CHEMISTRY RELATED TO THE PROCUREMENT OF VANADIUM ALLOYS*, D.L. Smith, H.M. Chung, H.C. Tsai (Argonne National Laboratory)

OBJECTIVE

The objective of this work is to evaluate the chemistry of vanadium alloys as it relates to production capability and low-activation characteristics.

SUMMARY

Evaluation of trace element concentrations in vanadium alloys is important to characterize the low-activation characteristics and possible effects of trace elements on the properties. Detailed chemical analyses of several vanadium and vanadium alloy heats procured for the Argonne vanadium alloy development program were analyzed by Johnson-Matthey (UK) as part of a joint activity to evaluate trace element effects on the performance characteristics. These heats were produced by normal production practices for high grade vanadium. The analyses include approximately 60 elements analyzed in most cases by glow-discharge mass spectrometry. Values for molybdenum and niobium, which are critical for low-activation alloys, ranged from 0.4 to 60 wppm for the nine heats.

INTRODUCTION

Vanadium alloys offer a potential for both high performance and low activation characteristics for fusion power applications. Chromium and titanium, which are the primary alloying elements for the candidate alloys for fusion applications, also exhibit favorable long-term activation characteristics. Therefore, trace elements, such as niobium and molybdenum, are the primary contributors to the long-term activation characteristics of vanadium alloys. Certain trace elements may also affect the mechanical properties of vanadium alloys, particularly after irradiation. A joint effort was conducted by Argonne National Laboratory and Johnson-Matthey of the United Kingdom to evaluate the low activation potential of vanadium alloys. Samples of three heats of vanadium and six heats of vanadium alloys were prepared from materials used in the test program at Argonne for analysis by Johnson-Matthey. These materials were produced by standard procedures used at the time for production of vanadium and vanadium-alloys. An important aspect of this effort was to identify which elements in these materials are the major contributors to the long-term activation and to evaluate whether these elements could be further reduced if necessary. Related information has been reported by Murphy and Butterworth [1] and Attaya [2].

MATERIALS AND PROCEDURES

Materials used in this investigation were obtained from the ANL stock of material used in the vanadium alloy development program. Three heats of unalloyed vanadium and six heats of candidate vanadium alloys were included in this study. These materials, which were produced by standard procedures used at the time of production, are summarized in Table I. One of the vanadium heats (BL-20) was produced in the 1960's for the breeder reactor program. Low activation material was not an issue at the time. Alloys of V-Cr-Ti produced at ANL for the breeder program were made from this material. The other two heats of vanadium were produced from Teledyne Wah Chang (TWC). The heat designated BL-51 was obtained from

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one of the ~300 Kg ingots of vanadium being produced by TWC in the late 1980's when they were producing several hundred ton of vanadium. Four of the vanadium alloys were produced by TWC for the ANL fusion program, one alloy (BL-43) was produced by ANL from TWC vanadium (BL-51) before TWC started producing these alloys, and the other alloy (BL-24) was produced by ANL in the 1960's for the breeder program.

The analyses were performed predominately by glow discharge mass spectrometry (GDMS). Exceptions to this method are noted.

RESULTS AND DISCUSSION

The analytical results obtained for the three heats of vanadium and six heats of V-Cr-Ti alloys are presented in Table 2 in units of parts-per-million by weight. Results for the light elements $Z \leq 12$ were not reported. A few other elements could not be analyzed because of interference with the spectra. A large fraction of the elements were below the limit of detection. In these cases the results are reported as "less than" the detection limit, which is typically a few parts-per-billion.

The dominant trace impurities are Al (5.7-380 wppm), Si (3.3-560 wppm), and Fe (15-200 wppm). Values for Nb and Mo, which are critical for long-term activation varied from 0.056 to 40 wppm for Nb and 0.53 to 60 wppm for Mo. Although the values are low, possible contamination by Ta from instrument parts was noted for all specimens. For the case of BL-46 (V-5 Ti), analyses for Sr, Zr, Nb, Mo and Te were obtained by SSMS techniques. The values obtained by the SSMS technique on the V-5 Ti alloy tend to be considerably higher than the concentrations obtained from the other specimens by the GDMS technique. Significant amounts of copper detected in some alloys may result from the use of copper heat sinks used in the alloy melting processes. A very high tungsten concentration was obtained for one vanadium specimen. The source of W in this case has not been determined. It appears that higher concentrations of some elements (eg, Sn) in the alloys may have originated from Cr or Ti since the concentrations in unalloyed vanadium are quite low.

These results indicate that high purity vanadium alloys can be obtained by current production processes. Further investigations can be conducted to evaluate which trace elements, if any, need to be further reduced to provide desirable low-activation properties. The values given in Table 2 represent typical trace element concentrations obtained in the alloys tested. It has been noted that at TWC, for example, the vanadium is processed in the same facilities that are used for processing niobium and that in some cases significant contamination of niobium will occur in first batches of vanadium. This has been observed by R. Johnson [3] in the production of a 1200 Kg heat of V-4Cr-4Ti alloy. It has also been concluded by R. Peterson [4] that niobium and molybdenum can be controlled to a great extent by selection of the source of raw vanadium.

Based on the information presented here and other analyses of vanadium alloys, we have concluded that vanadium alloys can be produced with trace element concentrations presented in Table 3 without a significant cost penalty. Further analyses and evaluation can be conducted to determine the desirability and cost of selectively reducing any of the trace elements to lower levels. Calculations of residual radioactivity, nuclear afterheat, and dose in a vanadium alloy first wall with the trace element concentrations in Table 3 have been presented by Attaya [2]. These types of analysis also indicate that the activation levels decrease substantially from the first wall to the back of the blanket.

REFERENCES

[1] D. Murphy and G.J. Butterworth, J. Nucl. Mat., 191-194 (1992), p. 1444.

[2] H. Attaya and D. Smith, The Effects of Impurities on the Activation of SiC, Vanadium, and Ferritic Alloys, Fusion Materials Semiannual Progress Report, DOE/ER-0313/18, July 1995, pp. 107-117.

[3] W. R. Johnson, J.P. Smith and R.D. Stambaugh, Fusion Materials Semiannual Progress Report for period ending December 31, 1995, DOE/ER-0313/19, April 1995, pp. 5-11.

[4] J.R. Peterson and D.B. Smathers, J. Nucl. Mat. 141-143 (1986) pp. 1113-1116.

Table 1. Vanadium and vanadium alloys included in this evaluation of trace element concentrations

Specimen Designation	Specimen ID	Source of Material
V	BL-20	ANL inventory from Breeder Reactor Program in 1960's
V	BL-51	From ~300 Kg ingot purchased by ANL Fusion Program from TWC in late 1980's
V	BL-52	Purchased by ANL Fusion Program from TWC
V-5Ti	BL-46	Produced by TWC for ANL Fusion Power Program
V-4Cr-4Ti	BL-47	Produced by TWC for ANL Fusion Program
V-9Cr-5Ti	BL-43	Produced by ANL from Vanadium procured from TWC (BL-51)
V-11Cr-5Ti	BL-40	Produced by TWC for ANL Fusion Program
V-10Cr-10Ti	BL-44	Produced by TWC for ANL Fusion Program
V-14Cr-5Ti	BL-24	Produced by ANL breeder reactor program in 1960's

Table 2. Trace element analysis of vanadium and vanadium alloy heats.

ANL ID NO.	BL 20	BL 51	BL 52	BL 46*	BL 47	BL 43	BL 40	BL 44	BL 24
Nom. Composition (wt. %)	V	V	V	V-5Ti	V-4Cr-4Ti	V-9Cr-5Ti	V-11Cr-5Ti	V-10Cr-10Ti	V-14Cr-5Ti
Al	5.7	270	380	350	400	100	100	100	100
Si	3.3	560	300	300	90	80	80	80	80
P	<0.005	26	9	15	4	4	4	1	1
S	0.34	69	17	27	3	10	10	3	3
Cl	0.086	0.041	0.13	0.16	2	0.6	0.2	0.6	0.6
K	<0.01	<0.04	<0.032	<0.022	0.6	2	0.2	2	2
Ca	<0.96	<1.5	<1.3	<0.92	0.6	0.6	0.2	2	2
Sc	0.01	0.0078	0.0046	0.027	0.2	0.2	0.2	0.6	0.2
Ti	1.3	3.2	5.7	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix
V	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix
Cr	----------	----------	----------	----------	Matrix	Matrix	Matrix	Matrix	Matrix
Mn	----------	----------	----------	----------	----------	----------	----------	----------	----------
Fe	15	23	28	86	100	30	80	200	200
Ni	2.1	0.66	0.83	6.4	3	3	3	3	3
Co	0.01	0.28	0.036	0.1	0.3	0.8	0.2	0.8	0.2
Cu	7.7	<0.018	0.33	40	0.4	10	1	40	100
Zn	0.16	<0.033	<0.032	0.58	0.6	0.5	0.5	2	0.5
Ga	----------	----------	----------	----------	----------	----------	----------	----------	----------
Ge	----------	----------	----------	----------	----------	----------	----------	----------	----------
As	----------	----------	----------	----------	----------	----------	----------	----------	----------
Se	----------	----------	----------	----------	----------	----------	----------	----------	----------
Br	<0.012	<0.017	<0.012	<0.012	<0.007	<0.006	<0.006	<0.006	<0.006
Rb	<0.001	<0.0022	<0.002	0.077	<0.005	<0.005	<0.005	<0.005	<0.005
Sr	0.018	0.012	0.038	0.05	<0.005	<0.004	<0.004	<0.004	<0.004
Y	3.8	2.2	4.2	0.2	<0.004	0.4	<0.04	<0.003	<0.003
Zr	0.65	2.1	12	20	3	2	7	7	0.7
Nb	0.056	5.4	18	40	4	0.4	1	4	4
Mo	0.53	3	34	60	6	2	20	20	50
Ru	<0.0098	<0.012	<0.0076	0.44	<0.03	<0.02	<0.02	<0.02	<0.02
Rh	0.032	<0.0016	<0.0014	0.18	<0.004	<0.04	<0.04	<0.04	<0.04
Pd	<0.0055	<0.0057	<0.0054	0.29	<0.02	<0.02	<0.02	<0.02	<0.02
Ag	<0.0078	<0.008	0.035	0.2	<0.009	0.08	<0.008	<0.008	<0.008
Cd	<0.032	<0.15	<0.14	<0.13	<0.02	<0.02	<0.02	<0.02	<0.02
In	<0.035	<0.036	<0.033	<0.031	<0.005	<0.005	<0.005	<0.005	<0.005
Sn	<0.041	<0.088	<0.081	0.93	<0.02	5	5	1	2
Sb	----------	----------	----------	----------	----------	----------	----------	----------	----------
Te	1.1	2.8	3.1	<0.006	<0.02	<0.02		<0.01	<0.01
I	----------	----------	----------	----------	----------	----------	----------	----------	----------
Cs	<0.001	<0.0026	0.12	0.33	<0.006	<0.005	<0.005	<0.005	<0.005
Ba	<0.001	<0.014	<0.014	0.29	<0.008	<0.05	<0.008	<0.007	<0.007
La	<0.001	<0.014	<0.0014	0.013	<0.006	0.6	<0.006	<0.005	<0.005
Ce	<0.001	<0.0014	<0.0013	0.03	<0.007	0.6	<0.006	<0.006	<0.006
Pr	<0.001	<0.0016	<0.0014	0.01	<0.006	<0.006	<0.006	<0.006	<0.005
Nd	<0.001	<0.0062	<0.0057	0.49	<0.02	0.7	<0.02	<0.02	<0.02
Sm	<0.0026	<0.0058	<0.0053	<0.0051	<0.02	8	<0.02	7	2
Eu	<0.0015	<0.0016	<0.003	0.025	<0.01	<0.01	<0.01	<0.01	<0.01
Gd	<0.0029	<0.0055	<0.0057	<0.0053	<0.03	<0.03	<0.03	<0.02	<0.02
Tb	<0.001	<0.0016	<0.0014	<0.0013	<0.007	<0.005	<0.006	<0.006	<0.006
Dy	<0.0025	<0.0055	<0.005	<0.0047	<0.03	<0.02	<0.02	<0.02	<0.02
Ho	0.0031	<0.0016	<0.0014	<0.0013	<0.007	<0.007	<0.007	<0.006	<0.006
Er	<0.0022	<0.0046	<0.0042	<0.0039	<0.02	<0.02	<0.02	<0.02	<0.02
Tm	<0.001	<0.0016	<0.0014	<0.0013	<0.008	<0.007	<0.007	<0.006	<0.006
Yb	<0.0023	<0.0049	<0.0045	<0.0042	<0.02	<0.02	<0.02	<0.02	<0.02
Lu	<0.001	<0016	<0.0014	<0.0014	<0.008	<0.007	<0.007	<0.007	<0.007
Hf	<0.0063	0.074	0.099	0.5	<0.02	<0.02	2	0.2	<0.02

*Sr, Zr, Nb, Mo and Te analyzed by SSMS for BL-46.

Table 2. Trace element analysis of vanadium and vanadium alloy heats. (Cont'd)

ANL ID NO.	BL 20	BL 51	BL 52	BL 46*	BL 47	BL 43	BL 40	BL 44	BL 24
Nom. Composition (wt. %)	V	V	V	V-5Ti	V-4Cr-4Ti	V-9Cr-5Ti	V-11Cr-5Ti	V-10Cr-10Ti	V-14Cr-5Ti
Ta	0.65	0.54	0.61	1.1	0.3	0.2	0.2	0.2	0.2
W	2800	0.21	1.8	8.2	<0.03	20	3	0.8	20
Re	<0.0016	<0.0025	<0.0023	<0.0021	<0.01	<0.01	<0.001	<0.01	<0.01
Os	<0.0018	<0.0038	<0.0035	<0.0032	<0.02	<0.02	<0.02	<0.02	<0.02
Ir	<0.0012	<0.0025	<0.0023	<0.0021	<0.01	<0.01	<0.01	<0.01	<0.01
Pt	1.1	<0.0046	<0.0042	<0.0039	<0.02	<0.02	<0.02	<0.02	<0.02
Au	23	0.072	0.032	0.067	<0.009	<0.008	<0.008	<0.008	<0.008
Hg	<0.011	<0.012	<0.011	<0.019	<0.03	<0.03	<0.03	<0.03	<0.03
Tl	---------	---------	---------	---------	---------	---------	---------	---------	---------
Pb	<0.0071	<0.015	<0.014	<0.013	<0.02	<0.02	<0.02	<0.02	<0.02
Bi	<0.0066	<0.014	<0.013	<0.012	<0.009	<0.008	<0.008	<0.008	<0.008
Th	<0.0018	<0.0023	<0.0014	<0.0013	<0.01	<0.009	>0.009	<0.009	<0.009
U	0.039	0.013	0.015	0.012	<0.01	<0.01	<0.01	<0.009	<0.009

*Sr, Zr, Nb, Mo and Te analyzed by SSMS for BL-46

Table 3. Trace element concentrations in vanadium alloys considered attainable by standard production practices.

V4CR4Ti																	
Element	C	N	O	Al	Si	P	S	Cl	K	Fe	Ni	Cu	As	Nb	Mo	Ta	W
wppm	50	100	200	100	500	30	10	.2	.1	40	4	1	0.1	1	4	2	2
appm	200	400	600	200	900	49	16	.29	.13	36	3.5	0.8	0.07	0.55	2.1	0.56	0.55