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Superconductivity and crystal structure of high-pressure phases in the vanadium–ruthenium–hydrogen system

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The composition and crystal structure were studied, and the superconducting transition temperatures T_c measured, for the phases formed in vanadium–ruthenium–hydrogen systems based on vanadium– ruthenium alloys containing 10, 18.5, and 34 at.% Ru at 300° C, at hydrogen pressures up to 70 kbar. The $V_{90}Ru_{10}$–H system showed a phase with a ratio of atoms $H/Me \approx 1$ and an fcc metal sublattice having $T_c \approx 3.0$ K, whereas all the initial vanadium–ruthenium alloys and other phases with interstitial hydrogen based on these were not superconducting at $T \geq 2$ K.

In this study, we continued the search for new materials whose hydrogenation yields phases with higher superconducting transition temperatures T_C. The state of progress and the specification of the problem have been quite recently formulated,[1] and it therefore seems useful to make here just the following comment.

Because there are no theories or empirical rules to use in looking for new superconducting hydrides in a purposeful way, we decided to use analogies. It has been shown[2] that electrolytic saturation with hydrogen of niobium–ruthenium alloys containing 20, 25, and 33 at.% Ru raises T_C from ≤ 0.25 K to ≈ 2-5 K. We have studied[1] solid solutions of hydrogen obtained at high pressures of hydrogen in an analog of niobium–ruthenium alloys, namely tantalum–ruthenium alloys with 22.6 and 31 at.% Ru; both of the tantalum–ruthenium–hydrogen systems studied showed phases having a hydrogen /metal atom ratio $n \approx 1$ based on an orthorhombically distorted hcp metal lattice having $T_C \approx 3$ K, whereas in the original tantalum–ruthenium alloys T_C was below 2 K. In the present research, we studied solutions of hydrogen in other analog alloys, namely vanadium–ruthenium containing 10, 18.5, and 34 at.% Ru; vanadium, niobium, and tantalum are in a vertical line in the periodic table.

1. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

To prepare the vanadium–ruthenium alloys, weighed amounts of electrolytic vanadium and ruthenium (99.998%) powder (∿40 mesh) were mixed, pressed into pellets at 20 kbar and room temperature, then remelted in an induction furnace, suspended in argon. The resulting ingots were annealed at 1200°C in a vacuum of ∿10^{-6} torr for 24 h, and then allowed to cool in the furnace. The samples were cut from the ingots by spark machining, a damaged surface layer ≈ 0.05 mm thick was ground off, and then a further layer ≈ 0.03 mm thick was removed by electropolishing in sulfuric acid. The final dimensions of the samples were $\approx 3 \times 3 \times 0.3$ mm.

The ruthenium content of the original powder mixtures was 10, 18, and 33 at.%. Chemical analysis of the samples with a CAMEBAX-MBX microanalyzer and a Link 860-500 energy dispersion x-ray spectrometer gave as the compositions of the resulting vanadium–ruthenium alloys respectively 10, 18.5, and 34 ± 0.4 at.% Ru, indicating that there was some loss of vanadium during the melting and the homogenization annealing.

The samples were hydrogenated by being held in an atmosphere of molecular hydrogen at 300°C with pressures up to 70 kbar for 24 h, followed by "quenching" under pressure to ≈ -180°C; the procedure has been described,[3] and preliminary experiments showed that there is almost no change in the hydrogen content and phase composition of the samples between 12 and 48 h. The error in the determination of the hydrogen pressure did not exceed ± 5%; the temperature was kept constant to within ± 7 C. To prevent loss of hydrogen from the prepared samples at atmospheric pressure, they were kept in liquid nitrogen.

At atmospheric pressure, the stability of the vanadium–ruthenium–hydrogen samples with respect to disintegration into metal and molecular hydrogen became less with increasing ruthenium content in the original vanadium–ruthenium alloys, and with increasing hydrogen content in each alloy. In particular, at room temperature, no evolution of hydrogen from $V_{90}Ru_{10}$–H samples with $n \leq 0.5$ was observed over a period of two weeks, but most of the hydrogen was released from $V_{66}Ru_{34}$–H with $n > 1$ in less than a minute. After keeping in liquid nitrogen for several months, there was no loss of hydrogen from any of the samples.

TABLE 1. Composition, Formation Pressure at 300°C, Structure, and Metal Sublattice Parameters at Atmospheric Pressure and 83 K of Vanadium–Ruthenium–Hydrogen Solid Solutions

At.% Ru	n	P_{H_2}, kbar	Structure	a, Å	c, Å	c/a	V_a, Å³/atom
10	0	—	α	3.011 ± 0.002	—	—	13.65 ± 0.02
	0.5	8	β	2.996 ± 0.002	3.302 ± 0.003	1.102 ± 0.001	14.82 ± 0.02
	1.04	from ≈11 to ≈32	γ_1	3.971 ± 0.004	—	—	15.65 ± 0.05
	2.0	≥ 38	γ_2	4.265 ± 0.005	—	—	19.40 ± 0.007
18.5	0	—	α	3.005 ± 0.002	—	—	13.57 ± 0.02
	1.12	13	ε	2.787 ± 0.003	4.688 ± 0.005	1.682 ± 0.003	15.77 ± 0.04
	1.36	70	ε	2.858 ± 0.003	4.696 ± 0.005	1.643 ± 0.003	16.61 ± 0.04
34	0	—	α^{or}	2.995 ± 0.002	—	—	13.43 ± 0.02
	1.24	24	ε	2.810 ± 0.003	4.577 ± 0.005	1.629 ± 0.003	15.65 ± 0.04
	1.34	70	ε	2.822 ± 0.003	4.572 ± 0.005	1.620 ± 0.003	15.77 ± 0.04

Note. α = bcc (volume per metal atom $V_a = a^3/2$); α^{or} = cesium chloride type ($V_a = a^3/2$); β = β V_2H type (values of a_6 and c_0 for the tetragonal pseudocell, $V_a = a_6^2 c_0/2$); γ = fcc ($V_a = a^3/4$); ε = hcp ($V_a = (\sqrt{3/4})a^2 c$).
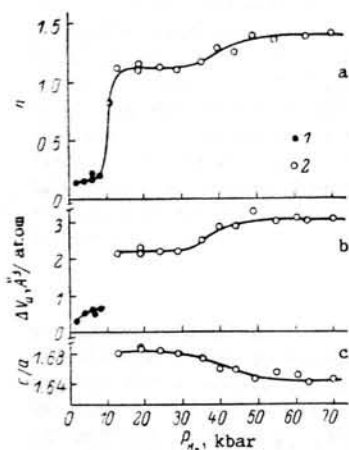

FIG. 1. Values of the hydrogen content n (a), the volume increase $\Delta V_a = V_a(n) - V_a(0)$ per metal atom (b), and the ratio c/a of the hcp metal cell parameters in ε solutions (c) for $V_{81.5}Ru_{18.5}$–H solid solutions obtained by heating at 300°C for 24 h with the hydrogen pressures shown as the abscissae: 1) results for α solutions; 2) results for ε solutions; the half filled symbols relate to two phase (α + ε) samples.
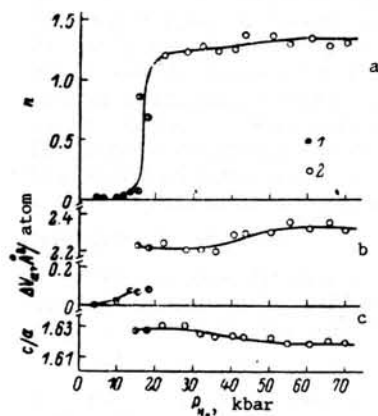

FIG. 2. Results of investigation of $V_{66}Ru_{34}$–H solid solutions; 1) for α^{or} solutions; the rest of the notation as in Fig. 1.

The hydrogen content in the samples was determined with relative error ± 5% from the amount of hydrogen evolved during thermal decomposition at up to 500°C; the method has been described.[1] The x-ray study was made photographically at 83 K with a DRON-2.0 diffractometer, using CuKα radiation; both the original vanadium–ruthenium alloys and the solutions of hydrogen in them were polycrystalline. The values of T_c were found by an inductive method at T ≥ 2 K.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The x-ray examination showed that at atmospheric pressure and 83 K the original vanadium–ruthenium alloys with 10 and 18.5 at.% Ru have a disordered bcc (α) structure, while that with 34 at.% Ru has an ordered cesium chloride type (α^{or}) structure. The structure types and the lattice parameter values (see Table I, lines with n = 0) are in agreement with published results.[4]

The superconducting properties of vanadium–ruthenium alloys have not previously been studied in this concentration range. Estimates by Miedema's method[5] with the parameter values[5] involved show that with 10, 18.5, and 34 at.% Ru T_c should not exceed ≈ 1.6, 0.2, and 0.004 K respectively. Our measurements showed that none of the three alloys is superconducting for T ≥ 2 K.

Figures 1 through 3 and Table I show the main results of this study of vanadium–ruthenium–hydrogen solid solutions. We began by examining those based on $V_{81.5}Ru_{19.5}$ and $V_{66}Ru_{34}$, in which the ruthenium contents are close to the limiting values for superconducting hydrides in the niobium–ruthenium[2] and tantalum–ruthenium[1] analogs.

Solutions $V_{81.5}Ru_{18.5}$ – H and $V_{66}Ru_{34}$ – H. It is seen from Figs. 1a and 1b that at 300°C increasing the hydrogen pressure to ≈ 8 kbar causes a monotonic rise in the equilibrium hydrogen concentration in the α alloy $V_{81.5}Ru_{18.5}$ to n ≈ 0.17, accompanied by an increase in the bcc lattice parameter of the alloy. At higher hydrogen pressures, the $V_{81.5}Ru_{18.5}$–H system shows a polymorphic transformation, and solutions with n > 1 are formed, which at atmospheric
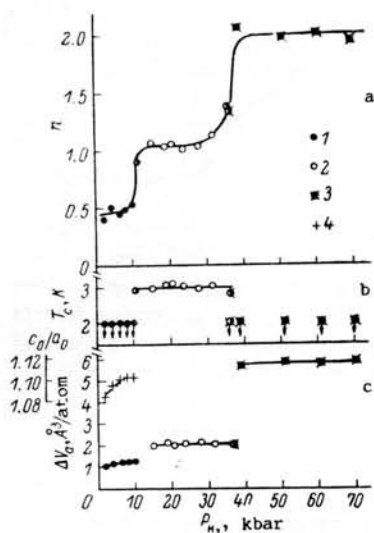
FIG. 3. Values of the hydrogen content n (a), the superconducting transition temperature T_c (b), the volume increase ΔV_a per metal atom, and the ratio c_0/a_0 of the tetragonal pseudocell parameters in the β solution (c) for $V_9 Ru_{10}$–H solid solutions obtained by heating at 300 C for 24 h with the hydrogen pressures shown as the abscissae: 1) results for β solutions; 2) for γ_1 solutions; 3) for γ_2 solutions; 4) c_0/a_0 for β solutions; the half filled symbols relate to two-phase samples. The arrows with the symbols in Fig. 3b show that the corresponding samples were not superconducting for $T \geq 2$ K.

pressure and 83 K have an hcp metal lattice (ε solutions). The greatest change among the dependences for ε solutions in Fig. 1 occurs at 30–50 kbar. The observed behavior of the ε solution properties in the $V_{81.5}Ru_{18.5}$–H systems is very similar to the transcritical behavior for the first-order amorphous transformation $\varepsilon_1 \leftrightarrows \varepsilon_2$, which is completed at the critical point with $pH_2 \sim 40$ kbar and $T \ll 300$ C (although other reasons[2] can no doubt exist for the presence of anomalies in these dependences, such as phase transformations in the hydrogen sublattice, the redistribution of hydrogen atoms between octahedral and tetrahedral interstitial positions, and ordering).

The dependence of the properties of $V_{66}Ru_{34}$–H solutions on the pressure used in producing them was qualitatively the same as in the $V_{81.5}Ru_{18.5}$–H system. It is seen from Fig. 2 that at pressures up to ≈ 13 kbar in the $V_{66}Ru_{34}$–H system the hydrogen content in solutions based on the α or lattice of $V_{66}Ru_{34}$ increases steadily to ≈ 0.04; at higher pressures, ε solutions with $n > 1$ are formed; the dependences of ΔV_a (the increase in the volume per metal atom when hydrogen is incorporated) and c/a (the ratio of the parameters of the metal sublattice hcp cell) for these ε solutions (Figs. 2b and 2c) show traces of the anomaly observed for $V_{81.5}Ru_{18.5}$–H ε solutions (Fig. 1).

The $V_{66}Ru_{34}$–H and $V_{81.5}Ru_{18.5}$–H ε solutions have another general feature: the width of the diffraction lines in the x-ray pictures does not vary monotonically with the reflection angle; this is most probably due to small distortions of the hcp metal sublattices. The presence of such distortions makes the vanadium–ruthenium–hydrogen ε solutions more similar to the superconducting tantalum–ruthenium–hydrogen ε' solutions investigated previously,[1] which have orthorhombically distorted hcp metal sublattices.

Another interesting point regarding the similarity of the effects observed in the two systems[1] is this. For $V_{66}Ru_{34}$, as for $Ta_{69}Ru_{31}$, but the almost complete (residual $\delta n < 0.01$) removal of hydrogen from samples with $n \geq 1$ after annealing in vacuum at 500°C caused the cubic lattice parameter to revert to its original value, but the ordered cesium chloride structure of the lattice was replaced by a disordered bcc structure. Superlattice reflections corresponding to cesium chloride type ordering of the lattice also disappeared from the x-ray picture of both alloys after surface grinding at room temperature. The reason for the effects observed is probably that the cesium chloride structure of these alloys is not in thermodynamic equilibrium at $T \leq 500°C$; this conclusion is in accordance with the results of extrapolating to these temperatures the phase transformation curves in the vanadium–ruthenium system, which have been studied[4] at $T \geq 1000°C$ (there are no published composition dependences of the temperatures for the corresponding transformations in the tantalum–ruthenium system).

The $V_{81.5}Ru_{18.5}$–H and $V_{66}Ru_{34}$–H systems were thus in many ways analogs of the tantalum–ruthenium–hydrogen systems studied previously.[1] However, whereas these ε' systems[1] were superconductors with $T_c \sim 3$ K, none of the vanadium–ruthenium–hydrogen systems based on alloys with 18.5 and 34 at.% Ru showed superconductivity at $T \geq 2$ K. Since the T_c values for the hydrides increased with falling ruthenium content in both niobium[2] and tantalum[1] alloys, it was reasonable to pursue the search for superconducting hydrides in the vanadium–ruthenium–hydrogen systems by examining alloys with a lower ruthenium content.

Solutions $V_{90}Ru_{10}$–H

The phases formed at 300°C in the $V_{90}Ru_{10}$–H system proved to be different from those in $V_{81.5}Ru_{18.5}$–H and $V_{66}Ru_{10}$–H (Fig. 3 and Table 1).

The hydrogen content in samples obtained at $1 \leq PH_2 \leq 10$ kbar was at the $n \approx 0.5$ level. Their diffraction patterns at atmospheric pressure and 83 K were indexable to a body-centered tetragonal (bct) cell; the corresponding solutions will be denoted by β. At hydrogen pressures between ≈ 11 and ≈ 32 kbar, solutions are formed which have an fcc metal sublattice with $n \approx 1$ (γ_1 solutions); for $PH_2 \geq 38$ kbar, there is likewise an fcc metal sublattice but with $n \approx 2$ (γ_2 solutions). It is seen from Figs. 3a and 3c that in the range where γ_1 and γ_2 solutions are formed their hydrogen contents and fcc metal sublattice parameter values are independent of the synthesis pressure.

The values of ΔV_a and of the ratio c_a/a_0 for the bct cell of $V_{90}Ru_{10}$–H β solutions agree well with the published values[6,7] for the bct pseudocells of vanadium–hydrogen β solutions with $n \approx 0.5$; these are actually[7] monoclinic with space group B2/m. Hence, it is very probable that the structure of $V_{90}Ru_{10}$–H β solutions is the same as for the vanadium–hydrogen β phase. The value of ΔV_a for the γ_2 phase in the $V_{90}Ru_{10}$–H system is 6–15% above the published values[7,8] for the VH_2 γ phase with an fcc metal lattice (calcium fluoride structure). Nevertheless, these phases too may be regarded as isomorphic, especially if we bear in mind the considerable spread of the ΔV_a values for γ–VH_2 reported by various authors. The γ_1 phase in $V_{90}Ru_{10}$–H has no analog among the vanadium–hydrogen system phases.
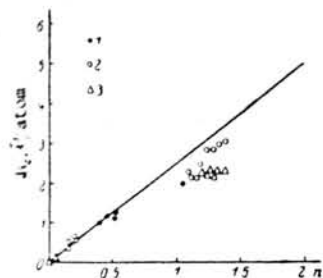
FIG. 4. Values of the volume increase $\Delta V_a(n)$ per metal atom, plotted against the hydrogen content n for solid solution of hydrogen in vanadium-ruthenium alloys with (1) 10, (2) 1.5, and (3) 34 at.% Ru; continuous line, see text.

Further measurements showed that in the $V_{90} \cdot Ru_{10}$-H system the γ_1 phase, and only this, is superconducting at $T \geq 2$ K. The temperature range of the superconducting transition in $V_{90}Ru_{10}$-H γ_1 samples was about 0.3 K; the centers of the range are plotted as T_C in Fig. 3b. It is seen that, within the experimental error, T_C is independent of the hydrogen pressure at which the γ_1 samples were synthesized; the mean $T_C \approx 3.0$ K.

The analogy method has thus proved satisfactory not only for tantalum-ruthenium-hydrogen solutions,[2] but also for vanadium-ruthenium-hydrogen ones: the addition of 10 at.% ruthenium to vanadium produced a new hydride phase with $n \approx 1$ based on the fcc metal lattice and having superconductivity with a higher value of T_C than in the original hydrogen-free alloy (note, incidentally, that no hydride phase in the vanadium-hydrogen system is superconducting above 2 K, whereas for vanadium we have[9] $T_C \approx 5.3$ K).

It is appropriate to represent the x-ray results for the various phases in the vanadium-ruthenium-hydrogen systems also as $\Delta V_a(n)$ (Fig. 4). This is because, for many transition metals and their alloys, $\Delta V_a(n)$ is almost linear over a wide range of hydrogen contents, and the slopes $(\partial/\partial n)\Delta V_a(n)$ are almost equal.[6] In particular, the values of $\Delta V_a(n)$ for all phases formed in the vanadium-hydrogen system are satisfactorily represented[6] by a linear dependence with slope ≈ 2.5 Å^3/H atom, as shown by the continuous line in Fig. 4.

Recent investigations have considerably extended the range of metal-hydrogen solutions studied, and have shown that in many cases considerable deviations from the "universal" $\Delta V_a(n)$ are observed.[10] It is seen from Fig. 4 that when $n \geq 1$ the $\Delta V_a(n)$ values deviate noticeably from those given by the continuous line for the vanadium-ruthenium-hydrogen solutions studied here also; the nonlinear variation of ΔV_a when the γ_1 phase with $n \approx 1$ and γ_2 with $n \approx 2$ are formed in the $V_{90}Ru_{10}$-H system is evident from Fig. 3c too. Nevertheless, it is very useful to acquire information about $\Delta V_a(n)$ for various phases, since, of all the quantities found in structural investigations, it is $\Delta V_a(n)$ that depends least on the type of metal that is hydrogenated,[6] and from ΔV_a we can, at least semiquantitatively, estimate the hydrogen content of the hydride phases that have been obtained for the first time. Such estimates are especially necessary in studying hydrides synthesized in non-equilibrium conditions (for example by electrochemical methods), when it is often almost impossible to make single-phase samples.

The results found for the tantalum-ruthenium-hydrogen[1] and vanadium-ruthenium-hydrogen systems allow some advice to be given, if only very tentatively, for the continued search for new superconducting hydrides.

So far, superconductivity has been found in hydrides of niobium alloyed not only with ruthenium[2] but also with rhodium and palladium,[9] that is, with all the 4d metals in group VIII. The discovery of superconducting hydrides for tantalum-ruthenium and vanadium-ruthenium alloys also, that is, for every d metal in group V with ruthenium, suggests that superconductivity in the hydrides of transition metal alloys is by no means exceptional, and the analogy in structure and properties indicates the alloys of group V transition metals with 4d and 5d metals in group VIII as offering promise for the synthesis of such hydrides.

There is not yet complete understanding of the crystal structures and hydrogen contents of superconducting hydrides of niobium with ruthenium, rhodium, and palladium. In the tantalum-ruthenium-hydrogen and vanadium-ruthenium-hydrogen systems, the superconducting hydrides are based on close-packed metal lattices, respectively hcp (slightly distorted) and fcc with $n \approx 1$. Another known superconducting transition metal hydride, that of palladium, also has a close-packed (fcc) metal sublattice, and its highest T_C occurs[9] for $n \approx 1$. Again using analogy, in the further search for such hydrides it is reasonable to look first at phases with $n \approx 1$ that are based on metal lattices having close-packed structures.

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