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Journal of Nuclear Materials 258–263 (1998) 1778–1783

journal of nuclear materials

Analysis of V–Cr–Ti alloys in terms of activation of impurities

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Abstract

Vanadium alloys offer many advantages including reduced neutron activation. However, activation of V–Cr–Ti alloys is controlled by impurities. This study analyzes four impurity levels for the alloy V–4Cr–4Ti. The first is an existing commercial heat of the alloy and the others are based on impurity levels attainable by three processes. One process uses a dedicated production plant; another uses a chemical recrystallization process, and the remaining one uses state-of-the-art laboratory purification. It was assumed that the alloys were irradiated as first wall and blanket structures in a fusion reactor operating for four full power years at a wall loading of 5 MW y/m^2. It was found that the two purest alloys and, with special selection, the three purest alloys will meet the criteria for shallow land burial after a cooling time of 50 years. However, none of the alloys were found to meet the criteria for hands-on reprocessing after a cooling time of 100 years.

1. Introduction

Vanadium alloys are being developed for use as first wall and blanket components in fusion reactors. Among the reasons for interest in vanadium alloys are that vanadium has a higher thermal stress capability than ferritic and austenitic stainless steels, resulting in a longer thermal fatigue life, is compatible with liquid lithium, and is capable of high operating temperatures. However, one of the most important properties of vanadium is the absence of neutron activation products with long half lives. If sufficiently pure, the latter property could allow vanadium from a decommissioned fusion reactor to be disposed of by shallow land burial or, even better, to be reprocessed and reused.

Common alloying elements for vanadium are chromium and titanium. Both of these elements share low neutron activation properties with vanadium and, therefore, make low activation alloys. A decay curve showing contact dose rate for pure V–4Cr–4Ti is shown in Fig. 1 for fusion first wall and blanket structures after an exposure of 20 MW y/m^2. Decay to very low levels after long times is demonstrated; however, impurities control long-term behavior [1]. A notable exception is that titanium must be limited to about 6% (because of ^{42}Ar) to meet the hands-on reprocessing criteria after cooling 100 years. Also shown in Fig. 1 is a corresponding curve for what may be the purest V–4Cr–4Ti alloy that can be made in the laboratory at the present time, as will be discussed later. Clearly it is the impurities that determine radiation exposure for times greater than about three years, and they will be the focus of this paper.

A V–4Cr–4Ti alloy with three levels of impurities will be examined for activation properties in a fusion reactor spectrum and activity determined after a decay period of 50 years, for land burial and 100 years for reprocessing.

2. Impurities in vanadium

The first alloy composition to be examined is shown in Table 1 and is designated 'WC 832665' to represent Wah Chang heat 832665 of V–4Cr–4Ti, analyzed by

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0022-3115/98/$19.00
PII: S0022-3115(98)00228-1

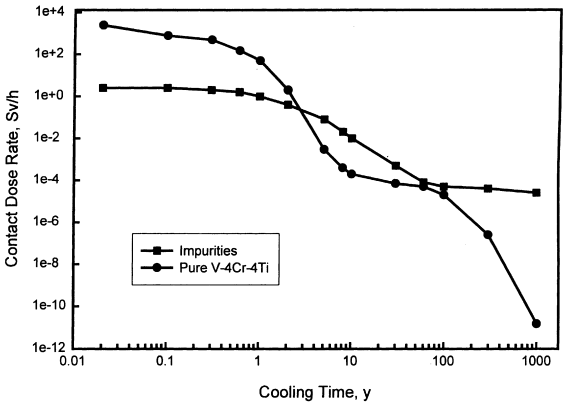

Fig. 1. Calculated contact dose rate for pure V–4Cr–4Ti and for the impurities present in the High Purity alloy resulting from state-of-the-art laboratory practice.

glow discharge mass spectrometry (GDMS). The values reported are the averages of two samples. GDMS is a very sensitive technique but requires a calibration standard for each impurity in the alloy. The result is that the reported values typically have as much as a factor of two uncertainty. Values for carbon, oxygen, and nitrogen were determined by inert gas fusion analysis on several rolled product forms from this heat. Since the concentrations of these interstitials may change significantly during processing, the values are only approximate.

The second alloy composition, designated 'Best Commercial' in Table 1 is a subjective composition that is proposed to be what is achievable using a dedicated production plant but employing only processing techniques in use today. As a first step in determining this composition, the composition of a recent random sample of V_2O_5 from Stratcor, [1] the supplier of feed stock to Wah Chang, was used. The composition was determined by inductively coupled plasma mass spectrometry (ICP-MS). This analytical technique requires that the sample be dissolved and, as a result, easily permits the use of standard solutions. Neutron activation analysis was used as a cross-check for the set of elements for which this technique is applicable. The composition is shown in Table 1, designated Stratcor V_2O_5. The composition of the actual V_2O_5 used to prepare WC 832665 was also used as guidance in selecting the achievable composition. The composition of the vanadium metal produced from this oxide and ultimately used to prepare WC 832665 was also examined. Its composition appears in Table 1, designated V820630. It is accompanied by the compositions of the Ti (920990) and Cr (21803) used to produce the alloy.

[1] Stratcor, A Division of US Vanadium Corporation, Hot Springs, AR 71901-8802, USA.

As will be shown in this analysis, two elements of critical importance for disposal, aside from holmium and terbium, which were not detected in these alloys, are molybdenum and niobium. Molybdenum is present in the V–4Cr–4Ti alloy (WC 832665) at a level of about 300 wppm. It is present in the feed stock vanadium at the same level, as seen from Table 1. However, molybdenum is present in the original V_2O_5 used to produce that particular heat of vanadium at a level of only <10 wppm. This leaves two likely sources for the molybdenum: the aluminum used to reduce the V_2O_5 and contamination from equipment at the production plant. A chemical analysis of the aluminum used for the reduction was not available, but aluminum is readily obtainable with molybdenum levels of a few wppm or less. Molybdenum could have come from contamination within the processing plant, but although Mo is used for alloy purposes, it is not produced there. To avoid such contamination, it is postulated that when commercial fusion power plants are being built that a virgin process line or even a new plant would be made available.

The level of molybdenum in the Stratcor sample of V_2O_5, 5 wppm, falls on the low end of concentrations of Mo in a representative group of V_2O_5 samples analyzed by Peterson and Smathers for which Mo ranges from 5 to 24 wppm [2]. Since material with 5 wppm Mo is readily and currently available, this level was considered the attainable level for Mo in the "Best Commercial" alloy. Only a small contribution is expected from the Ti and Cr since there was only 8 wppm Mo in the Ti and 6 wppm in the Cr used to produce WC 832665. These elements are further diluted since Ti and Cr make up less than 10% of the alloy.

Niobium was examined in a similar manner. It was found in the V–4Cr–4Ti alloy at a level of about 60 wppm, but it was found at levels <0.1 wppm in the Stratcor V_2O_5 sample and in the range of 2–8 wppm in the five high purity samples reported by Peterson and Smathers [2]. Significant niobium originated from the Cr but not enough to account for the level measured in the V–4Cr–4Ti alloy. It is believed to arise from contamination within the production plant since niobium is produced in the plant. A level of 5 wppm was chosen for the attainable level based on the Peterson and Smathers samples [2].

In a similar manner, each impurity element was examined and a value thought attainable without additional purification was determined. An interesting case is that of iron, which is present in the alloys at about 200 wppm and in the V_2O_5 at a level of 100 wppm. Perhaps some is added by the mechanical processing, and iron is added by the sulphuric acid used in leaching the ore and especially from the Cr and Ti used for making the V–4Cr–4Ti. It appears to be ubiquitous, and little is to be gained by its removal below this level.

Table 1
Compositions of V–4Cr–4Ti and feed stock materials (wppm unless specified)

Element	WC 832665	Best commercial	Chemical processing	High purity	Stratcor V_2O_5	Vanadium V820630	Cr 21803	Ti 920990	Stratcor NH_4VO_3
Ag	0.0775	0.1	0.1	0.07	27	0.26	0.11	0.38	
Al	355	250	250	80		530	1500	97	3
As	1.4	0.2				0.12 [a]	1 [a]	30 [a]	
Au	<.06	0.05	0.05	0.05		<0.15	0.06	0.09	
B	3.7	3			36	200	54	100	
Ba	<.26	0.2	0.2	0.05		0.25	0.07	0.2	
Be	<.0019					<0.1	<0.1	<0.1	
Bi	<.0068					<0.05	<0.05	<0.05	
Br	<.12								
C	170	200	200	200					
Ca	<.26	0.3			110	50	80	<50	140
Cd	<.16	0.1	0.1	0.1		0.5	<0.1	0.1	
Ce	0.019					<0.15	0.14	<0.05	
Cl	<.07								
Co	0.295	0.3	0.3	0.03		1.8	2.3	0.95	
Cr	3.25%	4.00%	4.00%	4%	11	37	Bal.	214	
Cs	<.019					<0.05	<0.05	<0.05	
Cu	0.84	0.8	0.8	0.04		<20	<20	Int.	
F	<.074								
Fe	205	200	200	200	110	300 [a]	2040	650 [a]	<10
Ga	1.4	1		0.2		0.3	100	<0.1	
Ge	<.03					0.1	<0.1	<0.1	
Hf	8.35					1.2	0.5	13	
Hg	<.035					2.76	3.48	0.47	
I	<.017								
In	0.066	0.05	0.05	0.01					
Ir	<.003					0.06	<0.05	0.06	
K	<.036					135	120	120	
La	<.00072					<0.05	0.06	<0.05	
Li	<.0016					0.3	<0.1	<0.1	
Mg	0.1715	0.2	0.2	0.05		14	8.5	190	
Mn	0.21	0.1	0.05	0.05		0.6 [a]	12.5	16.9	
Mo	315	5	1	3	4.8	275	6	8	
N	100		200	200					
Na	0.01215				70	30	<10	30	
Nb	60	5	1	0.05		22.4	109	12.4	0.2
Nd	<.0085					<0.05	<0.05	<0.05	
Ni	9.6	10	0.5	0.5	11	8.5	64	213	
O	330	350	350	350					
Os	0.008								
P	33	30	6	6		400	50	70	
Pb	<.0068					0.37	0.21	0.43	
Pd	0.14	0.1	0.1	0.05		0.6	0.4	0.8	
Pt	<.24	0.1	0.1	0.04		0.28	<0.05	0.11	
Rb	<.2					2.1	17	0.2	
Re	<.0041					<0.05	<0.05	<0.05	
Rh	<2.6	2	2			0.3	1.3	<0.1	
Ru	<1.4	1	1			3	17	0.3	
S	16.5	10	10	10					
Sb	0.17				165	0.6	23.3	12.6	46
Sc	<.012					<5	<5	1.3 [a]	
Se	<1	0.1	0.1			<10	<10	<10	
Si	785	800	800	800	60	2950	1690	6400	100
Sn	0.24	0.2	0.2	0.6		0.5	11.9	5.8	
Sr	<59	50	50			0.3	0.3	1.8	

Table 1 (Continued)

Element	WC 832665	Best commercial	Chemical processing	High purity	Stratcor V_2O_5	Vanadium V820630	Cr 21803	Ti 920990	Stratcor NH_4VO_3
Ta	<19	3	3			<0.05	0.76	0.56	
Te	<.083	0.08	0.08			<0.1	<0.1	<0.1	
Ti	4.05%	4.00%	4.00%	4%		28	390	Bal	
Tl	<.01					<0.05	<0.05	<0.05	
Th	0.00795					1.2	0.48	0.25	
U	0.0835	0.08	0.08			0.3	<0.01	<0.10	
V	Bal	Bal	Bal	Bal		Bal	<0.2		
W	25	2	2	0.1		27	27 [a]	5.5	
Y	<4.2	4	4	0.1		1.67	4.22	0.12	
Zn	0.115	0.1	0.1	0.1		80	70		
Zr	<46	5	5	2		70	16.9	89	

[a] Neutron activation analysis.
Int. = interference, bal = balance.

A third alloy was studied that is based on a chemical purification process. It is a common practice in commercial production to precipitate vanadium from a leaching solution with aqueous ammonia or ammonium sulfate to form ammonium metavanadate [2]. An additional purification stage has been developed by Stratcor to remove impurities. Following solvent extraction, dissolution and recrystallization of NH_4VO_3 is employed to take advantage of differing solubilities. This process is especially effective for removal of molybdenum. A sample of NH_4VO_3 produced by this process was analyzed and found to have a Mo level below the limit of detectability by ICP-MS and a Nb level of only 0.2 wppm (Table 1). Since NH_4VO_3 is already an intermediate in the processing of vanadium, the above process is not a difficult or expensive addition. It is estimated that such a process would add approximately \$1.00 kg^{-1} to the price of V_2O_5. A V–4Cr–4Ti alloy based on the purified NH_4VO_3 is given in Table 1 and designated, ''Chemical Processing''.

A fourth level of purity is represented by the alloy designated ''High Purity'' in Table 1. This represents estimates of impurity levels that are attainable with special purification techniques and is based on three materials. The first is a vanadium bar produced by Johnson Matthey [2] under contract with Euratom to investigate production of ultra-pure vanadium alloys [3]. The other two materials are high purity titanium (99.999%) and chromium (99.995%) available from chemical supply companies. These materials were used as a guide in formulating the composition of the attainable high purity alloy given in Table 1.

The Johnson Matthey material is the result of an extensive investigation into purification of vanadium. The purification was largely based on distillation of vanadium oxytrichloride, $VOCl_3$, followed by calcination, reduction by aluminum, and electron beam melting. State-of-the-art techniques were used to minimize contamination. The final product had a Mo level below 10 wppm, Nb below 0.2 wppm, and Ag, which is critical for reprocessing, below 0.2 wppm. The final vanadium bar contained 860 wppm nitrogen, a level several times higher than obtained in commercial processing of vanadium alloys. This resulted in a very hard material that was difficult to machine. Refinement of the process is likely to eliminate this contamination, so it was assumed that nitrogen will be about 200 wppm, an easily attainable level.

3. Activation calculations

The neutron activation calculations assumed a liquid lithium-cooled vanadium blanket consisting of a 3 mm first wall, a 0.5 m tritium breeding zone, and a 0.5 m reflector/plenum. The breeding zone was composed by volume of 7.1% vanadium alloy, 73.7% lithium, and the remainder void space. The reflector/plenum was made of 10% vanadium alloy (structures), 80% pure vanadium (non-structural), and 10% lithium. A neutron wall loading of 5 MW/m^2 at the first wall and a blanket lifetime of four full power years was assumed so that the total exposure was 20 MW y/m^2. The isotopic abundance of natural lithium was assumed. Details of the codes and calculations are presented elsewhere [4].

For the issue of disposal by shallow land burial, a cooling time of 50 years was selected. As shown in Table 2, only eight elements are of concern, for which the limiting concentration in vanadium is given. For each of the four alloys considered, the existing V–4Cr–4Ti and three proposed higher purity alloys, the concentration of the critical elements and the waste disposal rating (fraction of allowed concentration) is shown. The al-

[2] Johnson Matthey, Royston, Hertfordshire, UK.

Table 2
Allowable impurity concentrations and waste disposal ratings (WDR) for V–4Cr–4Ti for shallow land burial after 50 years cooling

Natural element	Limiting conc.	WC 839665		Best commercial		Chemical processing		High purity	
	wppm	wppm	WDR	wppm	WDR	wppm	WDR	wppm	WDR
Ag	16	0.08	0.0052	0.1	0.0065	0.1	0.0065	0.07	0.0045
Bi	40	0.0068	0.00017						
Dy	90								
Ho	0.7								
Ir	28	0.003	0.00011						
Mo	87	315	3.6	5	0.057	1	0.012	3	0.034
Nb	4.2	61	15	5	1.2	1	0.24	0.05	0.012
Tb	1.6								
Total WDR			19		1.3		0.26		0.051

Table 3
Allowable concentrations and reprocessing ratings for hands-on reprocessing of V–4Cr–4Ti after 100 years

Element	Limit for	WC 832665		Best commercial		Chemical processing		High purity	
	Recycling [a] wppm	wppm	Recycle Rating	wppm	Recycle Rating	wppm	Recycle Rating	wppm	Recycle Rating
Ag	0.025	0.0775	3.100	0.1	4	0.1	4	0.07	2.8
Al	353	355	1.006	250	0.708	250	0.708	80	0.227
Bi	0.12	0.0068	0.057		0.000		0.000		0.000
Ca	240 000	0.26	0.000	0.3	0.000		0.000		0.000
Cd	19	0.16	0.008	0.1	0.005	0.1	0.005	0.1	0.005
Co	20	0.295	0.015	0.3	0.015	0.3	0.015	0.03	0.002
Cu	1000	0.84	0.001	0.8	0.001	0.8	0.001	0.04	0.000
Hf	5.7	8.35	1.465		0.000		0.000		0.000
Ir	0.13	0.003	0.023		0.000		0.000		0.000
Mo	20	315	15.750	5	0.250	1	0.050	3	0.150
Nb	0.12	61	508.333	5	41.667	1	8.333	0.05	0.417
Ni	700	9.6	0.014	10	0.014	0.5	0.001	0.5	0.001
Os	20	0.008	0.000		0.000		0.000		0.000
Pd	2.4	0.14	0.058	0.1	0.042	0.1	0.042	0.05	0.021
Pt	630	0.24	0.000	0.1	0.000	0.1	0.000	0.04	0.000
Si	850 000	785	0.001	800	0.001	800	0.001	800	0.001
Ta	4330	19	0.004	3	0.001	3	0.001	0	0.000
Ti	58 000	40 500	0.698	40 000	0.690	40 000	0.690	40 000	0.690
W	2000	25	0.013	2	0.001	2	0.001	0.1	0.000
Zr	10 000	46	0.005	5	0.001	5	0.001	2	0.000
Total recycle ratio			531		47		14		4.3

[a] The following elements with recycling limits were not detected: Dy 1.7, Er 3.3, Eu 0.0038, Gd 0.57, Ho 0.019, Sm 1.2, Tb 0.0058, Tm 30.

lowed concentration is based on Federal Regulation 10CFR61 as evaluated by Fetter et al. [5].

For reprocessing, a cooling time of 100 years and a contact dose rate of 25 μSv/h was selected [6,7]. The results are shown in Table 3 in a similar fashion. The recycle rating is defined in a manner similar to the disposal rating. Since the criteria for hands-on reprocessing are more limiting, the list of critical elements is longer.

4. Discussion

As Table 2 shows, two of the alloys fail to meet the requirements for shallow land burial, the existing WC 832665 and the hypothetical 'Best Commercial' alloy. In both cases niobium contributes the highest activity, and in the existing alloy, molybdenum also causes the alloy to fail the criteria. It is important to note that the "Best Commercial" alloy is only 20% above the limit so that judicious selection of the source material alone might be

sufficient to achieve low activation. The alloy obtained by chemical processing was below the disposal limit by a factor of 4. Using the recrystallization purification step would permit shallow land burial with only a minimal increment in processing cost. The high purity alloy has the benefit of a wider margin of safety but at a much higher cost.

From the results for reprocessing, in Table 3, it can be seen that only Ag, Nb, Al, Mo, and Ti are of major concern. Titanium is, of course, an essential alloy constituent, but it must be kept below about 6% to render the alloy low activation for reprocessing. Silver remains above the allowable limit in all four alloys, but it enters the ''High Purity'' alloy through the chromium. If chromium were processed specifically to reduce silver, as was the case for the vanadium, it too might be low activation for reprocessing. The sum of the recycle ratings, similar to the waste disposal ratings, reveals that all four alloys fail the criteria for hands-on reprocessing. However, the High Purity alloy falls within a factor of 4. A slightly higher allowed activity level or a longer decay time could remedy this situation. However, caution must be used since Ti and Al alone contribute 0.92 to the reprocessing rating.

It should be considered that prototype fusion reactors will not be operational before the middle of the 21st century; commercial reactors will not be operating before the last quarter of the 21st century; decommissioning will not occur before the middle of the 22nd century, and waste will not be reprocessed before the middle of the 23rd century. The materials and their impurity levels that are used for fusion reactor construction late in the 21st century will determine what options will be available for waste handling in the 23rd century. As metals become more scarce and lower grade ores are used, vanadium that has been disposed of by shallow land burial might be dug up for reprocessing along with that stored from decommissioned reactors. Therefore, reprocessing will ultimately become more important than shallow land burial. With present processing technology and only a small increment in price, the ''Chemical Processing'' alloy can be produced, which is a factor of 14 from meeting the hands-on reprocessing criteria. For additional cost, the High Purity alloy can be produced today which will come within about a factor of 4 of the hands-on criteria. In addition, if isotope separation becomes cost effective, it would enable reprocessing criteria to be met [8]. Thus there is good reason for optimism in developing a low activation vanadium alloy.

5. Conclusions

1. With existing technology and present commercial practice, a low-activation V–4Cr–4Ti alloy that can be disposed of by shallow land burial can be produced.
2. Even with advanced laboratory processing, a low-activation V–4Cr–4Ti alloy meeting present requirements for hands-on reprocessing cannot be produced at the present time.
3. Since the present day criteria for hands-on reprocessing are within an order of magnitude of what can be achieved, research in purification techniques is likely to produce a hands-on reprocessing V–4Cr–4Ti alloy in the future.
4. Reprocessing of fusion reactor materials is the most attractive long-term disposition option and the one that will ultimately be used.

Acknowledgements

This work was sponsored by the Office of Fusion Energy Science, US Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation. The authors wish to thank J.W. Davis of McDonnell Douglass Corporation for helpful discussions on contamination of refractory metals.

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