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Influence of alloying and impurity element contents on V–Ti–Cr alloy properties

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Abstract

This work presents the results of a property study and analysis of V–Ti–Cr alloys with a total base component concentration of Ti + Cr in the range of 8–30% with consideration of the influence of impurity and possible transmutation elements. The effect of the base alloying elements (titanium, chromium) and impurity elements (iron, silicon, aluminum, scandium etc.) on the recrystallization temperature, hardness and mechanical properties of alloys at different temperatures has been estimated. The role of dynamic strain aging with respect to the increase of vanadium alloy strength and intermittence developed on a tensile stress–strain diagram at temperatures above 400 °C has been shown.

1. Introduction

The level and stability of V–Ti–Cr alloy properties are known to be defined not only by the ratio of the main alloying elements, namely titanium and chromium in this case, but also metallic and interstitial impurities. The influence of radiation induced impurity elements must also be taken into account. For this purpose vanadium alloys with a content of titanium from 4 to 30 at.% and with different contents of Al, Fe, Si, O, N, C, Sc were prepared. Two types of vanadium – vacuum remelting 1 and electrolytic 2 – as well vanadium alloys with various composition were assessed according to the environment and mechanical behavior.

2. Investigation of vanadium alloy properties with different content of titanium

Vanadium alloys possess good plasticity with moderate purity in comparison with other refractory metals. At present vacuum remelted vanadium containing interstitial impurities and process impurities such as iron, aluminium, silicon is most widely used for preparing low-activation vanadium alloys. These impurities, which form a solid solution in vanadium [1], may significantly affect the alloy mechanical properties and activation parameters [2–4]. In this work binary vanadium alloys with 10–35 at.% titanium were used to study the influence of impurities (Fe, Al, Si) on the alloy mechanical properties. The effect of annealing temperature for 1 h (800–1200 °C) on the alloy mechanical properties, recrystallization temperature and grain growth has also been determined.

To test, the alloys selected have been smelted on the basis of the two types of vanadium, i.e. vacuum remelted (1) and electrolytic (2), which are distinguished by different impurity content. For the type 1 vanadium in (%): Fe 0.06; Si <0.2; Al 0.16; C 0.02; N 0.01; H 0.001; O 0.03. For the type 2 vanadium in (%): Fe 0.04; Si 0.01;

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Al 0.01; C 0.01; N <0.015; H 0.01; O 0.1). The vanadium – base alloys were smelted in a L-200H furnace in a chemically pure He atmosphere. The alloys were remelted five times to eliminate the ingot heterogeneity. Because of the increase in the oxygen content in the electrolytic vanadium, the base alloys [1,3,4] were first smelted in an electron-beam furnace. Electrodes were made from titanium tubes, which were packed with electrolytic vanadium. The titanium reference tube to be used for smelting the alloy with 35 at.% titanium had an outside diameter of 40 mm and wall thickness of 2 mm. To smelt the alloy with 20 and 10 at.% titanium, the tube was grounded to a wall thickness of 1.0 and 0.5 mm, respectively. As a result of the small volumetric content of titanium, it constituted a minor amount of the impurity and metallic elements in the electrolytic vanadium-base alloy. The ingots of the electrolytic vanadium-base alloys (60 mm in diameter, 70–80 mm in height) were additionally remelted three times in a L-200H arc furnace in a chemically pure helium atmosphere to equalize the composition. Such a method of electrolytic vanadium-base alloy smelting resulted in a decrease in the oxygen content in the alloys to a level of 0.05%, which is close to its content in vacuum remelted vanadium.

Tension test results of the V–Ti alloys at room temperature before and after annealing are presented in Fig. 1.

Results have shown, that both the vacuum remelted and electrolytic binary vanadium–titanium alloys have practically the same values of hardness and slightly different strength properties. The increased hardness of cold-worked alloys compared to the annealed is due to work hardening.

For all the alloys studied their strength properties increased with increasing titanium content, which was determined by the distortion of the lattice by solid solution titanium. An increase in the annealing temperature of the cold-worked alloys from 800 to 1200 °C leads to a decrease in their hardness and strength properties (not shown). Electrolytic vanadium-base alloys containing minor amounts of impurities (Al, Fe, Si) had lower values of proportionality limit (σ_{pl}), yield stress ($\sigma_{0.2}$) and tensile strength (σ_B) in the cold-worked state. The results after annealing at 1000 °C for 1 h are similar. The same phenomenon is also observed for their plasticity characteristics (elongation δ and reduction in area $\psi = F/F_0$, where F and F_0 – sample resultant and initial cross-sections respectively). At elevated temperature (800 °C) the electrolytic vanadium-base alloys have slightly higher strength properties and lower plasticity.

The recrystallization temperature of alloys depends little on the metallic impurity content. For the binary alloys this temperature lies in the range of 900–1000 °C and for pure vanadium it is equal to 800 °C. In the vanadium–titanium binary alloys based on vacuum remelted and electrolytic vanadium the temperature of recrystallization increased from 800 °C for pure vanadium to 950–1000 °C for the alloy with 10 at.% titanium and it decreased to 850–900 °C with a further increase in titanium content (Fig. 2).

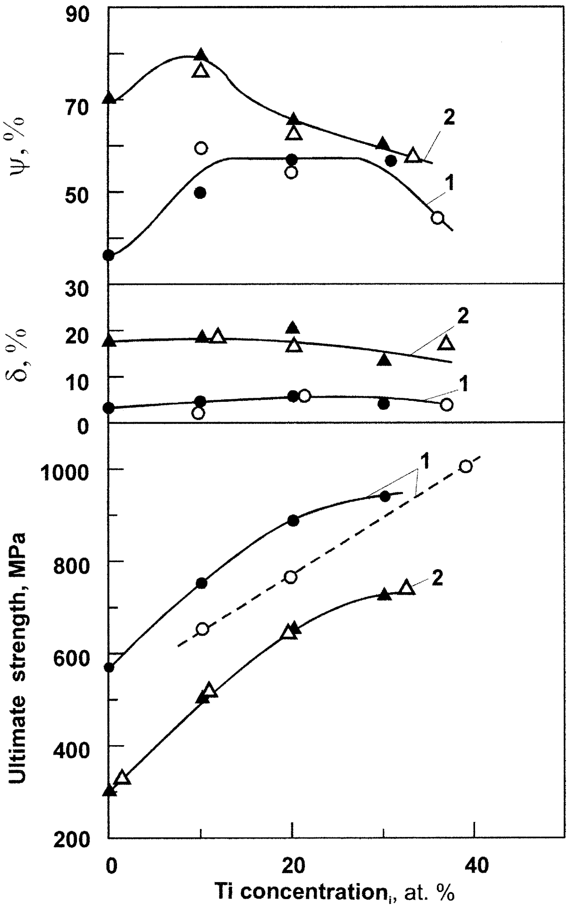

Fig. 1. Influence of titanium content on ultimate strength (σ_B), elongation (δ) and reduction in area (ψ) at room temperature of V–Ti alloys on a various basis (▲ △ – vacuum melted vanadium, ● ○ – electrolytic vanadium): 1 – cold worked (~30%); 2 – cold worked and annealed at 1000 °C for 1 h.

Investigations on the internal friction of vanadium alloys with 10–20 at.% titanium have revealed that the interstitial impurities are in the bound state, possibly in the form of titanium oxynitrides [5]. This promotes suppression of grain growth on recrystallization during annealing in the temperature range of 900–1400 °C. Such a change in grain size in the V–Ti alloys is correlated with the oxygen solubility versus titanium content in the alloys. According to the V–Ti–O phase diagrams [6], the vanadium alloys with 10–20 at.% titanium have a minimum oxygen solubility, which decreases with a

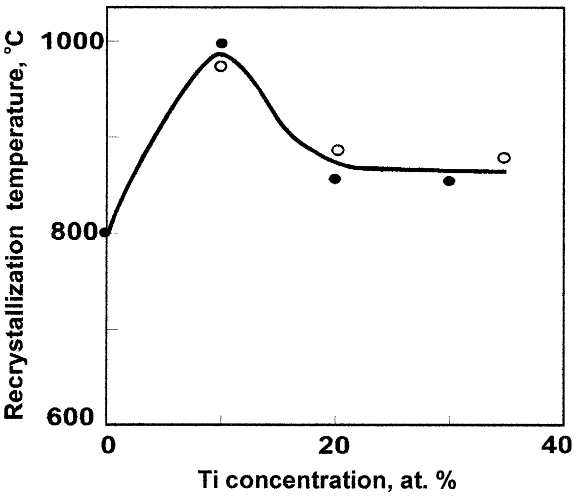

Fig. 2. Influence of titanium content on recrystallization temperature of binary vanadium–titanium alloys on a basis of vacuum melted (●) and electrolytic (+) vanadium.

reduction in temperature. The oxygen solubility increases with a further increase in titanium content. The V–Ti–N system has the same phase diagram [7]. All the above cause a suppression in grain growth in the alloys containing 10–20 at.% titanium.

It should also be noted that the alloys with higher titanium content, i.e. V–10Ti–5Cr, were found to be less strain rate sensitive than the less alloyed, such as V–4Ti–4Cr (see Table 1).

So, for V–10Ti–5Cr alloy tested at a strain rate from 1×10^{-4} to 1×10^{-2} s^{-1} the strength properties were not significantly deteriorated, while the yield stress of V–4Ti–4Cr was substantially reduced at a rate of 1×10^{-2} s^{-1} compared to the rates of 1×10^{-4} and 1×10^{-3} s^{-1}. The value of $\sigma_{0.2}$ for V–4Cr–VTi was 145 MPa at 500 °C at 1×10^{-2} s^{-1} and was 220 MPa at 1×10^{-4} and 1×10^{-3} s^{-1}.

3. Influence of transmutation elements on vanadium alloy structure and properties

The influence of metallic impurities on the alloy strength properties under irradiation must be taken into account, since concurrent with material volumetric and surface radiation damage the accumulation of gaseous and solid transmutation products takes place on exposure to high energy neutrons. As a whole, these impurities may have a marked effect on alloy physical and mechanical properties.

The transmutation elements such as Ti, Cr, Mn, Fe form continuous solid solutions or wide regions of solubility with vanadium. There is a wide region of solid solution in the V–Ti–Cr system. Therefore, the increase in content of these elements will lead to minor solid solution hardening (without change in phase), since the vanadium alloy mechanical properties have little sensitivity to small changes in titanium and chromium contents [4,8,9].

Proceeding from the available data, the transmutation elements (potassium and calcium) are not soluble in vanadium. Since calcium is more electro-negative, it may bind oxygen. This can result in the formation of calcium oxide or more complex oxide compounds [1,10, 11]. Since a small amount of calcium (stable isotope) is formed under irradiation and radioactive isotopes and isomers decay to form scandium, there will be a minor volumetric content of its oxides in the alloys, but that may not substantially affect the alloy mechanical properties.

Among the transmutation elements to be formed in the vanadium alloy, scandium is similar to the group IV elements (Ti, Cr and the others). The estimate of its effect on the vanadium alloy properties is of interest. This is of particular value, since based on the phase diagrams presented in [11], scandium with V, Ti and Cr has eutectic phase diagrams with rather narrow regions of solid solution. These become sharply narrower with a decrease in temperature.

Table 1
V–Ti–Cr alloy mechanical property dependence on strain rate

Alloy/state	Test temperature (°C)	Strain rate (s^{-1})	Strength (MPa)	Yield stress (MPa)	Total elongation (%)
V–10Ti–5Cr	250	0.0001	490	310	28
O 0.040 at.%		0.001	510	310	21
C 0.015 at.%	500	0.0001	520	320	24
N <0.01 at.%		0.001	550	340	20
Vacuum (1075 °C, 30 h)		0.01	520	330	25
V–4Ti–5Cr	250	0.0001	310	200	29
O 0.030 at.%		0.001	350	240	26
C 0.010 at.%	500	0.0001	390	220	27
N <0.01 at.%		0.001	380	225	20
Vacuum (1075 °C, 30 h)		0.01	330	145	25

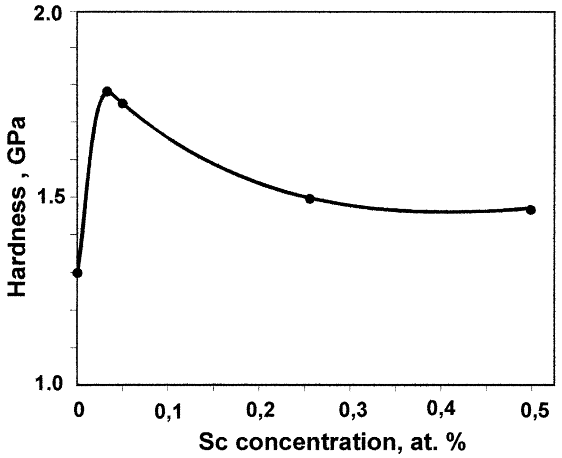

Fig. 3. Vanadium hardness versus scandium content.

The solubility of scandium in the V–Ti–Cr ternary alloys will be primarily determined by the vanadium composition. For small additions of chromium, the scandium solubility is similar to that in pure vanadium. At a content of titanium in the alloys in the range of 4–6 at.%, the solubility of scandium, which is higher than in vanadium and chromium, is not likely to increase. Some increase in scandium solubility in the alloys could take place on binding with V, Ti and Cr as compounds, but the phase diagrams indicate the absence of such compounds.

The estimate of the scandium effect on the mechanical properties of vanadium alloys is confirmed by our data. At contents of about 0.03 and 0.05 at.% Sc in vanadium an increase in alloy hardness up to 1760 and 1670 MPa, respectively, has been observed (Fig. 3). This is believed to be mainly due to its dispersion hardening through binding of interstitial impurities (oxygen) with scandium. The same increase in hardness of vanadium alloy with 1 at.% titanium is also to be known connected with precipitation of dispersion phases (titanium oxy-nitrides) [4]. The alloy hardness does not change with further increases in scandium content. In this case it is defined by vanadium hardening with scandium and its precipitation.

4. Mechanical properties of V–Ti–Cr alloys

As noted above, the high strength properties at high temperatures are considered to be one of the advantages of V–Ti–Cr alloys in comparison with other reactor materials. The vanadium alloys have a yield stress equal to 400 MPa at 800 °C, compared to austenitic and ferritic–martensitic steels, which soften at above 600 °C and above 500 °C, respectively. The creep rupture advantages of vanadium alloys are even greater [8,9]. At 700 °C for 10 000 h the long-term rupture strengths of V–4Ti–4Cr and V–10Ti–5Cr alloys amount to 140 and 180 MPa, respectively. At 600 °C these values are 230 and 300 MPa, respectively. This should be particularly emphasized, since under certain conditions the short-term strength cannot be considered as a criterion in evaluated materials. This is illustrated in Fig. 4, where the temperature dependence of short-term and long-term properties of V–4Ti–4Cr alloy specimens is given. At temperatures above 600 °C, it is useless to apply data on alloy short-term properties. However, taking into account the fact that the increase of yield stress is correlated with a decrease in creep rate [12], then strengthening is indicative of improvements in creep rupture behavior. Since the value of $\sigma_{0.2}$ for V–10Ti–5Cr alloy is superior by about 30% over that for V–4Ti–4Cr, it is believed that there will be a marked increase in creep rupture resistance of the first alloy compared to the second.

V–Ti–Cr alloys have high radiation resistance at 400–800 °C, although embrittlement and swelling data are lacking. However, the results of experiments differ greatly depending on the ratio of basic alloying elements (Ti, Cr) and concentrations of impurity elements (CO, N, C, H) in the alloy.

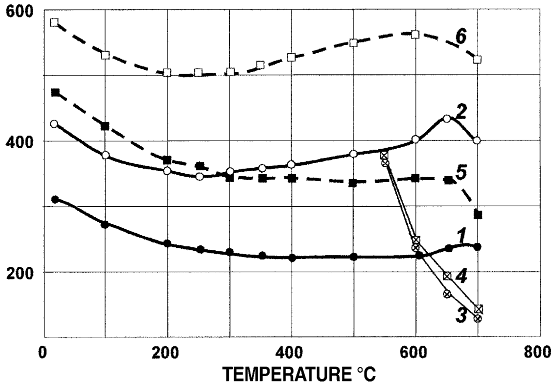

Fig. 4. Mechanical properties of the vanadium alloys. Ti–4Cr: 1 – yield stress, 2 – ultimate strength, 3 – long-term rupture strength (10 000 h), 4 – creep strength ($\varepsilon = 1 \times 10^{-4}$%h); V–10Ti–5Cr: 5 – yield stress, 6 – ultimate strength.

Table 2
Sample thickness of vanadium alloys before and after irradiation test in BN-600 reactor up to 45 dpa at 440 °C in flowing sodium

Alloy composition	Thickness (mm)		Thickness variation (%)
	Before	After	
V–20Ti–10Cr	0.40–0.42	0.40–0.42	0
V–17Mo–0.25Zr–0.16Y	0.36–0.38	0.15–0.18	50

Table 3
Mechanical properties of vanadium alloys before and after irradiation test in BN-600 reactor up to 45 dpa at 440 °C in flowing sodium

Alloy composition	σ_B (MPa)		$\sigma_{0.2}$ (MPa)		δ_{total} (%)		$\delta_{uniform}$ (%)	
	Before	After	Before	After	Before	After	Before	After
V–20Ti–10Cr	1070	1080	890	975	9.0	2.5	8.5	2.5
V–17Mo–0.25Zr–0.16Y	770	710	645	–	8.0	0.0	7.5	0.0

Under irradiation of vanadium alloys containing O 0.08; N 0.05; C 0.02 (1) and O 0.75; N 0.1; C 0.03 (2) by α-particles (~10 dpa) (5.3, 10–3 at.%) the changes in properties (especially δ and ψ) of the alloys with high contents of oxygen and nitrogen are much higher than those of the alloy with a low content of these impurities because of irradiation [13]. The nature of the environment is of importance for vanadium alloy during different tests.

Irradiation of vanadium alloys in flowing sodium in a fast reactor BN-600 with neutron fluence of 1.65 10^{23} n/cm^2 ($E > 0.1$ MeV) (>45 dpa) at a temperature of 440 °C showed [14] that the vanadium alloy specimens decreased substantially in thickness and showed brittle destruction (elongation after irradiation was 0). For alloys with Ti and Cr (1) the specimen thickness did not change, and ductility was retained (Tables 2 and 3). However, the values of elongation dropped (from 9 to 2.5), which may be explained by the oxynitride film on the specimen surface.

5. Conclusion

Based on the analysis of experimental data reported here and in earlier works

1. The influence of basic alloying elements, Ti, Cr and impurity (metallic) elements, Fe, Si, Al, Sc, on the recrystallization temperature, hardness and mechanical properties has been estimated. It is found that (a) mechanical properties depend on titanium content; (b) there is a weak dependence of mechanical properties on the concentrations of iron, aluminum and transmutated scandium.
2. Alloying of vanadium with titanium in the range of 8–11 at.% has been shown to be effective in terms of strength (including high-temperature strength) as well as radiation resistance and corrosion stability to various coolants.
3. Interstitial impurities, O, N, in certain concentrations (typical in commercial alloys) have been shown to affect mechanical behavior through strain ageing. Nevertheless, the provision of conditions which eliminate impurity gettering from coolants is imperative.

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