-particles in the Faraday cup.

3. Irradiations and measurements

For the γ-spectroscopic measurements a LN$_2$ cooled high purity Ge-detector has been used.

3.1. Reference measurements with pure niobium and molybdenum

In order to achieve high precision results, reference irradiations of pure niobium and molybdenum foils were made with the same experimental setup.

The impurity concentrations of molybdenum in the niobium foil and vice versa is less than 0.1% [1]. Since the excitation functions of both elements are in the same order, the impurity effect is below 10^{-3} and can be neglected.

The niobium and molybdenum foils were irradiated for

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[1] Goodfellow Metals GmbH, Bad Nauheim, Germany.

10 min at low beam current to a total dose of 2.1×10^{15} α-particles. The γ-spectroscopic measurements were done subsequently.

3.2. Niobium and molybdenum measurements in F82H-mod

In order to achieve a niobium and molybdenum activation above the detection threshold, an estimation of the irradiation time with the maximum applicable beam current of 3 μA has been made with the computer code LINDA (light ion induced activation and damage) [7]. The estimated irradiation time was 38 h. The experimentally applied dose was 1.1×10^{18} α-particles.

Due to side-reactions in other alloying elements of F82H-mod (mainly iron), after irradiation a cooling time of 2.5 days was applied. The γ-spectroscopic measurements lasted about two weeks. Since the half-lives of the nuclides to be measured are shorter than the measurement time period, the decay during acquisition (DDA) had additionally to be considered.

3.3. Data evaluation

The excitation functions for niobium and molybdenum have been derived for the following nuclear processes:

$\sigma({}^{nat}\mathrm{Nb} \rightarrow {}^{96}\mathrm{Tc})$: ${}^{93}\mathrm{Nb}(\alpha, n){}^{96}\mathrm{Tc}$

$\sigma({}^{nat}\mathrm{Mo} \rightarrow {}^{96}\mathrm{Tc})$: ${}^{94}\mathrm{Mo}(\alpha, pn){}^{96}\mathrm{Tc}$
${}^{95}\mathrm{Mo}(\alpha, p2n){}^{96}\mathrm{Tc}$
${}^{96}\mathrm{Mo}(\alpha, p3n){}^{96}\mathrm{Tc}$

$\sigma({}^{nat}\mathrm{Mo} \rightarrow {}^{97}\mathrm{Ru})$ ${}^{94}\mathrm{Mo}(\alpha, n){}^{97}\mathrm{Ru}$
${}^{95}\mathrm{Mo}(\alpha, 2n){}^{97}\mathrm{Ru}$
${}^{96}\mathrm{Mo}(\alpha, 3n){}^{97}\mathrm{Ru}$
${}^{97}\mathrm{Mo}(\alpha, 4n){}^{97}\mathrm{Ru}$

by means of Eq. (1)

$$\sigma = \frac{M_{\mathrm{Mol}}}{N_{\mathrm{A}} \rho d} \frac{T_{1/2}}{\ln 2} \frac{2e}{Q} A \tag{1}$$

with

$$Q = \int I(t)\,\mathrm{d}t,$$

where σ is the excitation function, M_{Mol} is the molar target mass, ρ is the target density, d is the target thickness, $T_{1/2}$ is the half-life, I is the electrical beam current, Q is the integrated beam current, A is the total nuclide activity, A' is the experimentally measured nuclide activity, N_{A} is the Avogadro number, T_{irrad} is the irradiation time, T_{real} is the measurement time and T_{cool} is the cooling time.

The analysis of these high purity foils, considering the statistical error in measurement and ±2 μm error in thickness, led to mean excitation functions of

$\sigma({}^{nat}\mathrm{Nb} \rightarrow {}^{96}\mathrm{Tc}) = 46.4$ mbarn (±8%),

$\sigma({}^{nat}\mathrm{Mo} \rightarrow {}^{96}\mathrm{Tc}) = 5.7$ mbarn (±9%),

$\sigma({}^{nat}\mathrm{Mo} \rightarrow {}^{97}\mathrm{Ru}) = 110.3$ mbarn (±8%).

The nuclide densities ρ of the nuclides produced in F82H-mod can be calculated by Eq. (2), and the nuclide concentration c (wt. ppm) is given by Eq. (3):

$$\rho = \frac{2e}{Q} \frac{T_{1/2}}{\ln 2} \frac{M_{\mathrm{Mol}}}{dN_{\mathrm{A}}} \frac{A}{\sigma}, \tag{2}$$

$$c = \frac{\rho}{\rho_{\mathrm{F82H-mod}}}. \tag{3}$$

The effects of the decay during irradiation (DDI), the cooling time and the DDA are corrected by Eqs. (4)–(6):

$$A = A'\,\mathrm{DDI}\,e^{-\ln 2(T_{\mathrm{cool}}/T_{1/2})}\,\mathrm{DDA}, \tag{4}$$

$$\mathrm{DDI} = \frac{\ln 2(T_{\mathrm{irrad}}/T_{1/2})}{1 - e^{-\ln 2(T_{\mathrm{irrad}}/T_{1/2})}}, \tag{5}$$

$$\mathrm{DDA} = \frac{\ln 2(T_{\mathrm{real}}/T_{1/2})}{1 - e^{-\ln 2(T_{\mathrm{real}}/T_{1/2})}}. \tag{6}$$

4. Results and discussion

The measurement of the impurity concentrations in F82H-mod led to 2.5 ± 1.0 wt. ppm for niobium and 46 ± 17 wt. ppm for molybdenum. In spite of the high background caused by many other activation reactions from the major constituents of the alloy, it was possible to undertake an evaluation of the γ-spectrum of the F82H-mod and to derive accurate results after correction of the molybdenum contributions. The critical detection levels of the γ-spectrometer, as described in Ref. [8], have been estimated to 0.4 ppm for niobium and 12 ppm for molybdenum.

The comparison of these values with results of the European laboratories CIEMAT (ICP-AES [2]) [9], FZK (ICP-OES [3]) [10] and VTT (ICP-MS [4]) [11] and with the data of the steel manufacturer NKK (ICP-MS) [2] is shown in Table 2.

The comparison, if niobium is considered, shows consistency for all measurements. The chemical analysis methods used in Refs. [9,10] are at the very limits of detectability. The data of VTT are compatible with the

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[2] Inductively coupled plasma atomic emission spectrometry.

[3] Inductively coupled plasma optical emission spectrometry.

[4] Inductively coupled plasma mass spectrometry.

Table 2
Comparison of the niobium and molybdenum concentrations in F82H-mod in wt. ppm. The data range of CIEMAT and VTT is given by measurements of different plates

Element	This work	NKK [2]	CIEMAT [9]	VTT [11]	FZK [10]
Nb	2.5 ± 1.0	1	< 100	2.2...3.0	< 8
Mo	46 ± 17	30	80...100	22...50	18 ± 1

data of this work and confirm the low niobium value of the manufacturer NKK in the steel F82H-mod.

If considering molybdenum, the different data show an incompatible picture. CIEMAT has measured the highest value. The measurement of FZK [10] is given with high precision, but lies by a factor of 2 below NKK. The measurements of VTT and of this work confirm the NKK specification.

From a practical point of view the actual molybdenum concentration is, however, not very critical for the overall long-term activation of the steel.

5. Summary and conclusion

A precise measurement of niobium and molybdenum impurity concentrations in the Japanese steel F82H-mod was made by an α-particle activation experiment. Comparing the measured values with the data given by the Japanese steel manufacturer NKK, one can state a good agreement. The very low content of the highly undesired element niobium as claimed by the manufacturer can be confirmed. Also the specified molybdenum concentration reasonably fits with the measurements.

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