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THE VANADIUM-GALLIUM SYSTEM IN THE REGION OF V_3Ga

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ABSTRACT

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Melted samples were studied by X-ray diffraction and metallographic techniques after slow cooling from 1100° C. The superconducting V_3Ga phase was found to exist over a very limited compositional range. V_3Ga exists in equilibrium with either V_6Ga_5 or a vanadium solid solution depending on composition. The microstructures of samples near 75 atomic percent vanadium (V_3Ga) were essentially identical whether compositions were slightly hypostoichiometric or slightly hyperstoichiometric. Both V_6Ga_5 and the vanadium solid solution are nonsuperconducting at 4.2° K.

Author

INTRODUCTION

The vanadium-gallium (V-Ga) system is of particular interest because it contains the superconducting compound V_3Ga. In reference 1, the critical field, H_c, at 0° K for this compound is estimated to be in excess of 500 kilogauss. Although superconductivity properties of V_3Ga have been presented in the literature, little metallurgical information is available. In addition to V_3Ga, the compunds V_5Ga_3, VGa, V_6Ga_5, and V_2Ga_5 have been reported (see refs. 2 to 5).

V_3Ga has a cubic beta-tungsten type structure, and several authors (refs. 1, 6, and 7) have alluded to the fact that this compound exists as a solid solution over a wide compositional range (66 to 80 atomic percent V). On the other hand, reference 8 reports a constant lattice parameter for V_3Ga

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within the composition range of 75 to 83 atomic percent vanadium and the presence of a second phase in the microstructure of such samples. These observations are indicative of limited solubility. Reference 5 also reports limited solubility of approximately 0.5 atomic percent at 800° C. Thus, there would appear to be some question as to the true compositional limits of the V_3Ga phase.

V_5Ga_3 is reported to be stable only in the temperature range from 935° to 1195° C (ref. 5); however, no structural information is available. Reference 5 discusses a VGa phase with a superlattice α-Fe structure, while reference 4 reports a V_6Ga_5 phase as hexagonal. Because of the proximity of the compositions of these phases and the possibility of ambiguous X-ray data, it is not possible at this time to clearly state that these are two distinct compounds. The V_2Ga_5 compound is reported (ref. 4) to have a tetragonal crystal structure (isostructural with Mn_2Hg_5) and to melt peritectically at 1085° C.

The objectives of this investigation were to obtain information regarding the solubility range of V_3Ga, to determine the phases in equilibrium with V_3Ga, and to ascertain the presence or absence of superconductivity in these phases. To this end, compositions were prepared by melting under an argon atmosphere. In an attempt to obtain equilibrium structures, all samples were annealed at 1100° C for $1\frac{1}{2}$ hours and slow cooled. Chemical analysis, X-ray diffraction patterns, and microstructures were obtained for each sample. Selected samples were tested for superconductivity at 4.2° K.

APPARATUS AND PROCEDURE

The vanadium and gallium used in this investigation were in chunk form with purities of 99.83 weight percent vanadium and 99.99 weight percent gallium, respectively. All compositions were melted in yttria-stabilized zirconia boats. No evidence of a reaction between the zirconia boats and the charge was found. Melting was accomplished in a tungsten resistance furnace that was first evacuated to a pressure of 10^{-5} millimeter of mercury and then backfilled with high-purity argon to a pressure of 500 millimeters of mercury.

The charge was heated to a temperature where liquefaction appeared complete (1600 to 1800° C depending on composition) as judged by visual examination through an optical pyrometer. The specimens were held at the liquefaction temperature for 1/2 hour and then cooled at a rate of approximately 20° C per minute. The samples were then annealed under an argon atmosphere at 1100° C for $1\frac{1}{2}$ hours followed by a slow cool (20° C/min).

Chemical analyses (both vanadium and gallium) and X-ray diffraction patterns were taken of all samples after annealing. Diffractometer patterns were taken after grinding the samples to -325 mesh powder. Nickel-filtered copper K_α radiation was used with a scanning speed of 1/8° per minute. Lattice constants were obtained from the X-ray diffraction patterns using a least-square analysis programed for the 7090 computer.

The superconductivity results were obtained from electrical resistivity measurements (voltage drop technique with sensitivity of 10^{-8} volt) at 4.2° K. Microhardness measurements were made using a diamond indenter with a 100-gram load. The values are reported as diamond pyramid hardness (DPH) numbers.

RESULTS AND DISCUSSION

The compositions investigated are listed in table I. For samples containing from 52.7 to 74.8 atomic percent vanadium, the only phases present were V_6Ga_5 and V_3Ga. All lines of X-ray patterns could be ascribed to either V_6Ga_5 or V_3Ga with the V_3Ga lines increasing in intensity as the vanadium content increased.

The sample containing 52.7 atomic percent vanadium consisted primarily of V_6Ga_5 with a small amount of V_3Ga present as a second phase. The microhardness of V_6Ga_5 was measured as 1000 DPH. The chemical analysis indicates this sample is within the limits reported for V_6Ga_5 in reference 4. The presence of V_3Ga, however, indicates that the actual composition of the V_6Ga_5 compound is less than 52.7 atomic percent vanadium.

TABLE 1. - SAMPLE COMPOSITIONS

As-mixed composition, atomic percent		Resulting composition after melting followed by 1100° C, 1$\frac{1}{2}$ hour anneal, atomic percent		Phases present
Vanadium	Gallium	Vanadium	Gallium	
51	49	52.7	47.2	V_6Ga_5 + V_3Ga
70	30	69.4	30.6	V_6Ga_5 + V_3Ga
73	27	74.5	25.3	V_3Ga + V_6Ga_5
75	25	74.8	25.1	V_3Ga + V_6Ga_5
74	26	76.2	23.4	V_3Ga + V-Ga solution
80	20	77.0	20.8	V-Ga solution + V_3Ga
85	15	85.6	14.3	V-Ga solution

The compound V_6Ga_5 (theoretical composition, 54.54 atomic percent vanadium) has been previously reported by two investigators (refs. 3 and 4). In reference 4, its composition is given as 54±2 atomic percent vanadium; V_6Ga_5 is reported to be hexagonal with lattice parameters of a_o = 8.496±0.001 angstroms and c_o = 5.174±0.001 angstroms. Whether this is the same compound reported in reference 5 as VGa is not clear at this time. The X-ray results of the present investigation are in agreement with those of reference 4; therefore, the compound in the vicinity of 50 atomic percent vanadium is referred to as V_6Ga_5 in this paper.

The microstructure of the sample containing 69.4 atomic percent vanadium is shown in figure 1. An X-ray pattern obtained from this sample at 1127° C[1] showed only V_6Ga_5 and V_3Ga phases present, while at 1327° C only V_3Ga lines were detected. Upon cooling to room temperature, the V_6Ga_5 lines reappeared. These results failed to show the presence of any high-temperature phase such as V_5Ga_3 reported by reference 5. Thus, it would appear that the microstructure of figure 1 is the result of either a eutectic or peritectic reaction occurring between 1127° and 1327° C. The microhardness measurements indicate that the white phase of figure 1 is V_3Ga. This phase exhibited a hardness of 920 DPH, which was identical to that measured for V_3Ga (discussed below).

As mentioned in the INTRODUCTION, there are conflicting views in the literature regarding the solubility limits of the V_3Ga phase. Attempts to obtain single-phase V_3Ga samples in this study were unsuccessful. Samples containing 74.5, 74.8, 76.2, and 77.0 atomic percent vanadium were examined, and none of these were single-phase materials. Typical microstructures of samples near the stoichiometric composition are shown in figures 2 and 3. A comparison of figures 2 and 3 reveals that essentially the same microstructure results regardless of whether the composition is slightly hypostoichiometric (atomic percent vanadium < 75, fig. 2) or hyperstoichiometric (atomic percent vanadium > 75, fig. 3). Evidence of a second phase is offered in figure 4. This electron photograph of the 74.8 atomic percent vanadium sample magnified 14,000 times definitely shows the particles of a second phase.

[1] High-temperature X-ray patterns were obtained using a helium atmosphere.

Quenching of near-stoichiometric samples from the annealing temperature of 1100° C resulted in essentially the same microstructure, although a somewhat finer distribution resulted. Reference 5 also shows a second phase present in near-stoichiometric compositions quenched from 800° C. However, the distribution of the second phase differs from that shown in figures 2 and 3. This difference may be due to the lower temperature and long annealing times (800 hr) used in reference 5.

X-ray diffraction of these near-stoichiometric compositions showed V_3Ga to be the major phase present. For hypostoichiometric compositions, V_6Ga_5 lines were identified in the X-ray patters; while at hyperstoichiometric compositions, vanadium lines were present.

The lattice parameter of V_3Ga also remained constant at 4.8165±0.0015 angstroms for both hypostoichiometric and hyperstoichiometric compositions. This is in agreement with the value given in reference 8 of 4.816±0.002 angstroms. The constancy of the lattice parameter observed here, the identification of second phases as equilibrium phases (either V_6Ga_5 or vanadium), and the characteristic microstructures of near-stoichiometric compositions all suggest that single-phase V_3Ga exists over a very limited compositional range. Microhardness measurements of the light matrix phase of figures 2 and 3 (V_3Ga) gave a value of 920 DPH.

A sample containing 85.6 atomic percent vanadium was examined metallographically and by X-ray diffraction and found to be a single-phase vanadium solid solution. The lattice parameter of this solid solution is 3.038 angstroms compared to 3.028 angstroms for pure vanadium (ref. 9).

The sample containing 77.0 atomic percent vanadium definitely contained V_3Ga in addition to the vanadium solid solution. The chemical analysis of this sample (Table I) suggests that some contamination has occurred. Subsequent analysis revealed approximately 1 weight percent oxygen. The sample containing 76.2 atomic percent vanadium also consists of V_3Ga and the vanadium solid solution.

SUPERCONDUCTIVITY MEASUREMENTS

The sample containing 52.7 atomic percent vanadium (primarily V_6Ga_5) was tested for superconductivity at 4.2° K and found to be normal. Reference 4 reported V_6Ga_5 to be normal to 2.1° K.

The sample containing 85.6 atomic percent vanadium was also tested and found to be normal at 4.2° K. This result indicates that the critical temperature, T_c, of vanadium is lowered more than 1° K by the addition of 14.3 atomic percent gallium in solution, based on a T_c of 5.3° K reported for pure vanadium (ref. 10).

These results indicate that the phases in equilibrium with V_3Ga are normal at 4.2° K. Therefore, for near-stoichiometric compositions at 4.2° K, the microstructure consists of superconducting V_3Ga containing particles of a nonsuperconducting second phase. These particles are generally of a continuous nature as opposed to isolated particles (figs. 2 to 4), and as such govern the size of the superconducting V_3Ga paths. Structures with the V_3Ga continuous path of the order of 2000 to 5000 angstroms wide have been observed in connection with this study. Critical field enhancement by decreasing the dimensions of the superconducting phase has been obtained in aluminum-lead composites (ref. 11) and a niobium-thorium eutectic alloy (ref. 12). In the case of V_3Ga, control of this dimension by heat treatment and/or compositional variations might offer a means of maximizing critical fields.

SUMMARY OF RESULTS

The following are the major results of this investigation:

1. The V_3Ga phase exists over a very limited compositional range near the stoichiometric composition.

2. The phases coexisting with V_3Ga at room temperature are V_6Ga_5 for hypostoichiometric compositions and vanadium with gallium in solid solution for hyperstoichiometric compositions.

3. Both V_6Ga_5 and a vanadium solid solution containing 14.3 atomic percent gallium are normal at 4.2° K.

4. The microstructural appearances of slightly hypostoichiometric and hyperstoichiometric compositions are essentially identical, with a second phase, either V_6Ga_5 or gallium saturated vanadium, present as precipitate particles in the V_3Ga matrix.

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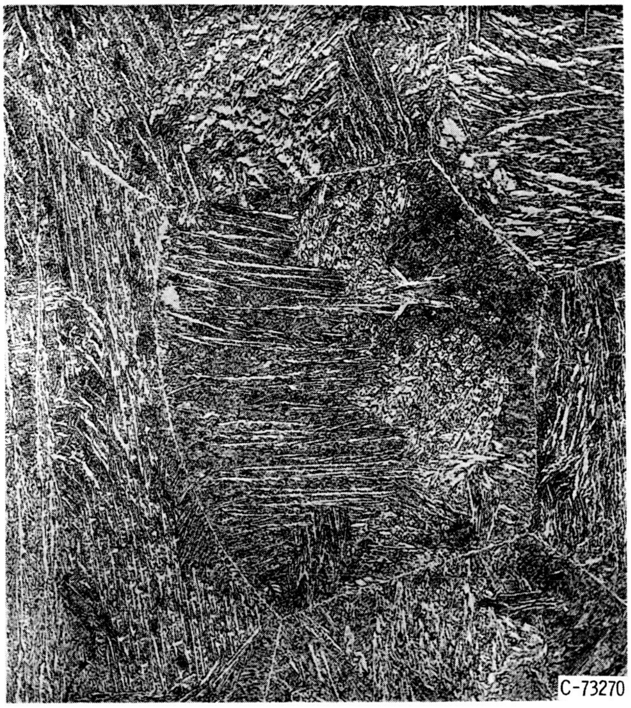

Figure 1. - Microstructure of sample containing 69.4 atomic percent vanadium. V_3Ga (white) + V_6Ga_5. Etchant, $4H_2O$-$3HNO_3$-1HF; X100.

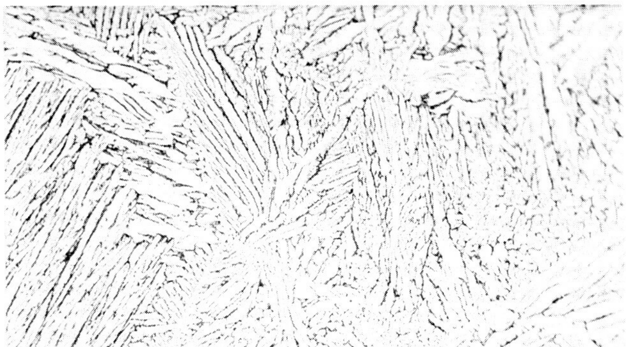

Figure 2. - Microstructure of sample containing 74.8 atomic percent vanadium. Primary phase, V_3Ga (white); secondary phase, V_6Ga_5. Etchant, $4H_2O$-$3HNO_3$-1HF; X250.

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Figure 3. - Microstructure of sample containing 76.2 atomic percent vanadium. Primary phase, V_3Ga (white); secondary phase, V-Ga solution. Etchant, $4H_2O$-$3HNO_3$-1HF; X250.

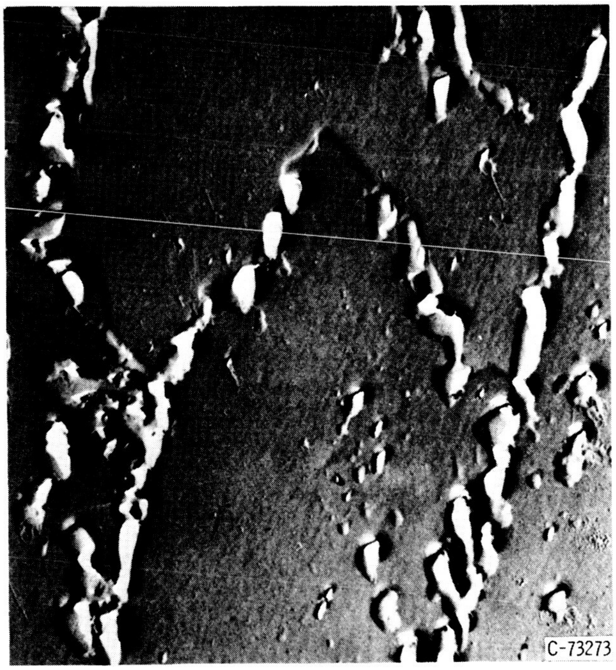

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Figure 4. - Electron micrograph of sample containing 74.8 atomic percent vanadium. Primary phase, V_3Ga matrix; second phase, V_6Ga_5. X14,000.