

Recycling of vanadium alloys in fusion reactors

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Abstract

The feasibility of reprocessing a vanadium alloy after its use as a structural material in a fusion reactor, in order to enable its subsequent hands-on recycling within the nuclear industry, has been determined. For less neutron-exposed components, clearance of materials has also been considered. A conceptual model for the radiochemical processing of the alloy has been developed and tested experimentally. Using di-2-ethyl-hexyl-phosphoric acid it is possible to purify the components of the V–Cr–Ti alloy after its exposure in a fusion reactor down to the required level of activation product concentrations.

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1. Introduction

Work to develop demonstration and commercial fusion reactors is currently underway in several countries. These reactors are designed to operate up to a fluence of 35 MW yr/m², which will cause considerable neutron-induced activation of structural materials. One of the candidate structural materials for fusion reactor in-vessel first wall, blan-

ket and divertor applications is the vanadium–chromium–titanium (V–Cr–Ti) alloy in which the content of the scarce and costly vanadium is up to 90 wt% [1].

There are several good reasons to consider the possible reuse of these materials [2], instead of disposing of them as radioactive waste (RW). However, to be able to safely handle a material without the need of complicated shielding procedures, it is necessary to bring its effective dose rate (EDR) down to a level of 10–12 μSv/h. For V-based alloys, this implies removal of the activation products from certain impurities, such as Co, Eu, Sm, Ni, Cu, Tb, Ag, Nb, Fe, Mo and some others, that give the main contribution to EDR in the long term.

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2. Computation of required purification factors

The purification factors sufficient to recover V, Cr and Ti with EDR below 12 $\mu\text{Sv/h}$ for a Russian DEMO-S fusion reactor with equivalent fluence of 35 MW yr/m² [1] were determined in earlier work [3–5]. These purification factors have been now recalculated for neutron-induced activation levels obtained from the EASY-2005 system [6] for conditions of the Plant Model 2 outboard blanket considered in the European fusion ‘power plant conceptual study (PPCS)’ with an equivalent fluence of 10 MW yr/m² [7].

The concentration of impurities in the alloy is given in Table 1. This corresponds to Russian standards and practically is the best composition of V–Cr–Ti alloys achieved by the Russian industry. Similarly, it corresponds to the best European, Japanese and US V–Cr–Ti alloys. Table 1 also shows contact dose rates $\text{DR}_{\text{imp}}^{100}$ from a structural material with 100% of the element, for three cooling times (10, 20, 30 yr). However three times are given, we recommend the adoption of a 30 yr cooling time in order to reduce the number of purification steps required.

Using these dose rates, the maximum allowable concentrations of radioactive impurities enabling manual refabrication of V–Cr–Ti alloy ($C_{\text{imp}}^{\text{max}}$) have been calculated:

$$C_{\text{imp}}^{\text{max}} = 12 \times 10^{-6} \cdot g_{\text{imp}} / \text{DR}_{\text{imp}}^{100},$$

where $0 < g_{\text{imp}} < 1$, depending on the impurity contribution to the total contact dose rate and on the cost of its removal. The results are shown in Table 2.

Finally, required purification factors have been calculated (see Table 3): they are the ratios of max-

Table 2

Maximum allowable concentrations of radioactive impurities enabling manual refabrication of the alloy

Radioactive impurity	$C_{\text{imp}}^{\text{max}}$ some years after the reactor shut-down (wppm)		
	10 yr	20 yr	30 yr
Co	1.6×10^{-5}	6×10^{-5}	2.3×10^{-4}
Eu	3×10^{-5}	6×10^{-5}	1.3×10^{-4}
Sm	1.5×10^{-4}	3×10^{-4}	7×10^{-4}
Ni	4×10^{-3}	0.016	0.06
Cu	6×10^{-3}	0.02	0.08
Tb	0.015	0.016	0.017
Ag	0.05	0.05	0.05
Nb	0.13	0.13	0.13
Fe	1.3	9	41
Mo	33	33	33

Table 3

Purification factors for radioactive impurities enabling manual refabrication of V–Cr–Ti alloy

Radioactive impurity	Decay time (yr)		
	10	20	30
Co	2×10^5	5×10^4	2×10^4
Ni	5000	2000	400
Eu	3100	1500	400
Sm	660	300	150
Cu	500	140	40
Fe	90	20	3
Nb	50	50	50
Tb	30	30	30
Mo	7	7	6
Ag	–	–	–

imum allowable concentrations of radioactive impurities enabling manual refabrication of V–Cr–Ti alloy ($C_{\text{imp}}^{\text{max}}$) to their initial concentration in the alloy (C_0) shown in Table 1.

Table 1

Impurity content and contact EDR from radioactive impurities and V at their 100% concentration ($\text{DR}_{\text{imp}}^{100}$, Sv/h)

Impurity	C_{im}^0 (wppm)	DR_{im} some years after the reactor shut-down (Sv/h)		
		10 yr	20 yr	30 yr
Co	3	7×10^5	1.9×10^5	5×10^4
Eu	0.1	4×10^5	1.8×10^5	9×10^4
Sm	0.1	8×10^4	4×10^4	1.6×10^4
Ni	20	2750	740	200
Cu	3	2000	500	140
Tb	0.4	760	730	700
Ag	0.03	230	220	220
Nb	6	90	90	90
Fe	120	9	1.3	0.3
Mo	200	0.4	0.4	0.4
V	9×10^5	1.1×10^{-4}	1.7×10^{-7}	9×10^{-8}

Irradiation corresponds to the outboard blanket of PPCS Plant Model 2: irradiation time = 5 yr, neutron wall load 2 MW/m².

3. Radioactive impurity extraction methods

The only method for reducing the dose rate of an activated V–Cr–Ti alloy is radiochemical processing. The task of decontaminating this sort of alloy from activation products is similar to separating irradiated nuclear fuel from fission products. The mass of the V–Cr–Ti alloy used in DEMO reactor structural applications is about 400 ton. To reprocess this tonnage in 1 yr, one needs a plant with a 400 ton/yr capacity; however, since the blanket is replaced every 5 yr only, even a plant with a capacity of 80 ton/yr would be sufficient. Such capacities are commensurable with the capacity of a standard radiochemical plant for reprocessing of fuel from nuclear power plants.

In this context, it would be reasonable to adopt an approach for alloy reprocessing similar to that used at radiochemical plants. At present, the only commercial technique for reactor fuel processing adopted by radiochemical plants throughout the world is the PUREX extraction process, in which uranium and plutonium are extracted from nitric acid solutions with tributylphosphate. Unfortunately, PUREX is not applicable to our case, because vanadium cannot be extracted from a nitric acid solution with tributylphosphate. Therefore we decided to use for this purpose another well-known extraction solvent – di-2-ethyl-hexyl-phosphoric acid (D2EHPA).

We investigated the extraction behaviour of V, Cr, Ti, and the main activation products, dissolved in nitric solutions of different acidity using a D2EHPA/dodecane (30/70) mixture as an extractant.

In our extraction experiments, we used a dissolved 90% V + 5% Ti + 5% Cr alloy. The behaviour of activation products was simulated by introduction into the solutions of radioactive isotopes ^{60}Co , ^{152}Eu , ^{110}Ag , ^{99}Mo and ^{55}Fe as well as of some milligrams of Nb.

Taking as a guide our estimates of element distribution between the aqueous and organic phases, we developed a schematic diagram of V–Cr–Ti alloy radiochemical reprocessing including the separation of alloy components and their purification from activation products [3,4]. During recent years this diagram was continually developed and made more accurate. The most recent version is given in Fig. 1.

The alloy is crushed and dissolved in 6–8 M/l nitric acid. The resultant solution comprises around 40 g/l metals and 1.0–1.5 M/l nitric acid. The tech-

nology of V, Cr and Ti recovery and separation is based on the difference in the extraction/reextraction behaviour of these metals. Each metal is extracted with a determined acidity in the solution. Titanium is extracted with Mo and Nb at 1.0–1.5 M/l HNO_3 – that is, directly after alloy dissolution, while the other alloy components (V, Cr and all the activation products, except Mo and Nb) remain in the aqueous phase (raffinate). The separation of Ti from Mo and Nb is accomplished at the reextraction stage using an alkaline solution. Mo and Nb pass into the aqueous phase, while Ti precipitates from the solution as a hydroxide.

Further extraction is conducted at lower acidity values. To reduce the acidity we use the method of chemical denitration with formic acid. Vanadium, together with rare earth elements (REE) and, to some extent, Fe and Ag, is extracted at pH 2.0–2.5. All the Cr, some activation products like Co and most of the Ag and Fe remain in the aqueous phase. At the reextraction stage, first the decontaminated vanadium is removed from the organic phase with a ~ 0.8 mol/l HNO_3 , and then the REE are washed out with a stronger acid.

The last component of the alloy extracted is Cr. For this metal, the most suitable extractant is not D2EHPA, as in the case of V and Ti, but a D2EHPA potassium salt. The latter is formed in the extraction process after the alkaline reextraction of Ti. The D2EHPA potassium salt has been successfully used for the recovery of Cr – albeit from sulfuric acid solutions – in the processing of non-ferrous metals. Cr is extracted at a pH of 4.0–4.5 and its reextraction is accomplished with 1 M/l nitric acid solution.

The final processes are denitration of solutions of V and Cr nitrates and calcination of Ti hydroxide precipitate. The end products of this processing are oxides of the three components of the V–Cr–Ti alloy. Molybdenum dissolved in an alkaline solution and other activation products dissolved in nitric acid are separated as radioactive waste.

The proposed conceptual model for the V–Cr–Ti alloy radiochemical processing is not final and will be adjusted under dynamic experimental conditions and in experiments with irradiated alloy samples.

Table 4 shows the separation factors for the V–Cr–Ti alloy components and activation products in the extraction process measured under static equilibrium conditions. They are defined as ratios of distribution factors of corresponding elements in an extraction process. Distribution factors are

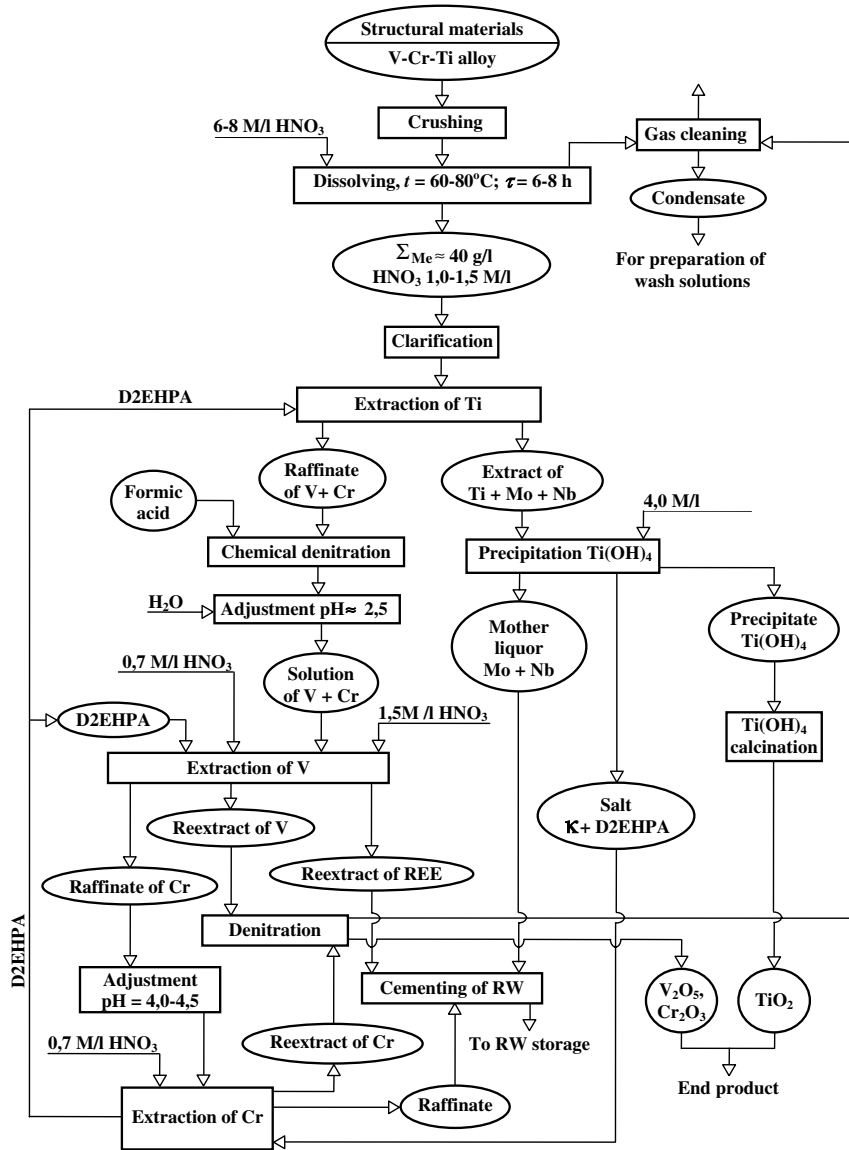


Fig. 1. Schematic diagram of V–Cr–Ti alloy radiochemical reprocessing.

Table 4
Separation factors for the V–Cr–Ti alloy components and radionuclides

Alloy component	⁹⁹ Mo	⁶⁰ Co	¹¹⁰ Ag	⁵⁵ Fe	¹⁵² Eu
V	2000	>10 ³	~10	>10	8
Ti	~10	10 ⁵	10 ⁴	200	10 ³
Cr	10 ⁴	10 ³	–	–	10 ³

$$D_{el} = C_{el}^{org} / C_{el}^{aq}$$

where C_{el}^{org} is the concentration of an element in the organic phase and C_{el}^{aq} is its concentration in the

aqueous phase. The separation factors appear to be quite significant.

Preliminary estimates suggest that the necessary purification of the V–Cr–Ti alloy from radioactive impurities and a 95% recycling of the alloy main components can be achieved using a 50-step extraction cascade. A possible way for reducing the number of extraction steps would be using a highly pure Vanadium alloy – result of a previous extraction process as the one here described – as a starting alloy. The remaining 5% of the alloy would be disposed of a low-level waste.

A preliminary technical and economic analysis has shown that the radiochemical processing is more attractive economically than V–Cr–Ti alloy burial as a solid RW [4]. This analysis take into account also the cost of the remote handling process and the disposal cost of 5% of the material as a low-level waste.

4. Conclusion

Using D2EHPA it is possible to purify the components of the V–Cr–Ti alloy after its operation in a fusion reactor to the level of activation product concentrations sufficient for recycling of highly neutron-exposed structures of these components.

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