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The role of component distribution in vanadium-based alloys in their resistance to hydrogen embrittlement

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Abstract: The influence of the distribution of components in vanadium alloys on the probability of hydrogen embrittlement of filters is analysed. Examining V-15Ni and V-15(Fe-Co-Cr-Ni) alloys with dendritic structures formed by solidification, it was demonstrated that microvolumes with vanadium concentrations as high as 91 at.% were present, exceeding the average value of 85 at.%. The equilibrium hydrogen solubility in such microvolumes is higher than average in the alloy. Therefore, even if the average hydrogen concentration in the alloy does not exceed the ductile-to-brittle transition concentration (DBTC), H/M = 0.2, this "safety" criterion will be violated locally in microvolumes with a higher vanadium content, increasing the probability of failure. To preserve the integrity of membrane filters, we propose a stricter criterion: the membrane operating parameters (pressure and hydrogen concentration at a constant temperature) must satisfy Sieverts' law. Even if the elements in the alloy are distributed unevenly, the probability of exceeding the local DBTC remains low. However, alloys that have a uniform distribution of components are preferred. Non-hydride-forming metals that are completely soluble in vanadium should be selected as alloying elements, and the alloy should solidify in a narrow temperature range. Chromium is one of such elements. Indeed, no microsegregation is observed in experimental V-23Cr alloy ingots after solidification.

Keywords: purification of hydrogen, membrane filter, vanadium-based alloys, ductile-to-brittle transition concentration, microsegregation

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1. Introduction

Purifying hydrogen of impurities is an important technological task. For example, it is necessary for the production of hydrogen by steam conversion of methane, as well as for separating H_2 from CH_4 during the transport of methane-hydrogen mixtures in pipelines. The membrane method of purification of hydrogen is a relatively simple alternative to the short-cycle adsorption method. In addition, it removes almost 100% of impurities, which is particularly important for powering low-temperature fuel cells in hydrogen vehicles [1].

Pd-23Ag alloy was the most widely used membrane material. In solid solutions of Pd-Ag alloys, the critical point of hydride formation shifts below room temperature, which prevents membrane destruction. However, the high price of palladium made the purification process itself expensive.

Metals of the fifth group, in particular vanadium, are considered a good alternative to palladium. Its promising application in membrane filters is due to the high diffusivity and solubility of hydrogen in vanadium as well as due to its cheapness and availability. However, like palladium, vanadium cannot be used in its pure form due to the risk of hydride formation, which can subsequently lead to failure. Therefore, the high solubility of hydrogen must be reduced by alloying with non-hydride-forming metals. To date, results on hydrogen solubility and permeability have been published for a wide range of compositions of vanadium-based membrane alloy. In particular, there are alloys with cobalt [2], iron [3], and nickel [4]. Ternary alloys [5] and quaternary alloys [6] were also studied. Although a large number of articles have been published on the subject, no practical results have yet been achieved.

It should be noted that vanadium alloys not only have applications in materials for hydrogen filters. They have several important features that make them useful for structural applications in fusion reactors, such as low induced activation and thermal stress coefficients, high strength at elevated temperatures, and ductility at low temperatures [7]. In this field, the most interesting alloys are V-4Cr-4Ti and related compositions [8].

In a first approximation, the flux density of hydrogen permeating a membrane is proportional to its solubility.

Therefore, it is obvious that substitutional elements should reduce the solubility of hydrogen in vanadium, but not too much. A compromise is necessary here, as the membrane must display both adequate permeability and sufficient resistance to embrittlement.

In [9], the authors introduced a criterion of the limit of hydrogen solubility that should not be exceeded to avoid membrane failure. This is the "ductile-to-brittle transition hydrogen concentration" (DBTC). The DBTC concept was then studied and applied extensively in many publications, for example in [10–12] etc. The maximum allowable dissolved hydrogen concentration is considered to be H/M = 0.2. However, there are also higher values, e.g. 0.36 H/M [6]. Some alloying elements, such as iron [3] or nickel [4,13], strongly suppress hydrogen solubility. Some other, such as chromium [14], suppress it less effectively, but it is clear that more chromium can be added to achieve a similar level of hydrogen solubility. In the latter case, a more significant decrease in the diffusion coefficient is expected than for pure vanadium. Therefore, from this point of view, alloying with chromium appears to be less attractive.

The question arises: which alloying components are preferable? The results of the study of the V-15Ni, V-15(Fe-Co-Cr-Ni) and V-23Cr alloys enabled us to address the following questions.

1. Did the compositions studied achieve the desired reduction in hydrogen solubility while maintaining embrittlement resistance?

2. In a recent study, we compared fluctuations in the concentrations of nickel, cobalt, iron and chromium in a vanadium solid solution formed after solidification. We observed microsegregations of alloying elements in the alloy, finding the greatest deviation from the average concentration for nickel and the smallest one for chromium. Nickel is known to suppress the solubility of hydrogen in vanadium more effectively than chromium. Does this mean that nickel is a more preferable alloying component than chromium? Does the uniformity of component distribution matter?

3. Can hydrogen embrittlement occur if the average hydrogen concentration in the alloy does not exceed the DBTC?

This paper does not discuss the results of hydrogen solubility measurements in membrane alloys. Instead, it focuses on analysing the distributional uniformity of alloying elements and hydrogen in vanadium-based solid solutions. To this end, we will use the results of our previous studies of V-15Ni and V-15(Fe-Co-Cr-Ni) alloys, some of which were published in articles [13,15,16], as well as our new results for the V-23Cr alloy. While the solubility and permeability of hydrogen in similar alloys have been investigated elsewhere [17], the uniformity of distribution of components has not yet been examined. This is a key factor for our analysis.

2. Materials and methods

Smelting of alloys was carried out using metals of at least 99.98% purity. This process was carried out in a vacuum arc furnace with a water-cooled copper mold, in an argon atmosphere, using a non-expendable tungsten electrode at a constant current. The samples were remelted at least six times to achieve a uniform chemical composition throughout the ingots. The ingots were not homogenized. Details of the samples preparation from V-15Ni and V-15(Fe-Co-Cr-Ni) alloys can be found in [15] and [16], respectively.

The microstructure and chemical composition of the samples were investigated using a MIRA 3 LMH (TESCAN) scanning electron microscope (SEM) with an accelerating voltage of 20 kV. The microscope is equipped with energy dispersive X-ray spectroscopy (EDS) and Aztec 3.0 software. Microstructural images were obtained using backscattered electron (BSE) mode.

3. Results and discussion

3.1. Analysis of the DBTC criterion

The study [18] determined the ductile-to-brittle transition of hydrogenated metallic membranes under temperature-pressure conditions close to operation ones by recording load–deflection curves during in situ small punch tests. It has been demonstrated that plastic deflection and failure load decrease dramatically if the hydrogen concentration in the membrane exceeds H/M = 0.2. Consequently, hydrogen-induced embrittlement of membrane filters is often associated with the loss of material strength, and the maximum allowable dissolved hydrogen concentration is considered to be H/M = 0.2.

Initially, the DBTC criterion H/M = 0.2 was considered a necessary condition, meaning this limit should not be exceeded, otherwise there is a high probability of hydrogen-induced failure. But over time, a rather common opinion emerged (we also followed it in [13]) that if this limit is not exceeded, there will be no problem with embrittlement-related failure [15,19,20]. That is, the DBTC criterion is now recognized as a sufficient condition, and its fulfillment excludes the failure of membranes. In our opinion, this is not the case. It can only be considered a necessary condition, not a sufficient one.

The solubility isotherms we obtained earlier for alloys V-15Ni [13] (green dots) and V-15(Fe-Co-Cr-Ni) [16] (blue squares) are shown in Fig. 1 for temperatures of 100, 200 and 300°C. The red vertical line shows the DBTC. The red vertical

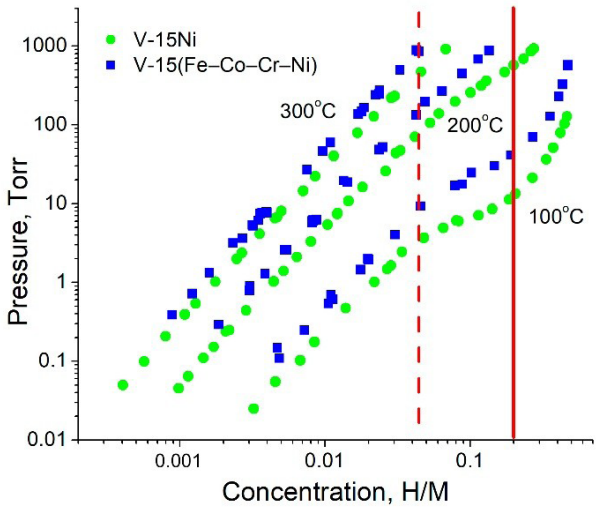


Fig. 1. (Color online) The solubility isotherms of the V-15Ni alloy (green dots) [13] and the V-15(Fe-Co-Cr-Ni) (blue squares) [16].

dotted line indicates the boundary of the zone in which the isotherms are linear and Siverts' law is valid.

As can be seen, the lower the temperature of the alloys, the greater the deviation from Sieverts' law. This indicates the potential danger of the hydrogenated alloy transitioning to a two-phase state. With a further decrease in temperature, hydrides can precipitate from the solid solution, causing embrittlement. For example, the maximum of hydrogen solubility in pure vanadium at 100°C is about H/M = 0.06 [21]. Alloying vanadium with non-hydride-forming metals at concentrations of 15 at.% and above decreases the temperature at which hydrides precipitate. However, it is unclear whether this reduction is sufficient. If the hydrogen concentration in the membrane below the one indicated by dotted line in Fig. 1, then embrittlement is not expected. These concentration values are less than H/M = 0.05, which is significantly less than the value of 0.2 implied by the DBTC criterion.

3.2. Dendritic structure as an additional problem

Note that the ductile-to-brittle transition concentration was initially measured experimentally in a pure metal [18]. However, consider the situation in which a dendritic structure with component microsegregations forms after the alloy has solidified, and the hydrogen concentration is close to the DBTC limit.

Both alloys V-15Ni and V-15(Fe-Co-Cr-Ni) had a dendritic structure. Figure 2a shows the distribution of vanadium and nickel concentrations in the V-15Ni alloy along the line depicted in the BSE image. Although the average vanadium and nickel concentrations are 85 and 15 at.% respectively, their values differ locally from these. The highest vanadium concentrations (and the lowest nickel concentrations) are observed in the darker regions of the BSE image, because vanadium has a lower atomic weight than nickel.

Figure 2b presents the fractions of microvolumes with different vanadium contents in the V-15Ni alloy. Microvolumes of the alloy containing more than 89 at.% of vanadium occupy 14 ± 3% of the total scan area. This fraction was calculated by dividing the sum of the section lengths of the scan lines containing more than 89 at.% of vanadium by the total length of the scanning lines (approximately 2 mm). It is clear that the equilibrium hydrogen solubility in the microvolumes with high vanadium content exceeds the average solubility in the alloy determined experimentally.

Figure 3 shows the experimentally obtained solubility isotherm for V-15Ni alloy at a temperature of 200°C (the same as in Fig. 1) as a green dotted curve (A). In microvolumes of the alloy with a vanadium concentration of about 90 at.%, the solubility of hydrogen should correspond with the isotherm on the right. In Fig. 3, this is represented by a speculative isotherm (curve B, the dark green dashed line). It is provided solely to demonstrate that, when the average hydrogen concentration in the alloy is H/M < 0.2, there are regions where the concentration is locally higher. The curve labelled C is also speculative and corresponds to areas of the

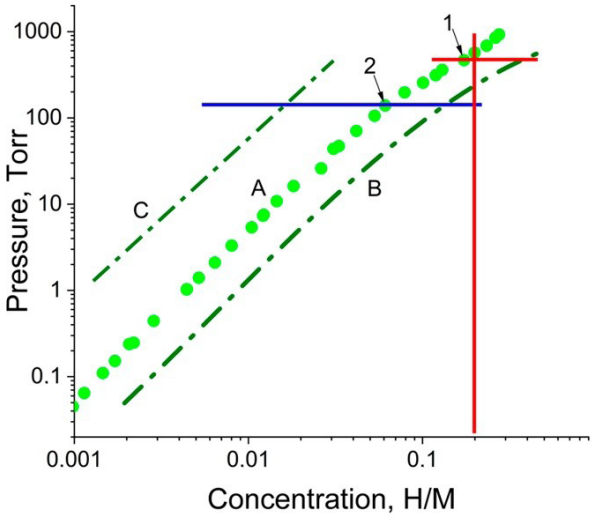


Fig. 3. (Color online) Experimental [13] and speculative solubility isotherms for the V-15Ni alloy at a temperature of 200°C.

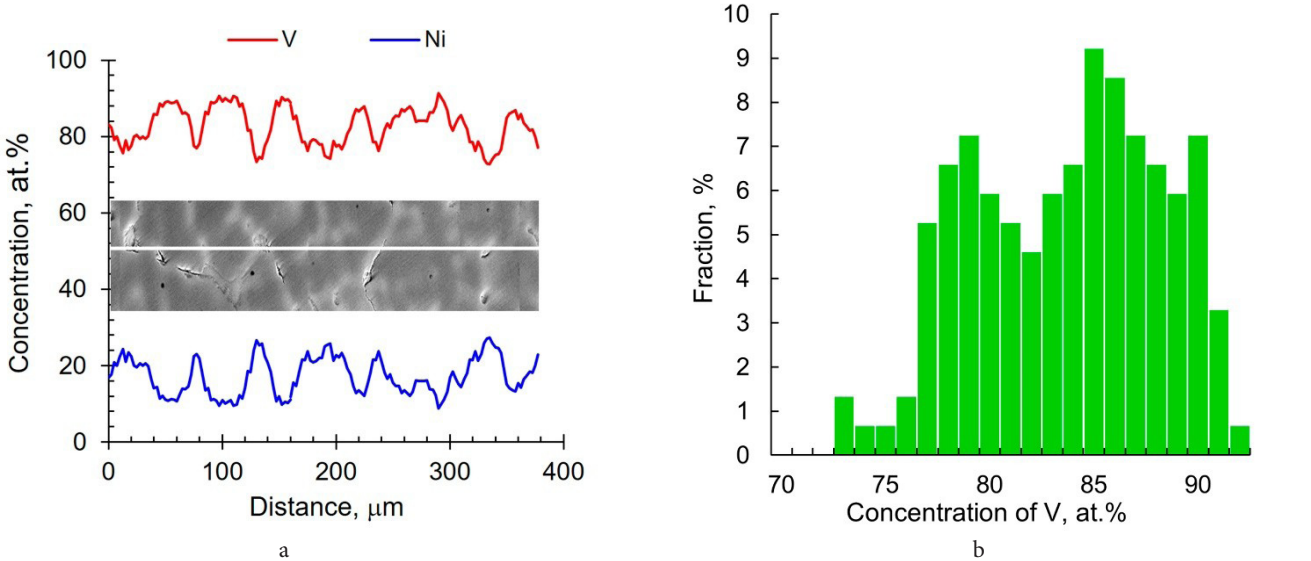


Fig. 2. (Color online) The fluctuation of vanadium and nickel concentrations along scan line (a), distribution of microvolumes with different vanadium content in the V-15Ni alloy (b).

alloy with vanadium concentrations of about 80 at.%. The red vertical line corresponds to DBTC = 0.2 H/M.

Let us consider point 1, which is indicated by the arrow on the graph. It corresponds to a hydrogen concentration of H/M = 0.17, which is less than the DBTC threshold. Therefore, there appears to be no risk of hydrogen embrittlement. However, the horizontal red line crossing curve B shows that local hydrogen solubility in microvolumes of the alloy with high vanadium concentrations can significantly exceed the DBTC. This indicates a high risk of failure.

However, if we had worked within the linear part of the experimental isotherm — for example, at point 2, as indicated by the arrow — the risk could probably have been avoided. The blue horizontal line indicates that, even in microvolumes with vanadium concentrations about 90 at.%, the DBTC concentration cannot be exceeded.

Therefore, in the presence of vanadium microsegregations (for example, in a dendritic alloy structure), the accepted DBTC criterion of H/M = 0.2 may be overestimated. One of our samples of the alloy V-15(Fe-Co-Cr-Ni) illustrates this statement; the saturation history of this sample is described in [16]. The maximum dissolved hydrogen concentration, H/M, was 0.102 and it was reached following sample exposure at 100°C. However, cracks were found in the sample (Fig. 4), even though the DBTC value was not reached.

Figure 5a demonstrates the change in component concentrations in alloy V-15(Fe-Co-Cr-Ni) along the line shown in the BSE image fragment. As noted above, chromium is the only component that distributes uniformly in the alloy. The concentrations of other components change periodically. The concentration of nickel and cobalt in microsegregations is almost twice the average for the alloy and reaches 7–7.5 at.%, whereas in microvolumes enriched with vanadium it decreases down to 1–2 at.%. The vanadium in this alloy is more evenly distributed and has a smaller variation range than in the V-15Ni alloy. Microvolumes with vanadium concentrations of over 89 at.% occupy only 5 ± 3% of the total scan volume (see Fig. 5b).

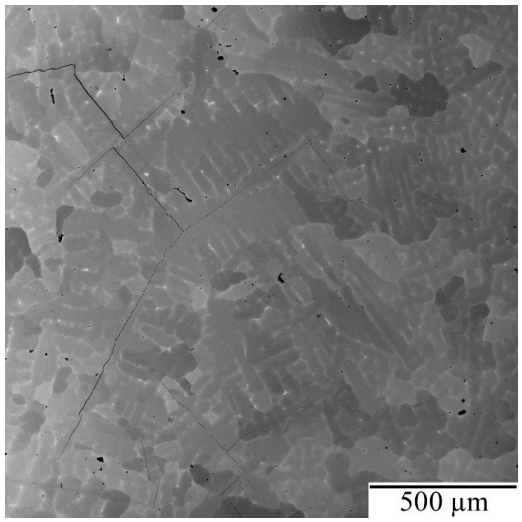
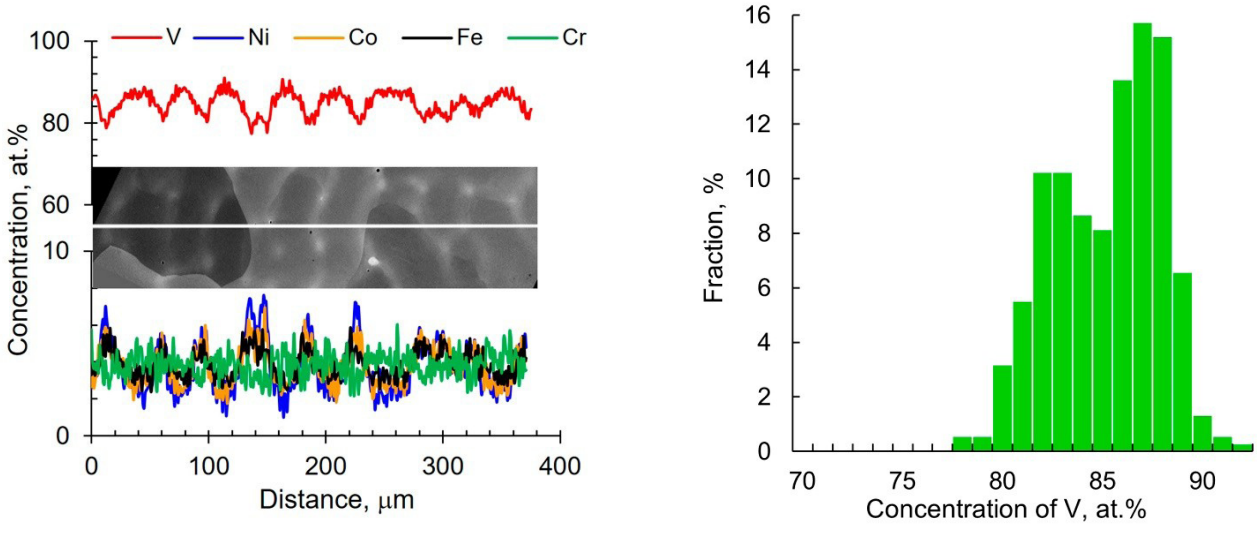


Fig. 4. BSE image of the sample of V-15 (Fe-Co-Cr-Ni) alloy with cracks [16].

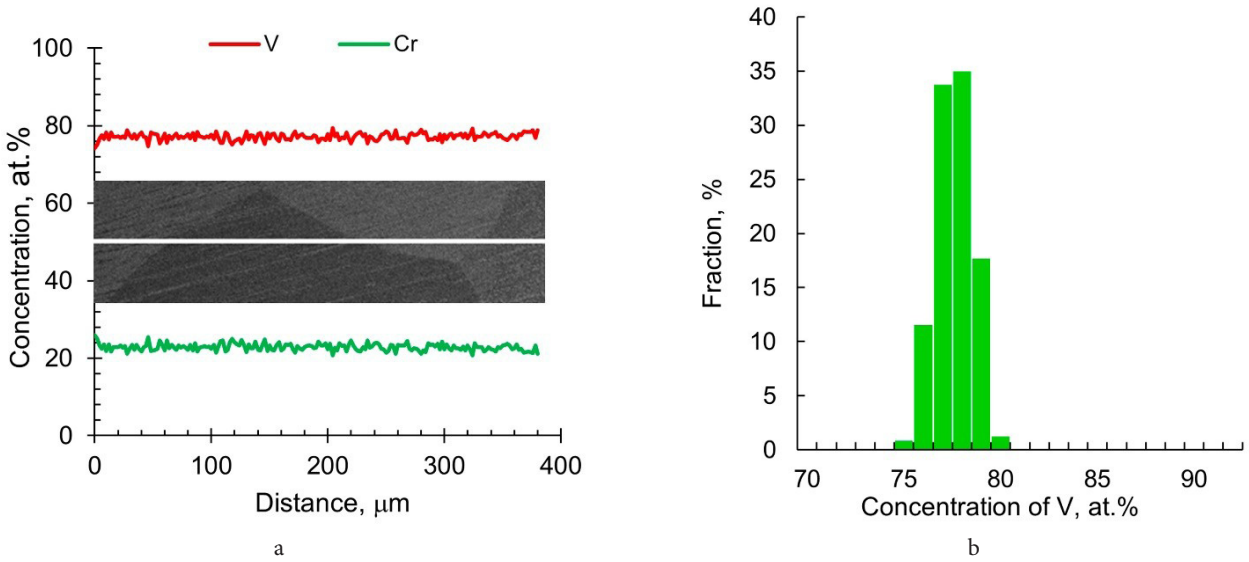
Note that the cracks (see Fig. 4) run predominantly along the dark areas of the BSE image, only crossing the light areas. It is reasonable to assume that the hydrogen concentration in the microvolumes with increased nickel, cobalt and iron content (the light areas) was less than H/M = 0.102. In contrast, in the microvolumes with increased vanadium content (the dark areas), the hydrogen concentration was higher. It is in these areas that the cracks appeared.

Thus, the uniform distribution of components in membrane alloys is of great importance. In case of non-uniform distribution of their concentration, even a small deviation from Sieverts' law is a real threat. This is because at the *average* hydrogen concentration value not exceeding H/M = 0.2, *locally* H/M > 0.2 will be met. There is a high probability of reduction in ductility and strength of the alloy caused by hydrogen. We gave an example of failure above at an average hydrogen concentration of H/M = 0.102.



a b

Fig. 5. (Color online) The fluctuation of component concentrations along scan line (a), distribution of microvolumes with different vanadium content in the V-15(Fe-Co-Cr-Ni) alloy (b).



a b

Fig. 6. (Color online) The fluctuation of vanadium and chromium concentrations along scan line (a), distribution of microvolumes with different vanadium content in the V-23Cr alloy (b).

Generally, H/M = 0.2 is a high hydrogen concentration for vanadium-based alloys and there is a high risk of a hydride phase formation at sufficiently low temperatures. However, within the limits of Siverts' law, this risk is almost eliminated, and therefore the probability of failure is low.

3.3. How to ensure uniform distribution of components in vanadium-based alloys?

Homogenisation is a common procedure used to eliminate microsegregation and dendritic structures. In [22, 23], experimental samples of the V-15Ni alloy were homogenised at temperatures of 1100–1200°C in vacuum. The samples were then cooled rapidly using argon flow to obtain a bcc single-phase structure and prevent the precipitation of low-temperature phases. The necessity of using a vacuum or protective atmosphere during the high-temperature processing of vanadium alloys, due to their high activity, makes the process very expensive.

To obtain a homogeneous single-phase bcc solid solution in vanadium-based alloys, we propose an approach similar to that implemented for Pd-Ag alloys. Non-hydride-forming metals (Me) should be selected as alloying elements which: i) are completely soluble in vanadium at the operating temperatures of membrane filters; and ii) solidify in a narrow temperature range.

Chromium seems to be the most promising element. Unlike nickel, chromium is completely soluble in vanadium [24]. Alloys of the V-Cr system solidify at a temperature of around 5–10°C under equilibrium conditions. It can be expected that solid solutions of V-Cr alloys after solidification will be significantly more homogeneous than solutions of V-Ni alloys, in which an increase in the nickel content from 4 to 15 at.% leads to an expansion of the range of equilibrium crystallization temperatures from 60 to 190°C.

Observation of the structure and EDX data (Fig. 6) confirmed that chromium is uniformly distributed in the experimental V-23Cr alloy ingots and that homogenisation is not required.

This means that in such a homogeneous alloy, one can achieve higher hydrogen concentrations without the risk of locally exceeding the DBTC and the occurrence of hydrogen embrittlement, unlike alloys with a dendritic structure. However, even with a uniform distribution of components, we believe that operation in a range of temperatures and hydrogen pressures, and not exceeding the applicability range of Sieverts' law, will allow one to more reliably prevent filter failure.

4. Conclusion

Analysis of the DBTC criterion, H/M = 0.2, revealed that, while its fulfilment is absolutely necessary, it is not sufficient to guarantee the absence membrane failure. Based on our study of the V-15Ni and V-15(Fe-Co-Cr-Ni) alloys, we have demonstrated that this is particularly critical for alloys with uneven component distribution (dendritic structures). This is explained by the fact that in microvolumes of solid solution with a reduced concentration of alloying components, the local hydrogen content can be higher than H/M > 0.2, which can lead to the failure of the material.

A more acceptable requirement for maintaining membrane strength and ductility is to comply with Sieverts' law, which assumes that isotherms are linear on a double logarithmic scale. Even if the alloy has a non-uniform distribution of components, the probability of local exceeding the DBTC is low.

Non-hydride-forming metals that are completely soluble in vanadium should be used as alloying elements, and the solidification temperature range of the alloy should be narrow. Chromium is one of such elements.

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